The Pennsylvania State University
The Graduate School
Department of Electrical Engineering

HIGH PERFORMANCE IONIC CAPACITIVE ENERGY STORAGE AND HARVESTING DEVICES

A Dissertation in
Electrical Engineering
by
Yue Zhou

© 2015 Yue Zhou

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

December 2015
The dissertation of Yue Zhou was reviewed and approved* by the following:

Qiming Zhang  
Distinguished Professor of Electrical Engineering  
Dissertation Advisor  
Chair of Committee

Shizhuo Yin  
Professor of Electrical Engineering

Chris Giebink  
Assistant Professor of Electrical Engineering

Qing Wang  
Professor of Materials Science and Engineering

Kultegin Aydin  
Professor of Electrical Engineering  
Head of Department of Electrical Engineering

*Signatures are on file in the Graduate School
ABSTRACT

Due to the deep concerns of environmental issues and the consumption of fossil fuels, such as petroleum, natural gas and coal, as well as the accelerated greenhouse effect, the renewable energy sources e.g., wind, solar and hydroelectricity have attracted enormous interests. The large fluctuations of these renewable energy sources in power output have brought the vigorous development of the area of energy storage system. Supercapacitors, which bridge the gap of power and energy between batteries and dielectric capacitors, have developed fast in the last decades among these energy storage devices. Although batteries can store a large quantity of energy, they release energy in a slow rate, resulting in a very low power density with a limited lifetime. On the other hand, dielectric capacitors can be charged and discharged at high rate and hence possess very high power density, but their energy density is low. With relatively high power, mid-high energy density and long cycle lifetime, supercapacitors are attractive for many applications, such as in grid scale renewable energy storage and in hybrid electric vehicles where high energy, high power and reasonable lifetime are all required. However, the current commercial supercapacitor product still suffers from the low energy density (less than 10 Wh/kg) and low power density (1 kW/kg). Hence, it is highly desired to further improve electrochemcial performance of supercapacitors cells for the advanced and wide applications. In this dissertation, different supercapacitor cells are introduced to improve the performance by several strategies such as controlling the nanomorphology of electrodes and optimizing the cell configuration.

The tortuous ion transport pathways formed in activated carbon, which is widely used as electrodes in the current commerical products, have influenced the power densisty of the cell. To overcome this drawback, the aligned carbon nanotubes (A-CNTs) were investigated in this dissetation due to the superior electrical conductivity and parallel ion pathways of electrodes.
Meanwhile, to achieve high volumetric energy and power densities of the cells, a unique mechanical densification method was developed to allow the density of A-CNTs to be tuned precisely over a broad range from 1% volume fraction (Vf) to 40% Vf while preserving the straight ion pathway between A-CNTs. As a result, the supercapacitors fabricated from 40% volumetric fraction (Vf) of A-CNTs as the electrodes with the thickness of 0.8 mm exhibit a power density of 25 kW L$^{-1}$ (50 kW kg$^{-1}$), which is much higher than that of the A-CNTs electrodes with similar thickness fabricated by other methods and that of activated carbon electrodes.

Pseudocapacitive materials, such as conducting polymers and transition metal oxides, can be incorporated into the electrode to increase the specific capacitance because the whole bulk (not only the surface for pure carbon electrode) of pseudocapacitive material has involved the electrochemical energy storage. Poly(ethylenedioxythiophene) (PEDOT) was studied as the pseudocapacitive materials in this dissertation. The conformal coating of PEDOT on A-CNTs can exhibit long cycle life compared with pure PEDOT or PEDOT coated on random CNTs since the A-CNTs can provide a mechanical structure to absorb the large volume change of PEDOT during the charge and discharge processes. The unique mechanical densification method was also used to densify the composite to 5% to improve the volumetric performance of the cell. Symmetric supercapacitors using the 5% compacted A-CNTs coated with 10nm thickness PEDOT as electrodes, as well as using BMI-BF4/PC as electrolyte can achieve the highest volumetric specific capacitance of 92.79 F cm$^{-3}$. Meanwhile, the QV curve based on CV curve or galvanostatic curve was firstly introduced. This new investigation method can be used to evaluate the cell energy loss and coulombic efficiency better compared with the conventional one.
The energy density and maximum power density of supercapacitor cells are strongly dependent with the operation potential which is limited by the electrochemical window of the interface between electrode and electrolyte. In order to expand the electrochemical window of the supercapacitor cell, the asymmetric configuration was introduced in this dissertation. One electrode can be pseudocapacitive materials and the other one is carbon materials so that the asymmetric configuration can make full use of the different windows and the advantages of two kinds of materials to expand the operation potential and enhance the performance of the cell. An asymmetric supercapacitor with high electrochemical performance has been developed with conformal coating of PEDOT on A-CNTs as one electrode and the ultra-high density A-CNTs as the other one in 2 M BMIBF₄/PC electrolyte. The positive and negative electrodes materials are individually tailored and work synergistically together in the asymmetric cell configuration so that the cell can be operated under the high operation voltage of 4 V to achieve energy and power densities with a long cycle life. Moreover, the EIS of each electrode is modeled by equivalent circuit elements to describe quantitatively the functions of pseudocapacitor and carbon electrode directly. The EIS of the asymmetric cell is also simulated based on the parameters from two electrodes which demonstrate the optimized asymmetric design.

In order to improve the electrochemical performance of asymmetric cell further, activated graphene electrode with the higher specific area (more than 3000 m²/g) were used in the high power side to replace the A-CNTs. The aligned microwave exfoliated graphite oxide electrode, fabricated via a self-assembly process, shows high specific gravimetric and volumetric capacitance for the high power electrode. As a result of complementary tailoring of the asymmetric electrodes, the layered device exhibits a wide 4V electrochemical window, and the highest power and energy densities reported thus far for carbon-based supercapacitors, 149 kW
L$^{-1}$ and 113 Wh L$^{-1}$ in volumetric performance and 233 kW kg$^{-1}$ and 177 Wh kg$^{-1}$ in gravimetric performance, respectively.

Finally, the mechanical and thermal energy harvesting devices based on high performance supercapacitor cells have been investigated due to the high specific capacitance and strong dependence with the pressure or temperature. For the mechanical energy harvesting devices based on supercapacitor cell, 40 mV open circuit potential change was obtained, resulting in the high energy harvested of 0.2 J/cc. For the thermal energy harvesting devices, 0.26 J/cc energy harvested per increasing/decreasing temperature cycle was achieved. The large energy harvested per cycle based on supercapacitor cells have surpassed all other energy harvesting devices based on pyroelectric and piezoelectric materials.
Table of contents

List of Figures .................................................................................................................................x
List of Tables .................................................................................................................................xvii
Acknowledgements .......................................................................................................................xviii

Chapter 1 .........................................................................................................................................1
  1.1 Introduction .................................................................................................................................1
    1.1.1 Energy Demand ......................................................................................................................1
    1.1.2 Energy storage technologies .................................................................................................3
  1.2 Energy storage devices-supercapacitor ......................................................................................9
    1.2.1 Main components and working principles of EDLC supercapacitor ................................. 10
    1.2.2 Pseudocapacitor ..................................................................................................................14
    1.2.3 Electrode materials ..............................................................................................................16
    1.2.4 Electrolytes ..........................................................................................................................25
  1.3 Research contribution and dissertation organization ...............................................................26

Chapter 2 .........................................................................................................................................28
  2.1 List of symbols .............................................................................................................................28
  2.2 Electrochemical characterization .................................................................................................29
    2.2.1 Cyclic voltammetry ..............................................................................................................30
    2.2.2 Galvanostatic charge/discharge .........................................................................................32
    2.2.3 Electrochemical impedance analysis ...................................................................................35
  2.3 Characterization set-ups .............................................................................................................38
    2.3.1 Electrochemical characterization set-ups .............................................................................38
    2.3.2 Scanning electron microscope (SEM) ..................................................................................41
    2.3.3 Thermogravimetric analysis (TGA) .....................................................................................42
    2.3.4 Activation of electrode materials .......................................................................................42

Chapter 3 .........................................................................................................................................44
  3.1 Introduction .................................................................................................................................44
  3.2 Supercapacitor cell fabrication .................................................................................................49
    3.2.1 CNT forest growth and densification ...................................................................................49
3.2.2 Cell assembly and characterization methods .................................................. 51
3.3 Results and discussion ................................................................................. 52
  3.3.1 Cyclic voltammetry .................................................................................. 52
  3.3.2 Galvanostatic charge/discharge ............................................................... 53
  3.3.3 Energy and power densities ..................................................................... 55
  3.3.4 Cycle life ................................................................................................. 58
  3.3.5 Nyquist plots ........................................................................................... 58
  3.3.6 Comparison with activated carbon supercapacitor .................................. 59
3.4 Conclusions .................................................................................................. 62
Chapter 4 ............................................................................................................. 63
  4.1 Introduction .................................................................................................. 64
  4.2 Preparation of PEDOT/A-CNTs supercapacitor cell ..................................... 68
    4.2.1 Preparation of PEDOT/A-CNTs ............................................................. 68
    4.2.2 Supercapacitor assembly ...................................................................... 70
  4.3 New method to investigate charge/discharge cycle ...................................... 73
    4.3.1 Nyquist plot .......................................................................................... 78
    4.3.2 Galvanostatic charge/discharge cycles ............................................... 81
    4.3.3 Energy and power densities ................................................................. 86
  4.4 Conclusion .................................................................................................. 87
Chapter 5 ............................................................................................................. 89
  5.1 Introduction .................................................................................................. 90
  5.2 Supercapacitor fitting based on equivalent circuit ....................................... 94
  5.3 Experimental .............................................................................................. 97
  5.4 Results and discussion ............................................................................... 98
    5.4.1 Electrochemical performance of each electrode based on three-electrode system .......... 98
    5.4.2 Asymmetric cell assembly ................................................................... 101
    5.4.3 CV and QV curves ............................................................................... 102
    5.4.4 Galvanostatic charge/discharge curve ............................................... 104
    5.4.5 Energy and power densities ................................................................. 107
    5.4.6 Equivalent circuit fitting ...................................................................... 109
5.5 Conclusions ......................................................................................................................... 113

Chapter 6 ................................................................................................................................. 115

6.1 Introduction ......................................................................................................................... 116

6.2 Experimental ..................................................................................................................... 120
  6.2.1 Fabrication of aligned aMEGO film ........................................................................... 120
  6.2.2 Fabrication of PEDOT/random CNTs composite ....................................................... 123
  6.2.3 Preparation of the asymmetric cell .......................................................................... 124

6.3 Results and discussion ...................................................................................................... 125
  6.3.1 Electrochemical performance of each electrode ......................................................... 125
  6.3.2 Asymmetric cell assembly and characterizations ...................................................... 131

6.4 Conclusions ....................................................................................................................... 138

Chapter 7 .................................................................................................................................. 140

7.1 Introduction ......................................................................................................................... 140

7.2 Energy harvesting based on variable capacitance ............................................................... 143

7.3 Circuit design .................................................................................................................... 145

7.4 Mechanical energy harvesting ......................................................................................... 146

7.5 Thermal energy harvesting ............................................................................................... 151

7.6 Conclusions ....................................................................................................................... 157

Chapter 8 .................................................................................................................................. 159

8.1 Conclusions ......................................................................................................................... 159

8.2 Future work ......................................................................................................................... 163
  8.2.1 Advanced hybrid electrode materials ....................................................................... 163
  8.2.2 Some improvements of energy harvesting devices based on supercapacitors .......... 164

References: ............................................................................................................................... 170
LIST OF FIGURES

Figure 1-1. U.S. energy consumption in the past and the prediction by DOE.[7] ............................................. 3

Figure 1-2. Flywheel energy storage system ........................................................................................................ 4

Figure 1-3. Compressed air energy storage system ............................................................................................. 5

Figure 1-4. Charge and discharge processes of rechargeable batteries .............................................................. 7

Figure 1-5. Ragone plots of different energy storage devices.[36] ......................................................................... 8

Figure 1-6. Different types of supercapacitor cells.[8] .......................................................................................... 9

Figure 1-7. The compositions of EDLC supercapacitor cell.[54] ........................................................................... 11

Figure 1-8. The different CV curves of pseudocapacitor and EDLC supercapacitor. .......................................... 14

Figure 1-9. Normalized capacitance change as a function of the pore size of carbon derived-carbide samples ................................................................................................................................. 17

Figure 1-10. Schematic of carbon family from 0 to 3 dimensions ...................................................................... 18

Figure 1-11. Specific capacitances of various supercapacitor electrode materials. ........................................... 24

Figure 2-1. Schematic CV curves for ideal EDLC, EDLC with resistance and cells based on carbon materials with chemical reactions ............................................................................................................. 31

Figure 2-2. Specific capacitance calculation from CV curve. ............................................................................. 32

Figure 2-3. (a) A typical galvanostatic charge/discharge curve (b) The IR drop region at the transmission from charge curve to discharge curve ................................................................................. 33

Figure 2-4. Simple equivalent circuit of supercapacitor cell. ............................................................................. 36

Figure 2-5. Frequency-response behaviors for different equivalent circuits of supercapacitor cells .............. 37

Figure 2-6. DropSens screen-printed electrode chips for three-electrode measurement. ................................ 39

Figure 2-7. (a) Split test cell and (b) coin cell for the supercapacitor measurement. .......................................... 40

Figure 2-8. (a) PARSTAT 2273 and (b) VersaSTAT 4 for electrochemical test .................................................... 41
Figure 2-9. FEI NanoSEM 630 FESEM. ................................................................. 42

Figure 2-10. MTI GSL-1100X tube furnace. ............................................................ 43

Figure 3-1. Schematic figure of how to "roll up" graphene sheet to nanotube. ...................... 45

Figure 3-2. Schematic of the tortuous ion transport paths in nanoporous electrodes formed, for example, from the activated carbons, and parallel ion pathways in the A-CNTs............................ 46

Figure 3-3. Ragone plot of the gravimetric performance of cell based on carbon material and the realistic data obtained from this plot. ............................................................................. 48

Figure 3-4. Schematic of A-CNTs growth process. .......................................................... 50

Figure 3-5. Optic images, schematic of mechanical densification process, and SEM images of 1% Vf and 40% Vf A-CNTs. .......................................................................................... 50

Figure 3-6. Chemical structure of EMI-BF$_4$. ................................................................. 52

Figure 3-7. Electrochemical performance of supercapacitors with A-CNT electrodes and EMI-BF$_4$/PC electrolyte at 4 V: a) gravimetric cyclic voltammograms and b) volumetric cyclic voltammograms of A-CNT electrodes with 1% and 40% Vf at 100 mV s$^{-1}$. The charge and discharge cycle curves are symmetric for both volume fractions of A-CNTs........................................................................................................ 53

Figure 3-8. Galvanostatic charge discharge curves at 1 A g$^{-1}$ for supercapacitors with electrodes of 1% and 40% Vf A-CNTs and EMI-BF$_4$/PC electrolyte. ............................................................................. 54

Figure 3-9. a) Gravimetric and b) volumetric specific capacitance for the supercapacitors with electrodes of 1% and 40% Vf A-CNTs at different discharge rates. ............................................................. 54

Figure 3-10. a) Gravimetric and b) volumetric Ragone plots for the supercapacitors with electrodes of 1% and 40% Vf A-CNTs. ..................................................................................................... 56

Figure 3-11. Cycle performance of 40% Vf A-CNTs supercapacitor with a voltage of 4 V at charge and discharge current density of 5 A g$^{-1}$. ....................................................................................... 58

Figure 3-12. Nyquist plots of 1% Vf and 40% Vf A-CNTs supercapacitors in the range of 100 kHz to 10 mHz............................................................................................................................ 59
Figure 3-13. a) Gravimetric and b) volumetric Ragone plots of supercapacitors with electrodes of 40% Vf A-CNTs and with electrodes of activated carbon. .................................................................60

Figure 3-14. The specific capacitance of supercapacitors with 40% Vf A-CNTs under different discharge current densities. .............................................................................................................61

Figure 4-1. Doping process in a conducting polymer. ..................................................................................................................65

Figure 4-2. Microstructures of the electrode materials. (a) SEM image of as-grown aligned carbon nanotubes. (b) SEM image of PEDOT/A-CNTs with 10 nm coating thickness. .........................67

Figure 4-3. Schematic figure of modified oCVD process chamber.[124] .................................................................69

Figure 4-4. Schematic illustration of A-CNTs (a) before and (b) after PEDOT coating.[112] ........70

**Figure 4-5.** TEM figure and scheme of composite, comprised of conformal PEDOT coating on A-CNTs. (The image was from our collaborator Prof. Wardle’s group in MIT) ...............................................................72

Figure 4-6. Scheme of working mechanism differences between EDLC and pseudocapacitor. ..................73

Figure 4-7. Typical QV curve of supercapacitor cell. ..........................................................................................74

Figure 4-8. (a) Volumetric and (b) gravimetric QV curves of cells with different electrodes. ........75

Figure 4-9. Coulombic efficiencies of cell with PA10 as electrode under the scan rates of 100 mV s^{-1} and 10 mV s^{-1}. .......................................................................................................................76

Figure 4-10. (a) Volumetric and (b) gravimetric specific capacitances of cell with PA10 as electrode under the scan rates of 100 mV s^{-1} and 10 mV s^{-1}. .......................................................................................................................77

Figure 4-11. Nyquist plot for symmetric supercapacitors with A-CNTs, PA3, PA6, PA10 at 5% volume fraction in 2 M BMI-BF$_4$/PC. ...........................................................................................................78

Figure 4-12. (a) Real part capacitance versus frequencies of cells with different electrodes. (b) The ratio of real and imaginary capacitance versus frequencies of cells with different electrodes.................79

Figure 4-13. Coulombic efficiencies and specific capacitances of cell with PA10 as electrode from CV and Nyquist measurements (one is for high voltage and one is obtained at low voltage). ..............80
Figure 4-14. (a) Galvanostatic charge/discharge curves for cells with A-CNTs, PA3, PA6 and PA10 as electrodes under different discharge current densities in 2 M BMI-BF$_4$/PC. (b) Coulombic efficiencies of different cells with conventional and new methods. ................................................................. 82

Figure 4-15. (a)Volumetric and (b) gravimetric specific capacitances of different cells versus discharge current densities. ........................................................................................................ 84

Figure 4-16. Capacitance retention property under 1000 cycles. .............................................................................. 85

Figure 5-1. SEM images of (a) as grown A-CNTs with 1% Vf and (b) densified A-CNTs with 40% Vf. 91

Figure 5-2. (a) SEM images of PEDOT/A-CNTs composite. (b) Scheme and high magnification TEM images of the composite. (The images were from our collaborator Prof. Wardle’s group in MIT) .... 92

Figure 5-3. CV curves of both electrodes at 100 mV s$^{-1}$ in 2 M BMIBF$_4$/PC. ....................................................... 93

Figure 5-4. Classical equivalent Circuit Model. ........................................................................................................ 95

Figure 5-5. Transmission line network model of a supercapacitor. ............................................................................ 96

Figure 5-6. The ladder model................................................................................................................................. 97

Figure 5-7. Galvanostatic charge/discharge curves of both electrodes at 1A g$^{-1}$ 2 M BMIBF$_4$/PC................. 99

Figure 5-8. Specific (a) volumetric and (b) gravimetric capacitances at different discharge densities of both electrodes. ................................................................................................................. 100

Figure 5-9. CV curves of asymmetric cell at different scan rates of 10, 20, 50, 100 and 200 mV s$^{-1}$ between 0 and 4 V in 2 M BMIBF$_4$/PC electrolyte. ................................................................. 102

Figure 5-10. QV curve of cell at different scan rates between 0 and 4 V ................................................................. 102

Figure 5-11. Coulombic efficiency of asymmetric cell with different scan rates. ................................................. 103

Figure 5-12. Galvanostatic charge/discharge curves of device at a current density of 2 A g$^{-1}$ ................. 104

Figure 5-13. Cell (a) volumetric and (b) gravimetric capacitances of cell at different discharge current densities. ............................................................................................................................. 106

Figure 5-14. Cycle life vs number of cycles. .............................................................................................................. 107

Figure 5-15. (a) Volumetric and (b) gravimetric Ragone plot of asymmetric cell. ............................................. 108
Figure 5-16. Equivalent impedance circuit of each electrode.................................................................109

Figure 5-17. Nyquist plot and fitting curve for (a) PEDOT/A-CNTs electrode, (b) densified A-CNTs electrode........................................................................................................................................111

Figure 5-18. Nyquist plot and fitting curve for asymmetric cell.................................................................113

Figure 6-1. Schematic of the KOH activation process for MEGO.[47].........................................................117

Figure 6-2. VASAA of nano-porous aMEGO sheets to produce high density highly aligned aMEGO sheets.[146].................................................................................................................................................118

Figure 6-3. Nanostructured electrodes in asymmetric supercapacitors. (left) Low and high magnification TEM micrographs of the negative electrode (negative ions are shown schematically in the PEDOT layer), comprised of conformal oCVD PEDOT on A-CNTs, and (right) SEM images of a-graphene flakes electrode..........................................................................................................................................................119

Figure 6-4. Filtration equipment for A-aMEGO films..................................................................................121

Figure 6-5. Unique pore structure of Anodisc filter..................................................................................122

Figure 6-6. (a) As-filtered aMEGO film, (b) aMEGO film after applying the floating method.[42]........123

Figure 6-7. (a) CV curves of PEDOT/A-CNTs and (b) CV curves of a-graphene flakes at 5 mV s⁻¹ in 2 M BMIBF₄/PC..................................................................................................................................................125

Figure 6-8. Galvanostatic charge/discharge curves of A-MEGO electrode................................................126

Figure 6-9. (a) Volumetric and (b) gravimetric specific capacitance at different discharge densities of A-MEGO electrode........................................................................................................................................127

Figure 6-10. Galvanostatic charge/discharge curves of PEDOT/A-CNTs composite a current density of 2 A g⁻¹. ......................................................................................................................................................128

Figure 6-11. (a) Volumetric and (b) gravimetric specific capacitance at different discharge densities of PEDOT/A-CNTs electrode..................................................................................................................129
Figure 6-12. Cycle performances of symmetric supercapacitors with the PEDOT/A-CNTs electrodes and the PEDOT deposited on randomly packed CNT networks under driving voltages of 1 V and 2 V, respectively, at current density of 5 A g\(^{-1}\)................................................................. 130

Figure 6-13. (a) CV curves of PEDOT/A-CNTs//a-graphene asymmetric supercapacitor at different scan rates between 0 and 4 V in 2 M BMIBF\(_4\)/PC electrolyte. (b) Galvanostatic charge/discharge curves of asymmetric device at different current densities................................................................. 132

Figure 6-14. (a) Volumetric and (b) gravimetric cell capacitances of asymmetric cell at different discharge current densities ........................................................................................................... 133

Figure 6-15. Cycle capacitance retention of the asymmetric supercapacitor under a voltage of 4 V at a current density of 5 A g\(^{-1}\) in 2 M BMIBF\(_4\)/PC electrolyte. ................................................................. 134

Figure 6-16. Nyquist plot of the asymmetric cell using 1 M BMIBF\(_4\)/PC as electrolyte. ......................... 135

Figure 6-17. (a) Volumetric and (b) gravimetric Ragone plots of asymmetric cell................................. 136

Figure 6-18. (a) CV curves of each electrode using 1 M Et\(_4\)NBF\(_4\)/PC as electrolyte. (b) Cell capacitance of asymmetric cell ............................................................................................................. 137

Figure 6-19. (a) Volumetric and (b) gravimetric Ragone plots of asymmetric cell using 1 M Et\(_4\)NBF\(_4\)/PC as electrolyte. ............................................................................................................. 138

Figure 7-1. Schematic energy flow in a mechanical energy harvesting system. ......................................... 141

Figure 7-2. (a) QV curve and (b)CF curve during the energy harvesting process........................................... 143

Figure 7-3. A simple switch circuit energy harvesting devices based on variable capacitance.................. 144

Figure 7-4. Parallel electrode configuration for testing the porous electrodes for mechanical energy harvesting...................................................................................................................... 147

Figure 7-5. Normalized capacitance change of supercapacitor cell with stress......................................... 148

Figure 7-6. Face-to-face electrode configuration for mechanical energy harvesting.............................. 150

Figure 7-7. Open circuit potential change after applying a stress of 2 MPa from t=1041 seconds to t=1055 seconds......................................................................................................................... 151
Figure 7-8. DSC curves of BMIBF₄ electrolyte........................................................................................................... 152

Figure 7-9. CV curves for the cells with BMIBF₄ as the electrolytes with the scan rates of (a) 100 mV s⁻¹ and (b) 5 mV s⁻¹. ....................................................................................................................................................... 153

Figure 7-10. Normalized capacitance and volumetric capacitance of cells with the BMIBF₄ vs. temperature from -60 °C to 80 °C at the scan rate of 5 mV/s.......................................................................................................................... 155

Figure 7-11. Open circuit potential change with temperature change for the CNT/P(VDF-CTFE) nanocomposites with what electrolyte as the temperature was reduced from 80 °C to -20 °C ............... 155

Figure 7-12. Open circuit potential change of Gold Cap 2.5 V 10 F supercapacitor cell with temperature change from 80 °C to -20 °C. ................................................................................................................................. 157

Figure 8-1. Leakage current with time of samples assembled in (a) air and (b) N₂, respectively............. 165

Figure 8-2. Thermal conductivity of aligned and un-aligned carbon nanotubes.[168]............................... 167

Figure 8-3. (a) Structure of PN junction and (b) detail of the junction area.[170] ........................................... 169
LIST OF TABLES

Table 1-1. The advantages and drawbacks of the two supercapacitor cells......................................................... 15
Table 1-2. Capacitances and physical properties of carbon or carbon based materials. ......................................... 19
Table 2-1. List of symbols and their meanings. ......................................................................................................... 28
Table 4-1. The volumetric energy density and power density of all cells in 2 M BMI-BF₄/PC. ......................... 86
Table 5-1. Fitting parameters for the EISs of two electrodes. ............................................................................... 113
Acknowledgements

I would like to express the deepest and sincerest gratitude to my advisor Professor Qiming Zhang for his constant guidance, vision, encouragement and support. I am very fortunate to have him as my research advisor and deeply thankful for his attention on my scientific and personal development. His insights into this area led my dissertation to a level which I was incapable to achieve on my own.

I gratefully acknowledge my committee members Professor Shizhuo Yin, Professor Chris Giebink and Professor Qing Wang. They have spent a lot of their precious time on reading my thesis, making constructive comments and advancing critical suggestions in my research process, and setting great examples of being a mature and serious researcher for me.

I would like to sincerely thank all my colleagues in the lab, especially Dr. Minren Lin, Dr. Yang Liu, Dr. Mehdi Ghaffari, Mr. Chad Welsh, Mr. Omar Alzaabi, Dr. Jiping Cheng, Dr. Xiaoshi Qian, Mr. Lei Mei and all my fellow students and group members for their assistance and friendship during my PhD study.

In addition, I would like to thank my collaborators: Professor Brian Wardle and Professor Karen Gleason and their groups at MIT, Professor Rodney Ruoff and his group at UT-Austin, Professor Andy Burke. Some of their group members I closely worked with are Dr. Noa Lachman at MIT for her persistency in research, Dr. Roberto Guzmán de Villoria, Dr. Dhiman Bhattacharya, Dr. Asli Ugur Katmis and Dr. Tae-Young Kim.

Furthermore, I appreciate the financial support by AFOSR under grant number FA9550-11-1-0192 and NSF under grant number CMMI-1130437.
Last but foremost, I would like to thank my parents and my wife Tianying Jin for their eternal love, understanding, and support. The dissertation cannot be completed without their accompanying. Special thanks to my daughter Yolanda, who lifts my spirit all the time and brings tremendous happiness to my family.
Chapter 1

Introduction

1.1 Introduction

Nowadays, our society relies heavily on the fossil fuels, such as petroleum, natural gas and coal, for the energy source to sustain the needs of both industries and the current life all over the world.[1] Although these fossil fuels are convenient to transport and handle, and can produce significant amounts of energy per unit weight or volume, however, they are depletive and have side effect of producing toxic emissions and greenhouse gases attributing the global warming.[2-4] Under this background, the development of replacing old energy products with new ones has become critical. The penetration of renewable energy sources and other forms of potential distributed generation sources has attracted many countries’ interests. These renewable energy sources, such as wind, solar, and wave (in ocean), often rely on the weather or climate to work effectively. It should be mentioned that one drawback is that large fluctuations in power output may presence in monthly or even annual cycles due to the directly harnessing the power from the nature.[5, 6] Hence, in order to making full use of these renewable energy sources as a reliable source of energy, energy storage technologies play an important role in the clean energy field. Here I will briefly introduce several conventional energy storage devices including flywheels, pneumatic storage, hydrogen storage, batteries and supercapacitors storage.

1.1.1 Energy Demand

Demand of energy has increased dramatically in the last twenty years. The trend will still grow in the future because of the economic recovery and population growth. As shown in the
The department of energy has predicted more than 50% increase in U.S. energy consumption from 2010 to 2030. Although energy production has several forms, the fossil fuel together takes most part of all the energy sources. In 2010, they accounted for more than 80 percentage of total energy production although renewable energy has increased. Among the fossil fuel sources, liquids fuels (majority of which are petroleum based) remains the largest part. The historical trends show that the liquids fuels increase from 35 quadrillion (35 q) units used in 1980 to 42 q in 2012. Despite some fluctuation between 1980 and 1995, there was a steady increase, which is predicted to continue, reaching to 47 q in 2030. As we discussed above, with the rapid depletion of fossil fuels and environmental pollution caused by vast fossil fuel consumption, there is a high demand to make efficient use of energy and to seek renewable and clean energy sources. A vast majority (around 82%) renewable and clean energy sources is from hydropower and wind power. Solar power is currently still a “niche” source of new energy that requires optimization in both technology and cost. However, as exhibited in Figure 1-1, the energy consumption from renewable energy sources such as solar/wind and hydropower increase with relatively low speed or remain constant. One of the reasons is that the power output of these energy sources is not as reliable and easy to adjust to changing demand cycles as the output from the conventional power sources. Therefore, energy storage is a crucial factor to make sure these renewable sources to be completely safe and stable as main sources of energy.
Figure 1-1. U.S. energy consumption in the past and the prediction by DOE.[7]

1.1.2 Energy storage technologies

Depending on the applications, the energy storage systems have different requirements, such as charge/discharge efficiency, power (charge/discharge rate), the amount of energy stored, whether stationary or mobile, gravimetric/volumetric performance and the cost. There are plenty of methods that can be used to store energy including mechanical, thermal, gravitational and chemical methods.[8-12]

Flywheel storage is one kind of mechanical energy storage technologies which is carried out by conversion between electrical energy and mechanical energy at demand. As shown in Figure 1-2, the flywheel energy storage system is mainly composed of a column-shaped rotation part and a magnetic suspension axletree as supporting component. The electrical energy converted into kinetic energy in the flywheel is achieved by an electromotor to drive the flywheel with a high speed (~50000 rpm). When the flywheel slows down (~6000 rpm), the
kinetic energy is converted back into electrical energy and thus the storage and release of electrical energy is realized. The main advantages of flywheel storage systems are the high charge/discharge rates, high energy density, high energy storage efficiency and wide working temperature range. The light weight and high-strength composite rotors can achieve specific energy of 100 Wh/kg. There are several disadvantages of this energy storage system such as the high cost and the relatively high standing losses. Self-discharge rate for the flywheel storage systems is very high, usually with minimum rate of 20 percentage of the stored capacity per hour.[13-15]

**Figure 1-2.** Flywheel energy storage system

Pneumatic energy storage technologies are mainly based on compressed air or compressed gas to achieve energy storage. For the former technology, the operation principle is involved the compression and expansion of a trapped volume of gas (N₂) taking place in a storage vessel. The volume and pressure are adjusted by the amount of fluid/liquid in the vessel. There are several severe disadvantages so that the technology is still limited at research stage, such as low energy density (3.2 to 5.55 Wh/kg), large self-discharge and leakage, and low energy
efficiency (~73 percentage). For the compressed air energy storage, cheap off-peak electric power is deployed to compress air, and at peak load the compressed air is then released and used for electric power generation. The compressed air is usually stored in underground caves or abandoned mines as shown in Figure 1-3. The major constraint of this technology is that it is dependent on favorable geography. In other words, it is only economically feasible for power plants that have nearby rock mines, salt caverns, and aquifers or depleted gas fields.[16-19]

Figure 1-3. Compressed air energy storage system

There are mainly four hydrogen storage technologies currently. Hydrogen pressurization and hydrogen adsorption in metal hydrides are the two mature and developed technologies. Hydrogen pressurization technology is based on highly permeable materials to hydrogen and to their mechanical stability under pressure of 200–250 bar. Stronger and stable materials are required for the hydrogen storage with high pressure. The use of metal hydrides as storage mediums depends on the excellent hydrogen absorption properties of these compounds. Because of the exothermic reaction during absorption of hydrogen and the endothermic reaction during desorption of hydrogen, thermal management plays an important role. [20-23]
Batteries energy storage technology is based on the rechargeable electrochemical system. The chemical energy is delivered in the form of electric energy, which is generated from the electrochemical reactions. The battery cell is mainly composed of electrodes, separator and electrolyte. The anode provides the electrons to the load and could be oxidized during the electrochemical reaction. The cathode accepts electrons and could be reduced during the electrochemical reaction. The electrolyte provides the medium for the ions transfer during the reaction and the porous separator provides the electrical insulation for the cell. The electrochemical reaction is involved the transfer of electrons from one electrode to the other through an external electric circuit/load as shown in Figure 1-4. There are many types of rechargeable batteries depending on the electrodes materials, such as lead-acid, nickel-based, lithium ion batteries (LIBs), sodium ion batteries and so on. Lead-acid batteries are the oldest rechargeable batteries (secondary cells) and are composed of lead dioxide as cathode, lead metal as anode and sulphuric acid as the electrolyte, with a typical operation voltage of 2 V, energy density of around 30 Wh/kg and power density of around 180 W/kg. The lead-acid batteries have very low self-discharge rates (2% per month), high energy efficiencies and relatively low level of maintenance. However, the relatively low energy density, environmentally unfriendly (lead and electrolyte) and limited number of full discharge cycles have some limitations on the wider application of lead-acid batteries. In the last decades, the LIBs energy storage technologies have been developed fast because of plenty of advantages such as high operation voltage, high energy density (around 150 Wh/kg), high energy efficiency, low self-discharge rate and relatively safety. Nowadays, they have got wide applications from potable electronic devices (mobile phones and laptops) to electric vehicles (Tesla). However, the properties of LIBs still need to be improved further. Current researches mainly focus on the electrode materials optimization to improve the
energy density and power density as well as the cost reduction. The power density now gets more attentions because the charge/discharge speed is anticipated to be faster to meet different demands especially in the electric vehicles field. [24-31]

![Figure 1-4](image)

**Figure 1-4.** Charge and discharge processes of rechargeable batteries.

Supercapacitors (also called ultracapacitors), which store charges through electrical double layers (EDL), bridge the power and energy gap between batteries and dielectric capacitors shown in Figure 1-5.[32-35] Although batteries can store large quantity of energy, they release energy slowly, resulting in a very low power density (1 kW L$^{-1}$) and they suffer from very limited lifetime (<1000). On the other hand, dielectric capacitors with long lifetime can be charged and discharged at high rate (< microseconds) and hence possess very high power density (> 10$^5$ kW L$^{-1}$), however their energy density is low, often below 0.3 Wh L$^{-1}$. The relatively high power (> 10 kW L$^{-1}$), mid-high energy density (> 10 Wh L$^{-1}$) and long cycle lifetime (>millions)
of supercapacitors make them attractive for many applications such as in the grid scale renewable energy storage and in hybrid electric vehicles where high energy, high power and reasonable lifetime are required.[36-39] Depending on the electrodes materials, the supercapacitors can be categorized into two types, electrochemical double-layer capacitors (EDLCs) and pseudocapacitors as shown in Figure 1-6. The hybrid capacitors are a category combined the EDLCs and pseudocapacitors. The working principle of EDLCs is based on the ions absorption/desorption at the interface of electrode and electrolyte while that of pseudocapacitors is based on the redox reactions inside the electrodes. The components, electrodes materials and some more details of supercapacitors will be discussed in the following section.

Figure 1-5. Ragone plots of different energy storage devices.[36]
The chemist started to investigate the charge storage mechanism at the interface between electrodes and electrolytes since late 18th and earlier 19 century. The first electrochemical charge storage devices based on double layer charge storage using carbon materials was patented by Becker from General Electric company in 1957. SOHIO company made the first attempt to exhibit the EDLCs with porous carbon materials using tetralkylammonium salt as electrolyte in the market place in 1969. In 1978, the Nippon Electric Company (NEC) fabricated the commercial EDLCs and used the term “supercapacitor” for the developed device. Around the same time, Panasonic developed its own commercial supercapacitor cell called “Goldcap”. In the late 1970s, Prof. Conway in the University of Ottawa carried out extensive
research on another mechanism for electrochemical capacitors by introducing RuO$_2$ as electrodes materials.[41] This charge storage mechanism was based on faradic electrochemical reactions of the electrode materials and was named as pseudocapacitance. In late 90’s, the supercapacitors researches obtained tremendous attentions. They were applied in many areas from potable electronic devices to hybrid electric vehicles. Nowadays, several other companies including Maxwell technologies, Cap-XX, NNC, AVX, Cooper, ELNA, and several others have made tremendous efforts on the development of supercapacitors.

1.2.1 Main components and working principles of EDLC supercapacitor

As shown in Figure 1-7, the typical EDLC supercapacitors are composed of two porous electrodes with high surface area, two current collectors, a semi-permeable membrane as separator and an electrolyte. The separator is sandwiched by the positive and negative electrodes to prevent the electric shorting between the two. Porous activated carbon is usually as the electrodes, especially in the commercial product. Recent advancements also employ carbon nanotube, carbide-derived carbon, onion-like carbon and graphene as supercapacitor electrodes.[34, 42-48] Aqueous solutions based on acids or bases (H$_2$SO$_4$, KOH) could be used as electrolytes with limited operation voltage of around 1 V because of the electrochemical decomposition of water, although this kind of electrolytes will lead to low equivalent series resistance (ESR) and hence high power density. Organic electrolytes using propylene carbonate (PC) or Acetonitrile (An) as solvent are also used in some works with electrochemical window up to 3 V.[49, 50] Recently, Ionic Liquids (ILs) have been used because of the wide electrochemical window of 4 V to 5 V.[51-53] The working principles of EDLC supercapacitors are similar with those of dielectric capacitors with the feature of electrostatic process. During the charging process that voltage is applied, charges accumulate on the electrode surfaces. Due to the
electric field between the charged electrodes created by the applied voltage, the electrically
charged ions in the electrolyte migrate through the porous separator towards the electrodes with
opposite polarity. Hence, the separate charged double layer is produced at each electrode.

Figure 1-7. The compositions of EDLC supercapacitor cell.[54]

For the EDLC supercapacitor, following the expression of parallel-plate dielectric
capacitors, the specific capacitance $C$ (F g$^{-1}$) of each electrode is generally assumed to be
exhibited as

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$$ (1-1)

Where $\varepsilon_r$ represents the relative permittivity of electrolyte, $\varepsilon_0$ (F m$^{-1}$) is the permittivity of the
vacuum, $A$ (m$^2$ g$^{-1}$) is the specific surface area of the electrode that can be accessible to the
electrolyte ions, while $d$ (m) is the effective thickness of electrochemical double layer which is
also represented as Debye length. Compared with conventional dielectric capacitors, the EDLC
supercapacitors have much high electrode surface area to store more charges per unit weight/volume, coupled with the much smaller effective double layer thickness with only a few molecular diameters (~ nm), leading to much higher specific capacitance and energy density. Supercapacitor cells with the capacitance of 5000 F have been reported with the gravimetric energy density up to 5 Wh/kg compared to 0.5 Wh/kg of conventional capacitors. Current advanced studies have improved the energy density by several times thanks to the optimized electrodes with large surface area, electrolyte with wide electrochemical window and cell structure.

Different with the charge storage mechanism of batteries, there are no chemical reactions or compositions changes during the charge/discharge process in EDLC supercapacitors. Due to the non-faradaic processes, the charge/discharge processes in EDLC supercapacitors are highly reversible, which allows them to achieve very high cycling stabilities. There is minimal degradation even in deep discharge or overcharge. EDLC supercapacitors generally operate with stable performance characteristics for large amount of charge/discharge cycles, typically as many as $10^6$ cycles. On the other hand, the stability of electrochemical batteries is generally limited to only about $10^3$ cycles. Meanwhile, the electrochemical reactions free will lead to the fast charge/discharge processes, hence the power density of the EDLC supercapacitors will be improved largely. The extremely power density of 10 kW/kg has been achieved in commercial product. As a comparison, the power density of batteries is a few orders of magnitude lower.

The maximum energy stored and power delivered for a single supercapacitor cell can be expressed as Equations (1-2) and (1-3), respectively.

\[ E = \frac{1}{2} CV^2 \]  

(1-2)
\[ P = \frac{V^2}{4 \times ESR} \]  

where \( V \) (V) is the operation voltage, \( C \) (F) is the total series capacitance of the supercapacitor cell, and ESR is the equivalent series resistance with the unit of ohms.[55] All of these parameters are crucial to the final performance of the supercapacitor cell. The capacitance of the cell is related strongly to the electrode materials and also the interface between the electrode and electrolyte. The cell voltage is limited by electrochemical window of the electrolyte solution. The ESR can be from various types of resistances associated with the intrinsic electronic resistance of the electrode matrix and electrolyte solution, mass transfer resistance of the ions in the electrode matrix, and contact resistance of the interface between the current collector and the electrode. Hence, all of these demands, such as large specific capacitance, high operation voltage, and minimum ESR, should be satisfied simultaneously when considering the performance of a supercapacitor cell. It is thus obvious that the development of both electrode materials and the electrolyte solutions are the key factors in order to optimize and improve the overall performance of the supercapacitor cell.

The following criteria should be considered further to evaluate the performance of the supercapacitor cell. The power density should be much larger than that of batteries with acceptably high energy density (larger than 10 Wh/kg). Excellent cycle ability with more than \( 10^6 \) charge/discharge cycles should be obtained. The property of relatively high self-discharging rate compared with batteries should be optimized. Safe operation and low cost should also be considered. It should be noted that the time constant which can be expressed as internal resistance times capacitance is another important factor in evaluating the performance of a supercapacitor in terms of the leakage current and self-discharge rate.
1.2.2 Pseudocapacitor

Pseudocapacitor is based on the reversible Faradaic charge transfer processes occurring at the surface or in the bulk of the electrode.\textsuperscript{[56, 57]} The potential at which charge is being passed has a strong relationship with the charge accumulated. Unlike ideal Nernstian behavior in batteries in which the operation potential is constant and independent with the reactions, during the process in the pseudocapacitor, the charge transfer coming from these electrochemical reactions is dependent with the applied voltage. Hence, the capacitive phenomenon occurs and the working principle is not electrostatic EDLC supercapacitor. ‘pseudo’ is denoted in order to differentiate it from electrostatic capacitance. The difference in EDLCs and pseudocapacitor is shown in Figure 1-8, which means that difference depends on whether the capacitance is related with the operation potential. And the advantages and drawbacks of EDLCs and pseudocapacitors are discussed in Table 1.

![Figure 1-8. The different CV curves of pseudocapacitor and EDLC supercapacitor.](image)
Table 1-1. The advantages and drawbacks of the two supercapacitor cells.

<table>
<thead>
<tr>
<th>Electric Double Layer Capacitor</th>
<th>Pseudocapacitor</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase angle 90°</td>
<td>Phase angle 45°</td>
<td>More transmission like behavior</td>
</tr>
<tr>
<td>Low specific energy density</td>
<td>High specific energy density</td>
<td>Good capacity of charge storage</td>
</tr>
<tr>
<td>High reversibility</td>
<td>Moderate reversibility</td>
<td>Reasonably good cyclic life</td>
</tr>
<tr>
<td>Capacitance remains constant with voltage</td>
<td>Capacitance changes with voltage</td>
<td>Small leakage effect</td>
</tr>
<tr>
<td>Narrow potential window (1-3V)</td>
<td>Large potential window (1-5V)</td>
<td>Broad range of applications</td>
</tr>
<tr>
<td>High Power due to good diffusion</td>
<td>Low Power due to Kinetic limitations</td>
<td>High diffusion resistance</td>
</tr>
</tbody>
</table>

Pseudocapacitance occurs with the extent of reaction, the charge is the continue function of operation potential. Thus the pseudocapacitance can be expressed by following function

\[
C = \frac{\Delta Q}{\Delta V}
\]  

(1-4)

Where \(\Delta Q\) is the amount of charge stored and is proportional to the potential difference \(\Delta V\).

For the pseudocapacitors, there are two kinds of electrochemical reactions that can lead to charge transfers which are voltage dependent. They are adsorption of ions and redox reactions. For the former phenomenon, the ions coming from the electrolyte will occupy the surface sites of the electrodes progressively. And for the latter one, it is related to the redox process by ions and electrodes that the potential of the redox system has a logarithmic function of the oxidized and reduced activities. The two above processes are principally based on surface mechanisms. The redox pseudocapacitance can also arise from the oxidation/reduction of the conducting polymer electrode materials in which the bulk of electrode is involved the electrochemical reactions. Although the specific surface area of the conducting polymer materials is not critical for high
capacitance, relatively high surface area with micropores/mesopores plays an important role in the insertion and desertion of ions between the electrolyte and the electrode matrix. High electronic conductivity of electrodes is highly required to distribute and collect the electron current in the pseudocapacitors. Overall, Many factors can influence the performance of pseudocapacitors, such as the specific surface area of the electrodes, the porosity of materials, the conductivity of electrodes, particle sizes, electrolyte and design of cell. Generally the capacitance of pseudocapacitors shows much more compared with that of EDLC supercapacitors. Meanwhile there are some drawbacks that cannot be neglected such as cycle retention and reliability of a device.

1.2.3 Electrode materials

The selection of electrode materials is significant to determine the electrochemical performance of supercapacitors. Due to surface process in the supercapacitor cells, especially in the EDLCs, the surface characteristics in the electrodes greatly influence the capacitance. Carbon materials are widely used currently as cell electrodes including the electrodes in the commercial products. The considerable research of transition metal oxides and conducting polymer are also conducted widely nowadays.

Thanks to various advantages including high specific surface area, high conductivity, low cost, good thermal and chemical stability, and environmental friendliness, carbon materials have gained considerable interests in the past decades. High specific surface area is highly desired for the carbon materials with the order of 1000 m²/g as well as electrode conductivity to be optimal for today’s state of the art supercapacitor cells. Although the surface area can be increased generally by adjusting the porosity of the carbon materials, the specific capacitance does not
need to have direct proportional relationship to the surface area of the electrode. Charge is stored in the pores at the interface between the electrolyte and carbon electrode. If the ions in the electrolyte cannot access in the pores, this part of surface area cannot contribute to the specific capacitance. Therefore, the surface area that can be occupied by ions is the ultimate factor to influence the capacitor, rather than simply emphasizing a high surface area. In other words, the pore size distribution of the carbon materials is crucial to the electrochemical performance of supercapacitors. Hence, treatment of carbon materials is significant to make the pore size suitable for the electrolyte ions transport and storage and thereby ensure the pore size distribution to be optimal depending on the size of ions. In the past several years, many research groups have investigated different ways to control the porosity in the mesoporous range (2 to 10 nm) and microporous range (below 2 nm) to maximize the capacitance.

Figure 1-9. Normalized capacitance change as a function of the pore size of carbon derived-carbide samples.
Figure 1-9 shows a study using a solvent free electrolyte in which both cation EMI+ and anion TFSI have a maximum size of around 0.7 nm.[33] The carbide-derived carbon was used as the electrodes. It could be found that the maximum capacitance was achieved with the pore size around 0.7 nm, demonstrating a strong correlation between the capacitance and the match of pore size and ion size.

So far there are several forms of carbon for the supercapacitor electrodes such as activated carbon (AC), carbon nanotubes (CNTs), carbon aerogels and graphene existing with various micro textures (fibers, powers, fabrics, foams, nanocomposites) in different dimensionality from 0 to 3D, as shown in Figure 1-10.

Figure 1-10. Schematic of carbon family from 0 to 3 dimensions.
Table 2 compares the capacitances and diverse physical properties of different carbon and carbon-based materials.

**Table 1-2.** Capacitances and physical properties of carbon or carbon based materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>SSA (m²/g)</th>
<th>Density (g/cm³)</th>
<th>Specific capacitance in aqueous electrolyte</th>
<th>Specific capacitance in organic electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbons (ACs)</td>
<td>1000-3500</td>
<td>0.4-0.7</td>
<td>&lt;200</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Particulate carbon from SiC/TiC</td>
<td>1000-2000</td>
<td>0.5-0.7</td>
<td>170-220</td>
<td>100-120</td>
</tr>
<tr>
<td>Functionalized porous carbons</td>
<td>300-2200</td>
<td>0.5-0.9</td>
<td>&lt;120</td>
<td>90</td>
</tr>
<tr>
<td>Carbon nanotube (CNT)</td>
<td>500-1315</td>
<td>0.6</td>
<td>50-100</td>
<td>&lt;60</td>
</tr>
<tr>
<td>Templated carbons (TC)</td>
<td>500-3000</td>
<td>0.5-1</td>
<td>120-350</td>
<td>100-140</td>
</tr>
<tr>
<td>Activated carbon fibers (ACF)</td>
<td>1000-3000</td>
<td>0.3-0.8</td>
<td>120-370</td>
<td>80-200</td>
</tr>
<tr>
<td>Carbon cloth</td>
<td>2500</td>
<td>0.4</td>
<td>100-200</td>
<td>24-40</td>
</tr>
<tr>
<td>Carbon aerogels</td>
<td>400-1000</td>
<td>0.5-0.7</td>
<td>100-125</td>
<td>&lt;80</td>
</tr>
<tr>
<td>TC–RuO₂ composite</td>
<td>600</td>
<td>1</td>
<td>630</td>
<td>&lt;630</td>
</tr>
<tr>
<td>CNT–MnO₂ composite</td>
<td>234</td>
<td>1.5</td>
<td>199</td>
<td>&lt;300</td>
</tr>
<tr>
<td>AC–polyaniline composite</td>
<td>1000</td>
<td>-</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td>Graphene</td>
<td>1000-3000</td>
<td>0.3-0.7</td>
<td>100-140</td>
<td>&lt;150</td>
</tr>
</tbody>
</table>

*: data not reported

AC is a widely developed material for the supercapacitor electrodes due to the highly economic fabrication process, high mechanical property and high specific surface area. The activation process of AC is usually based on physical, chemical or electrochemical methods. High surface area electrode materials with the randomly sized porous matrix can be obtained by activation processes. The resulting overall accessible surface area activated carbon is in the range
of 500 to 3000 m²/g, which leads to the specific capacitance range from 50 to 100 F/g in both aqueous and organic electrolytes. Some binders are usually required in AC powders to fabricate electrode films. However, these inactive components occupying a significant fraction of the total electrode weight will attribute to relatively low specific capacitance and energy density. Meanwhile, the control of pore size distribution and pore structure in the AC electrodes is still a challenge.

Besides activated carbons, carbon aerogels have also attracted many interests for the electrode materials of supercapacitor cells. Aerogels is a kind of suspension of carbon nanoparticles with low density within a gel where the liquid components of gel are replaced by gas. There are several advantages of carbon aerogels compared with AC. The uniform particles and mesopores, as well as the interconnected pore structure, leads to low ESR, high power and high specific capacitance although the specific surface area is relatively lower (400 - 900 m²/g). Meanwhile, the binder free structure can improve the capacitance, cycle life and power density further, making carbon aerogels as promising supercapacitor electrode materials.

CNTs have become another option of electrode materials for the supercapacitor cells due to their unique nanostructure and remarkable properties such as high specific surface area, high electrical conductivity and interconnectivity, unique pore structure and chemical stability. CNTs can be classified in two types that are single wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs), depending on the synthesis methods. The first supercapacitor cell based on CNTs electrodes was reported in 1997 by Niu et al.[58] The functionalized CNTs with nitric acid were fabricated and the specific capacitance of 102 F/g and energy density of 0.5 Wh/kg in a sulfuric acid solution were obtained. Ever since, many significant research have been developed on the optimization of nanotubes to improve the electrochemical performance of
assembled cell. However, the rate of improvement is still limited and the cycling stability is a problem. Recent highlights of supercapacitor research based on CNTs focus on the nano-engineering of nanotube forests with dense, nano ordered, or vertically aligned nanostructure. For example, Futaba et al. fabricated SWCNT-based electrode with aligned nanostructure and a specific capacitance of 80 F/g was obtained in 1 M Et$_4$NBF$_4$/PC electrolyte.[59] The vertical aligned nanostructure provides regular pore structure and high specific surface area to improve the electrochemical performance of cells, such as low ESR, low ion diffusion resistance, high life cycles and much high power density. However, there are still some limitations in the supercapacitor cells based on aligned carbon nanotubes (A-CNTs), that will influence the real application in the market. One of those is that the density of as-grown A-CNTs is very low (around 0.1 g/cm$^3$) so that the volumetric electrochemical performance of the cells is influenced a lot. Although there are several methods to densify the nanotube forests such as liquids collapse, the volume fractions (Vf) of forests cannot be controlled precisely and some of the arrays are sacrificed. These issues will be discussed further in Chapter 3 by introducing a unique densification method to control the Vf from 1% to 40% without scarification. Meanwhile, the supercapacitor cell with this method shows significant enhanced volumetric specific capacitance, low ESR, high cycle lifetime and high energy and power densities.

Graphene is a promising electrode material with many attractive properties, such as large theoretical specific surface area (2630 m$^2$/g), high Young’s modulus (~1.1 TPa), high intrinsic mobility (200,000 cm$^2$V$^{-1}$s$^{-1}$) and high thermal conductivity (~5,000 W/mK). The large theoretical specific surface area attracts plenty of interests on developing graphene electrodes for supercapacitor cells. The first graphene-based supercapacitor cell was reported in 2006 in a U. S. Patent Application by Jang’s group where the exfoliated graphite flakes were deployed as
supercapacitor electrodes.[60] From that time, several groups have devoted their attentions on utilizing graphene materials for supercapacitor applications with different configurations.[61-75] Many methods have been used in fabricating graphene sheets as electrode materials including mechanical cleavage of graphite,[76] unzipping carbon nanotubes,[77] chemical exfoliation of graphite,[78] solvothermal synthesis,[79] chemical vapor deposition,[80] etc. Stoller et al. utilized chemically modified graphene (CMG) sheets as supercapacitor electrode and the specific capacitance of 135 and 99 F/g in aqueous and organic electrolytes were obtained, respectively.[81] Vivekchand et al. fabricated graphene through a thermal exfoliation of graphene oxide (GO) and obtained specific capacitance of 117 F/g in an aqueous H$_2$SO$_4$ electrolyte.[62] Zhu et al. fabricated microwave exfoliated GO (MEGO) as electrodes with specific surface area up to 3100 m$^2$/g.[47] The specific capacitance of 166 F/g was achieved with 1-butyl-3-methyl-imidazolium tetrafluoroborate (BMIBF$_4$)/acetone nitrile (AN) as electrolyte. In addition, graphene/metal oxide and graphene/conducting polymer composites have also been investigated as supercapacitor electrodes with very high specific capacitance up to 1000 F/g. Although graphene-based electrodes have exhibited some excellent properties, they still suffer from various limitations such as re-stacking, random nanomorphology, low density, etc. We will discuss and try to overcome these shortcomings in the following chapters.

Transition metal oxides are attractive candidates for electrode materials in supercapacitor cells due to their high specific capacitances and low resistances. Utilizing of metal oxides in pseudocapacitance research has been started with ruthenium oxides (RuO$_2$). Since 1970, RuO$_2$ as electrode was investigated extensively because of its excellent pseudocapacitive and stability characteristics. So far, the supercapacitor cells based on RuO$_2$ as electrodes in an aqueous system has exhibited the specific capacitance as high as 1000 F/g in H$_2$SO$_4$ electrolyte at room
temperature. However, this kind of material is a noble metal and far too expensive to be applied for many commercial products. Most of the early work on RuO$_2$ was conducted for military applications, where cost was of less concern. Current academic works mainly focus on some lower cost metal oxides to be deployed in more practical supercapacitor cells. Candidates of oxides of manganese, iron, nickel and cobalt are considered potential materials for the supercapacitor electrodes due to low cost, environmental friendliness, high theoretical specific capacitance more than 1000 F/g, and excellent capacitive behavior. Vanadium oxides are another class of metal oxides that attract many attentions as a low-cost alternative to ruthenium oxides for supercapacitor cells. The electrochemical characteristics are strongly related to the broad range of morphologies and their discharging curves of supercapacitor cells demonstrate a typical capacitive-like behavior. There are still some concerns that should be considered by utilizing metal oxides as pseudocapacitors, such as electrolyte limitation and short cycle lifetime.

Conducting polymers offer a new possible choice for supercapacitors electrode. The storage of charges is performed through redox processes. Ions are transferred to the polymer backbone when oxidation occurs, that is the doping process. Meanwhile the dedoping process can be described that the ions are released back into the electrolyte when reduction occurs. During the charging process, the ions are charged not just on the surface of the conducting polymers as in the case with carbon but throughout the bulk volume of the electrodes. The high levels of specific capacitance can be obtained due to this working principle. The most common types of conducting polymers used in supercapacitor cells are polyaniline (PANI), poly (3, 4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPY), polythiophene (PTh), poly(3-arylthiophene), poly-3-(3,4-difluorophenyl) thiophene, poly-3-(4-cyanophenyl) thiophene, poly-(3-parafuorophenyl)thiophene and poly[bis(phenylamino)disulfide].[82-92] The
charging/discharging mechanism in conducting polymers can be classified to n type and p type. One of the shortcoming of using conducting polymers as electrodes is that the volume of electrode will change a lot during charging/discharging process, leading to poor cycle retention. We will discuss this shortcoming and provide our solution in the following chapters.

**Figure 1-11.** Specific capacitances of various supercapacitor electrode materials.

It should be mentioned that the hybrid composite materials, made of one or more materials including metal oxides, CNTs, graphene, activated carbon and conducting polymers as supercapacitor electrodes have also been studied in order to exploit the full advantage of pseudocapacitor materials and hence to improve the performance of a device. Figure 1-11 summarizes the specific capacitances reported based on different supercapacitor materials in the literature.
1.2.4 Electrolytes

The choice of electrolyte for a supercapacitor cell is as significant as that of the electrode material. The operation potential of a supercapacitor cell will depend on the breakdown voltage of the interface between electrode and electrolyte, and hence the energy density has strong relationship with the electrolyte. Meanwhile, the power density is related with the ESR and ion diffusion resistance, which are strongly dependent on the conductivity electrolyte. There are mainly two types of electrolyte in use in supercapacitor cells including aqueous and organic solutions.

Supercapacitors based on aqueous electrolytes exhibit higher specific capacitance compared to those using organic electrolytes because of the smaller size and higher mobility of ions in aqueous electrolytes. However, due to the thermodynamic decomposition of water solvent, the electrochemical potential window for the supercapacitors using aqueous electrolytes is limited to around 1 V. In contrast, the organic electrolytes can provide a much wider operation voltage window (more than 2 V) for supercapacitors. Organic electrolytes based on aprotic solvents such as AN or PC have been widely used in the academic and commercial supercapacitor cells. On the other hand, organic electrolytes also suffer from some disadvantages including high cost, flammability, low conductivity, and toxicity.

As a class of promising electrolytes for the supercapacitor cells, ionic liquids (IL), known as room temperature molten salts, have attracted much attention due to large electrochemical stability range (up to 6 V) in addition to the high thermal and environmental stability, low melting point and high ion conductivity. Several studies recently have shown that the CNTs-based or graphene based supercapacitors using BMIBF$_4$ or 1-ethyl-3-
methylimidazolium tetrafluoroborate (EMIBF₄) as electrolyte provide a specific capacitance of more than 150 F/g with the cell voltage of more than 3 V. \cite{47, 93, 94} In this dissertation, most of our supercapacitors cells are based on ILs to enhance the electrochemical performance of these cells.

1.3 Research contribution and dissertation organization

This dissertation develops an in-depth understanding of the working mechanism in energy storage devices, specifically in supercapacitors and provides solutions to improve the electrochemical performance, including specific capacitance, energy density, power density and cycle life.

In Chapter 2, important parameters, characterization methods, experiments and characterization set-ups will be introduced. For the commercial supercapacitor products, activated carbon is usually used as electrode which has the tortuous ion transport pathways influencing ion transport. In Chapter 3, A-CNTs were used to replace the activated carbon electrodes. The superior electrical conductivity and parallel ion pathways formed by A-CNTs lead to high electrochemical performance of as-assembled supercapacitor cells. A unique mechanical densification method was used to allow the density of A-CNTs to be tuned precisely over a broad range from 1% volume fraction (Vf) to 40% Vf while preserving the straight ion pathway between A-CNTs.

In order to improve the specific capacitance of supercapacitor electrode further, the incorporation of pseudocapacitive material PEDOT in the hybrid electrodes is introduced in Chapter 4. PEDOT electrodes can store larger amount of charges per unit compared with EDLC supercapacitor cells do because the whole bulk (not only the surface) of PEDOT has involved the
electrochemical reactions. The conformal coating of PEDOT on A-CNTs can exhibit long cycle life compared with pure PEDOT or PEDOT coated on random CNTs since the A-CNTs can provide a mechanical structure to absorb the large volume change of PEDOT during the charge and discharge processes.

In Chapter 5 and Chapter 6, high performance asymmetric supercapacitor cells are investigated. The energy density and maximum power density of supercapacitor cells are strongly dependent on the operation potential which is limited by the electrochemical window of the interface between electrode and electrolyte. Although the pseudocapacitors can bring relatively larger specific capacitance, the electrochemical window with electrolyte is very narrow (2 V even for organic electrolyte). In order to expand the operation potential, the asymmetric configuration was introduced in the supercapacitor cell. The positive and negative electrodes materials are individually tailored and work synergistically together in the asymmetric cell configuration so that the cell can be operated under a high operation voltage of 4 V to achieve energy and power densities with a long cycle life.

In Chapter 7, the supercapacitor cells, replacing the piezoelectric and pyroelectric material, are used for the mechanical and thermal energy harvesting devices, due to the high specific capacitance and electric energy density and their strong dependence on stress (pressure) or temperature.

Finally, conclusions of this dissertation and the suggestions for future works are presented in Chapter 7.
In this chapter, a brief introduction to this dissertation work on experiments is provided. A list of symbols containing most parameters exhibited in this dissertation is presented in Section 2.1. In Section 2.2, several typical electrochemical characterization methods are introduced. Finally, Section 2.3 provides some details of characterization tools and set-ups such as electrochemical measurements tools, optical measurements and thermal analysis, etc.

2.1 List of symbols

Table 2-1 exhibits all the symbols that are frequently used in this dissertation. The ones that are not listed in the table will be explained as they appear.

Table 2-1. List of symbols and their meanings.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance or concentration</td>
</tr>
<tr>
<td>d</td>
<td>Distance</td>
</tr>
<tr>
<td>dl(subscript)</td>
<td>Double layer</td>
</tr>
<tr>
<td>e(subscript)</td>
<td>Effective layer or electrical</td>
</tr>
<tr>
<td>I</td>
<td>Momentum of inertia or Current</td>
</tr>
<tr>
<td>j</td>
<td>Imaginary unit</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
</tr>
<tr>
<td>Q</td>
<td>Charge</td>
</tr>
<tr>
<td>R</td>
<td>Radius or Resistance</td>
</tr>
</tbody>
</table>
\( t \) Thickness or Time
\( E \) Energy
\( V \) Voltage or Volume
\( V_f \) Volume fraction
\( w \) Width
\( wt \) Weight
\( Z \) Electrical complex impedance
\( \varepsilon_0 \) Vacuum permittivity
\( \varepsilon_R \) Relative permittivity
\( \phi \) Complex impedance phase angle
\( \omega \) Angular frequency \((2\pi f)\)
\( \tau \) Time constant
\( \sigma \) Conductivity
\( \mu \) Mobility
\( \rho \) Density
\( \eta \) Efficiency

### 2.2 Electrochemical characterization

The characterization methods on the performance of a supercapacitor cell have to be quantitative and effective in order to make direct comparisons among different devices and technologies, which can also provide directions to improve the device performance. There are several standard characterized techniques that can be used to study energy storage systems including cyclic voltammetry, galvanostatic charge/discharge (constant current charge/discharge) and electrochemical impedance analysis. We will briefly introduce the fundamental principles of these methods and discuss some significant parameters related to these methods in this section.
2.2.1 Cyclic voltammetry

Cyclic voltammetry (CV) is one of the most widely used techniques in electrochemistry to study the EDLC cells as well as pseudocapacitors due to its simplicity and versatility. It provides both quantitative and qualitative information of the electrochemical system in details. In this technique, the current density at the interface between working electrode and electrolyte is monitored as a relationship with the operation potential which is being swept over a given voltage range at a constant scan rate. This dynamic parameter, rate of the potential cycling can be variable depending on different reactions, is expressed as the unit of mV/s. Overall, this characterization method is used to evaluate whether the electrochemical system is stable and the degree of reversibility of the ion absorption/desorption or electrode reactions. Specifically, for the EDLC supercapacitor, the obtained voltammograms can be used to investigate how close the cell is to the ideal capacitor which has a very low ESR. Meanwhile for the pseudocapacitor, the CV curves reveal the information related to the electrochemical potentials at which the oxidation and reduction processes occur, and how fast these processes can occur. The scan rates, switching potentials, as well as anodic peak potential and cathodic peak potential, the magnitudes of the anodic peak current, cathodic peak current, are the significant parameters of cyclic voltammetry measurements. Furthermore, CV curve can be deployed to investigate the property of stability of the cell during multiple charge/discharge cycles. Meanwhile, the CV curves obtained under different scan rates are often exhibited on the same graph to demonstrate the rate of charging and discharging characteristics corresponding to different power levels. Faster scan rates indicate the higher power levels.

For the supercapacitor with ideal capacitive property, the relationship between current and scan rate can be expressed as (assuming that the capacitance will not change with the operation potential)
where $dV/dt$ represents the scan rate of linear voltage ramp. An ideal EDLC supercapacitor cell (ESR=0) is expressed in the form of rectangular of CV characteristic shown in Figure 2-1. [95]

![Figure 2-1. Schematic CV curves for ideal EDLC, EDLC with resistance and cells based on carbon materials with chemical reactions.](image)

In an ideal supercapacitor, the sign of the current is immediately reversed with the reversal of the potential sweep, showing that it is a purely electrostatic process and the current is independent of the operation potential. However, there will be a rise of the current with the potential because of the ESR in the real cell as shown in Figure 2-1. The larger ESR the supercapacitor cell has, the more distortion the CV curve will be have. For the pseudocapacitor, a large deviation from the rectangular shape and reversible redox peaks related to the electrochemical reactions can be found in the CV curve as also shown in Figure 2-1. In this kind
of cell, the charge accumulated in the capacitor is strongly dependent on the potential applied to
the electrodes. [95, 96]

**Figure 2-2.** Specific capacitance calculation from CV curve.

Based on the CV curves, the capacitance can be calculated by integrating the discharge
part of CV curve and then divide it by scan rate and operation voltage as shown in the following
equation and Figure 2-2. [97]

\[
C = \frac{\int I dV}{\Delta V \times S}
\]

(2-1)

where \( I \) is the current, \( V \) is the potential, \( \Delta V \) is the potential range and \( S \) is the scan rate.

**2.2.2 Galvanostatic charge/discharge**

Galvanostatic charge/discharge characterization method, also known as constant current
charge/discharge, is one of the standard and widely used techniques in evaluating the
electrochemical capacitive performance and cycle retention property of supercapacitor. The
capacitance and resistance values can be determined quantitatively for such cells. In this experiment, a constant current is applied across the electrochemical cell between the two electrodes. The potential is monitored until a final set voltage is reached (charge process) and afterwards the cycle reverses to reach the initial set potential (discharge process) under the same current with opposite sign. The results for this experiment are plotted for the potential of cell as a function of time that is shown in Figure 2-3a for example.

![Figure 2-3](image)

**Figure 2-3.** (a) A typical galvanostatic charge/discharge curve (b) The IR drop region at the transmission from charge curve to discharge curve.

Based on the discharge half part of this potential-time curve, the gravimetric specific capacitance of electrode can be expressed as (Assuming the capacitance and mass of two electrodes are the same):

\[
C = \frac{I}{m \times \frac{dV}{dt}}
\]  

(2-2)

where I is the applied constant current, m is the active materials mass of the two electrodes and \(dV/dt\) is the slope of the discharge potential-time curve (marked as the red line). The volumetric
specific capacitance can be determined by multiplying the gravimetric capacitance by the electrode density. Similar to the CV characterization method, different currents are usually applied on the cell to investigate the responses to different power levels in order to meet different demands. It should be mentioned that there is a voltage drop also called IR drop at the beginning of the discharge curve as shown in Figure 2-3b. The IR drop can be calculated as

\[ V = \Delta I \times ESR \] (2-3)

where \( \Delta I \) is the current change from the positive constant current to the negative constant current. For example, if a current of 1 A is applied during the charge process and that of -1 A is applied during the discharge process, \( \Delta I \) equals 2 A.[97]

From the galvanostatic charge/discharge curve, the amount of charge stored or released during the charge/discharge process can be calculated by:

\[ Q = I \times \Delta t \] (2-4)

where \( \Delta t \) is either the charge or discharge time. It is obvious that the amount of charge during each complete cycle can be calculated by measuring the time for that cycle.

Another important characteristic in evaluating the electrochemical performance of supercapacitor cell is the coloumbic efficiency which is the ratio between the amount of charge that can be released during the discharge process and the amount of charge that enters in the cell during the charge process. The coloumbic efficiency can be expressed as

\[ \eta = \frac{Q_d}{Q_c} = \frac{\Delta t_d}{\Delta t_c} \] (2-5)
where $\Delta t_d$ and $\Delta t_c$ are the discharge and charge time in the galvanostatic curve, respectively.[97] This characteristic is used to investigate the charge or energy loss during the charge/discharge process.

The energy stored in the supercapacitor cell can also be obtained from the galvanostatic discharge curve given by the formula below:

$$E = \int I dV$$

(2-6)

Then the gravimetric or volumetric energy density can be calculated by dividing the obtained energy by mass or the volume of the two electrodes.

2.2.3 Electrochemical impedance analysis

In the electrochemical devices, impedance analysis is a powerful characterization method to evaluate the complex ratio of the voltage to the current in an alternating current signal with different frequencies. It will provide the information about charge dynamics of mobile charge either in the bulk or in the interfacial between electrode and electrolyte. In this experiment, the impedance of an electrochemical cell is measured by applying a low amplitude alternative voltage $\Delta V$ to steady state potential $V_s$, with the relationship as follows:

$$\Delta V(\omega) = \Delta V_{max} e^{j\omega t}$$

(2-7)

where $\omega$ is the angular frequency, $\Delta V_{max}$ is the signal amplitude and $t$ is the time. Then this input signal leads to a sinusoidal output current which can be expressed as

$$\Delta I(\omega) = \Delta I_{max} e^{j(\omega t + \phi)}$$

(2-8)

where $\Delta I_{max}$ is the signal amplitude and $\phi$ is the phase angel of the obtained current versus voltage. Hence the electrochemical impedance can be calculated as
\[ Z(\omega) = \frac{kV}{\Delta l} = |Z(\omega)|e^{-j\varphi} = Z'(\omega) + jZ''(\omega) \] (2-9)

where \( Z'(\omega) \) is real part of the electrochemical impedance and \( Z''(\omega) \) is the imaginary part of the impedance. Hence the impedance of the cell can be defined as

\[ |Z(\omega)|^2 = Z'^2 + Z''^2 \] (2-10)

Considering the simple equivalent circuit of supercapacitor cell shown in Figure 2-4 in which the frequency of cell can be described to associate a serial resistance \( R_s \) and the cell capacitor \( C \).

\[ Z = R_s + \frac{1}{jC \times \omega} \] (2-11)

\( Z \) is often represented in the so-called Nyquist plot, where the \( Z'' \) is plotted as a function of the real part \( Z' \) with different frequencies. Since equivalent circuit models can be used to investigate the contributions of various components in the electrochemical system on the impedance behavior of the cell, they have been widely used to analyze the Nyquist plot.[97]
Figure 2-5. Frequency-response behaviors for different equivalent circuits of supercapacitor cells.

As exhibited in Figure 2-5, modeled Nyquist plots shape can be various forms from simple lines to complex multi-component plots depending on the chosen equivalent circuit models. For an ideal capacitor that there is no serial resistance, the Nyquist plot is only a vertical line along the $Z''$ axis. Considering the capacitor in series with a resistor, a vertical line parallel to the $Z''$ axis intersecting $Z'$ axis at an equal value to the serial resistance of $R_s$ could be found in the Nyquist plot. For the more realistic equivalent circuit models, a
A semicircle is exhibited at the high frequency region and the plot intersects the $Z'$ axis at the value equal to the series resistance. Depending on the interface between electrodes and electrolyte as well as ion propagation behavior in the porous electrode, the size of this semicircle can be different, which provides information on the ion distribution mechanisms in the electrochemical system. Basically, the size of semicircle is related to the ion diffusion resistance of $R_F$ as shown in the figure. We will discuss the Nyquist plots of our devices in details in the following several chapters. From the impedance data for the ideal case, the real and imaginary capacitance can be expressed as:

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2}$$ (2-12)

$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2}$$ (2-13)

### 2.3 Characterization set-ups

#### 2.3.1 Electrochemical characterization set-ups

In this dissertation, both three-electrode and two-electrode measurements were performed to investigate the electrochemical performance of single electrode and the cell. For the three-electrode configuration, DropSens screen-printed electrode chips shown in Figure 2-6 were used for the experiments.
As shown in the figure, the electrode attached on the inner platinum circle was used as the working electrode, the outer platinum circle was used as the counter electrode and the silver circle was used as the reference electrode. All the electrodes were immersed in the electrolyte in the N₂ atmosphere to evaluate the electrochemical performance of single electrode. For the two-electrode configuration that mainly was employed to investigate the performance of the entire cell, a home-made split test cell and coin cell were used as shown in Figure 2-7(a) and Figure 2-7(b), respectively. The current collectors were deposited a thin layer of gold to optimize the electrical contact between current collectors and electrodes.
Both systems were connected to a Princeton Applied Research PARSTAT 2273 Potentiostat shown in Figure 2-8a with PowerSuit software to investigate the impedance performance of the electrodes and cells, both with or without a biased voltage. This equipment has the built-in analyzer from 10 μHz to 1MHz. The CV characterization method was also employed in this equipment. In order to evaluate the galvanostatic charge/discharge cycling performance of the samples, a Princeton Applied Research Versastat 4 Potentiostat with VersaStudio software was employed as shown in Figure 2-8b. We will provide more details of
each instrument in different chapters. It should be noted that all the experiments were performed in the glove box filled with N\textsubscript{2} to remove with moisture and other impurities.

![Image of the PARSTAT 2273 and VersaSTAT 4 electrochemical test instruments.]

**Figure 2-8.** (a) PARSTAT 2273 and (b) VersaSTAT 4 for electrochemical test.

### 2.3.2 Scanning electron microscope (SEM)

SEM is widely used to study the micro- or nano-structures of active materials. The images can be obtained by scanning the surface of material with a high energy beam of electrons in a raster scan pattern. In this dissertation, a FEI NanoSEM 630 FESEM, as shown in Figure 2-9, was used to get the SEM images of A\textsuperscript{-}CNTs and activated graphene. Field emission gun provides the source that can improve the resolution up to around 1.7 nm using back scattered electron detector.
2.3.3 Thermogravimetric analysis (TGA)

A TA Instruments 2050 TGA was employed to determine the polymer content in the composite electrode of conducting polymer/A-CNTs samples from room temperature to 800 °C. The coating thickness of conducting polymer on the nanotube could be determined based on the weight ratio of polymer and A-CNTs. Different coating thickness was studied to investigate the working principles of doping/dedoping of conducting polymer.

2.3.4 Activation of electrode materials

Activation of supercapacitor electrode material was performed inside a quartz tube furnace (MTI GSL 1100X) that can be used to heat treat small samples up to around 1100°C shown in Figure 2-10. This kind of furnace can be programmed up to 30 steps of heating, dwelling and cooling steps with temperature accuracy of +/- 1 °C. A nitrogen or
argon inlet was connected to the furnace’s flange in order to control the atmosphere inside the furnace with accurate gas flow rate.

Figure 2-10. MTI GSL-1100X tube furnace.
Chapter 3

Supercapacitors Based on Ultra high density Aligned Carbon Nanotubes

In this chapter, EDLC supercapacitors using ultra-high density A-CNTs as electrodes with controlled nanomorphology will be investigated. The superior electrical conductivity and parallel ion transport pathways formed by A-CNTs lead to high electrochemical performance of the supercapacitor cells. To achieve high volumetric energy and power densities, the low volume density of the as-synthesized A-CNT (<5%) should be densified. In this chapter, we demonstrate a mechanical densification method that allows the density of A-CNTs to be tuned precisely over a broad range while preserving the straight ion pathway between A-CNTs. The supercapacitors fabricated from 40% volumetric fraction (Vf) of A-CNTs as the electrodes with the thickness of 0.8 mm exhibit a power density of 25 kW L$^{-1}$ (50 kW kg$^{-1}$), which is much higher than that of the A-CNTs electrodes with similar thickness fabricated by other methods and that of activated carbon electrodes.

3.1 Introduction

As we mentioned in Chapter 1, due to their excellent electrical, mechanical and thermal properties, CNTs have attracted a lot of attentions since 1990s for the various applications, such as clothes and sports gear, semiconductor materials and high-tech equipment.[98-105] Depending on shell number of graphene sheets of the CNT, the nanotubes could be classified into SWCNT and MWCNT. SWCNTs technically can be defined as a cylinder fabricated by rolling a sheet of graphene as shown in Figure 3-1. The range of diameter of the nanotube can vary from 0.7 nm to 3 nm which depends on the direction of rolling. As shown in Figure 3-1, a
pair of indices \((n, m)\) can be used to determine the rolling direction of the graphene. The zigzag nanotubes can be formed when \(m=0\) while armchair nanotubes can be formed when \(n=m\). For other situations, nanotubes are called chiral.

**Figure 3-1.** Schematic figure of how to "roll up" graphene sheet to nanotube.

Recent advances in A-CNTs have demonstrated many attractive features as the nanoporous electrodes for supercapacitors. The superior electrical conductivity of the A-CNTs and the parallel ion pathways formed by the A-CNTs reduce the electric resistance and improve the ion transport, as schematically illustrated in Figure 3-2 with a comparison with randomly arranged nanoporous electrodes, such as those constructed from the activated carbons, which possess tortuous ion transport pathways.[43, 106-111] Consequently, supercapacitor cells with
A-CNTs exhibit much less equivalent series resistance (ESR) values and have the potential to achieve much higher power and energy density than the supercapacitors fabricated from activated carbons and randomly packed CNTs.[33, 112]

**Figure 3-2.** Schematic of the tortuous ion transport paths in nanoporous electrodes formed, for example, from the activated carbons, and parallel ion pathways in the A-CNTs.

However, as-synthesized A-CNT forests have a low nanotube volume fraction (< 5%) and direct use of the A-CNT forests for the supercapacitor electrodes will lead to low volumetric electrochemical performance because of the low volumetric specific electrode surface area. Therefore, A-CNTs should be densified to reach higher CNT number per unit area in order to fully realize high volumetric power and energy density of the devices which are critical for a broad range application in electric and electronic systems which require compact device size and increased functions within a limited device volume.
In the past decade, several groups have worked on approaches to densify the as-grown A-CNTs to high CNT density in order to achieve high volumetric capacitance, energy density, and power density. For example, Futaba et al. introduced a liquid collapsing method to densify A-CNTs in which the surface tension of liquid forces the A-CNTs to collapse to a high density.[42] Compared with the liquid-induced collapse densification method, the mechanical densification method introduced in this paper for fabricating high volume fraction (Vf) A-CNT electrodes offers several advantages, including the ability to tune the density of the A-CNTs precisely, ranging from the original 1% Vf A-CNTs to more than 40% Vf, while maintaining the nanomorphology of the A-CNTs. Hence this method provides a realistic approach for large scale manufacturing of supercapacitors employing A-CNTs with desired volume fraction while preserving the nanomorphology of the easy ion transport pathways.

It is significant to mention what is the distinction between gravimetric and volumetric electrochemical performance of supercapacitor cell and why we should emphasize the volumetric performance in this dissertation. Although gravimetric properties are used to evaluate the performance of cells in many recent publications, the volumetric properties are the more accurate parameters to investigate the real performance of the cells. Gogotsi et al. discussed these claims as shown in Figure 3-3. It could be found that the reporting data based on the weight of only the active material cannot give a clear picture on the electrochemical performance of the real cell.[113] The reason is that an assembled cell contains not only the active material, but also separator, electrolyte, binder, current collectors and packaging. The active electrode materials are usually assumed to occupy only around 30% of the total weight considering a packaged commercial device. Hence, the factor of 3 to 4 has to be taken into consideration in
evaluating the supercapacitor cell performance based on the active electrode materials performance.

**Figure 3-3.** Ragone plot of the gravimetric performance of cell based on carbon material and the realistic data obtained from this plot.

For example, if the active material system shows an energy density of 20 Wh/kg as indicated by the green curves in Figure 3-3, only 5 Wh/kg can be achieved for the packaged device as shown in the blue curve in Figure. Moreover, because the thickness of commercial supercapacitor electrode is around 200 μm, an additional factor of 4 to 5 is also used to investigate the film performance for the reported sample with the thickness of electrode as 50 μm. If the same material system exhibited the energy density of 20 Wh/kg, the value of real device performance will then be further decreased to around 1.5 Wh/kg as shown in the pink curve in Figure 3-3.[44, 113] Hence, it is not accurate to take into consideration of
only the weight for the active electrode material to report the real device performance. On the other hand, it is highly desired to consider volumetric properties to evaluate the real electrochemical performance of real assembled device. For example, one kind of graphene material with normal density of 0.3 g/cm$^3$ and 20 Wh/kg for the energy density exhibits volumetric performance of 6 Wh/l, providing more accurate metric for the real assembled supercapacitor cells.

In this chapter, we report the investigation of supercapacitors fabricated from A-CNTs in the volume fraction from 1% to 40%. The supercapacitor cells based on A-CNTs with high volume fraction exhibit excellent electrochemical performance using the unique mechanical densification method. As a result, the supercapacitors fabricated from A-CNTs with 40% Vf A-CNTs exhibit volumetric and gravimetric power densities of 25 kW L$^{-1}$ and 50 kW kg$^{-1}$, respectively, for the capacitor cell with 0.8 mm thick A-CNT electrodes, compared with 1.1 kW L$^{-1}$ and 2.5 kW kg$^{-1}$ for the capacitor cell with 0.8 mm thick activated carbon electrodes and 13.4 kW L$^{-1}$ and 24 kW kg$^{-1}$ for the supercapacitors using smaller 0.5 mm thick A-CNTs densified by the liquid collapsing method.

3.2 Supercapacitor cell fabrication
3.2.1 CNT forest growth and densification
The A-CNTs here were synthesized via a modified chemical vapor deposition (CVD) method on silicon substrates using iron (Fe) on alumina as a catalyst as shown in Figure 3-4.[114] The as-grown A-CNT forests have a 1% volume fraction (Vf) of CNTs with densities of $10^9$–$10^{10}$ CNTs cm$^{-2}$. The average diameter of these CNTs is 8 nm (multiwall CNTs with 3-5 shells of walls) and the CNT-CNT spacing (center to center) is approximately 80 nm in the as-grown A-CNT forest.
Figure 3-4. Schematic of A-CNTs growth process.

<table>
<thead>
<tr>
<th>Optical Photo</th>
<th>Illustration</th>
<th>SEM Image</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Optical Photo" /></td>
<td><img src="image2" alt="Illustration" /></td>
<td><img src="image3" alt="SEM Image" /></td>
</tr>
<tr>
<td><img src="image4" alt="Optical Photo" /></td>
<td><img src="image5" alt="Illustration" /></td>
<td><img src="image6" alt="SEM Image" /></td>
</tr>
</tbody>
</table>

Figure 3-5. Optic images, schematic of mechanical densification process, and SEM images of 1% Vf and 40% Vf A-CNTs.

For the high volume fraction A-CNT fabrication, the CNT forests were released from the silicon substrate and then subjected to a mechanical biaxial densification process in two orthogonal directions as illustrated in Figure 3-5. In this method, the released A-CNT forests were placed in a specially designed sample holder. The height of the sample holder was the same as the height of the A-CNT forest so that the top and bottom of the forest remained flat during
the densification process. The A-CNT forest was densified along one direction first (see Figure 3-5) to a fixed amount using a mechanical bar, and then another mechanical bar in the orthogonal direction was used to press the A-CNT forest to the final density. (The densifications in the two directions were the same for the A-CNTs studied in this work). By varying the inter-CNT distance in densification process, A-CNT forests with different volume fractions can be achieved. The density of the 40% Vf A-CNTs is 0.52 g cm$^{-3}$, determined by directly measuring the weight and volume of the electrode (without any electrolytes).

3.2.2 Cell assembly and characterization methods

The A-CNT forests (0.8 mm thickness) were used as the electrodes of the supercapacitors. Thick A-CNT samples are easier to characterize and handle. A porous paper (> 50% porosity, 40 μm thickness) was used as the separator. An IL/ML mixture, 3 M EMI-BF4 (1-ethyl-3-methylimidazolium tetrafluoroborate) with the chemical structure shown in Figure 3-6 in PC (propylene carbonate), was used as the electrolyte which has a higher ionic conductivity compared with that of pure ionic liquid EMI-BF4.[115] The A-CNT/separator/A-CNT unit was placed between two pieces of Au coated steel plates (2 mm x 2 mm x 1.6 mm) which served as the current collectors, and the whole assembly was housed in a Teflon cell. As a comparison, supercapacitor electrodes of the activated carbon powders (Sigma-Aldrich) with 10 wt% PTFE and 10 wt% carbon black were also fabricated using the standard method repeated in the literature.[42] Since the charge/discharge times of supercapacitors depend on the electrode thickness, in addition to the electrode nanomorphology, the activated carbon electrodes and the A-CNT electrodes had the same dimensions for the supercapacitor performance comparison.
In this work, cyclic voltammetry and impedance spectroscopy were performed using a potentiostat/frequency analyzer (Parstat 2273). Galvanostatic cycling was measured with different currents using a VersaSTAT 4 (Princeton Applied Research).

3.3 Results and discussion

3.3.1 Cyclic voltammetry
The electrochemical experiments of supercapacitor cells based on A-CNTs were performed using two-electrode system in the glove box filled with nitrogen. Figure 3-7a presents the cyclic voltammetry curves at 100 mV s⁻¹ scan rate of supercapacitors with 1% Vf and 40% Vf of A-CNTs and with 3 M EMI-BF₄/PC electrolyte. As we mentioned in Chapter 1, the specific capacitance can be obtained based on the integration of the discharge part of CV curve. The data reveals that there is very little drop of the gravimetric capacitance as the A-CNT volume fraction increases from 1% Vf to 40% Vf, indicating that the densification process maintains the nanomorphology of parallel ion pathways formed by the A-CNTs. On the other hand, increasing the A-CNTs volume fraction from 1% to 40% results in a marked increase in the volumetric capacitance, as shown in Figure 3-7b.

Figure 3-6. Chemical structure of EMI-BF₄.
Since there is no faradic reaction in these supercapacitors, the curves exhibit symmetric charge and discharge rectangular shape, showing ideal capacitive behavior.

**Figure 3-7.** Electrochemical performance of supercapacitors with A-CNT electrodes and EMI-BF₄/PC electrolyte at 4 V: a) gravimetric cyclic voltammograms and b) volumetric cyclic voltammograms of A-CNT electrodes with 1% and 40% Vf at 100 mV s⁻¹. The charge and discharge cycle curves are symmetric for both volume fractions of A-CNTs.

### 3.3.2 Galvanostatic charge/discharge

The galvanostatic cycles between 0 and 4 V for the supercapacitors with 1% Vf and 40% Vf A-CNT electrodes under 1 A g⁻¹ current density are presented in Figure 3-8. The symmetric metric of charge/discharge curve exhibit the ideal capacitive behavior of A-CNTs supercapacitor cells. From the slope of the galvanostatic curves, \( dV/dt \), the capacitance of the cell can be determined:

\[
C = I / (dV/dt)
\]  

(3-1)

where \( I \) is the constant current density, \( V \) is the voltage, and \( t \) is time. Figure 3-9a and Figure 3-9b present the specific gravimetric capacitances at different discharge currents (in gravimetric units) and the volumetric capacitances at different discharge currents (in volumetric units), respectively. Although the electrodes with 1% Vf of A-CNTs show a very high specific gravimetric capacitance, > 270 F g⁻¹, their volumetric capacitance is very low (~ 3 F cm⁻³).
Figure 3-8. Galvanostatic charge discharge curves at 1 A g\(^{-1}\) for supercapacitors with electrodes of 1% and 40% Vf A-CNTs and EMI-BF\(_4\)/PC electrolyte.

Figure 3-9. a) Gravimetric and b) volumetric specific capacitance for the supercapacitors with electrodes of 1% and 40% Vf A-CNTs at different discharge rates.

It should be pointed out that the 1% Vf A-CNTs have a very low active material density of 0.013 g/cm\(^3\). For electrodes with such a low active material density, the majority of the electrode volume is filled with electrolytes whose weight is not included in evaluating the gravimetric
electrochemical performance. Hence, the gravimetric data for electrodes with very low active material density do not provide meaningful information of the practical electrochemical performance of package supercapacitors. Instead, the volumetric values should be used when comparing electrodes with large difference in the active material density. For the purpose of illustration, the gravimetric electrochemical performance data are still presented for the electrodes with 1% Vf A-CNTs besides the volumetric values. The specific volumetric capacitance of 40% Vf A-CNT electrodes is about 40 times higher than that of 1% Vf A-CNT electrodes, indicating that the mechanical densification method developed here preserves the nanomorphology of the A-CNTs.

### 3.3.3 Energy and power densities

From the capacitance and the equivalent series resistance (ESR), the power density and energy density of the supercapacitors can be obtained. The Ragone plots for the supercapacitor cells under 4 V were presented in Figure 3-10a and Figure 3-10b. The energy of the cell in each discharging cycle, $E$, is determined by integrating the discharge curves,

$$E = \int IV(t)dt$$  \hspace{1cm} (3-2)

The equivalent series resistance (ESR) is determined from

$$ESR = \Delta V / \Delta I$$  \hspace{1cm} (3-3)

where $\Delta V$ is the voltage drop as the current is switched from a positive value to a negative value, such as from 1 A g$^{-1}$ to -1 A g$^{-1}$ ($\Delta I=2$ A g$^{-1}$). The power density, hence, can be deduced from (and dividing by the cell volume or cell active materials weight to obtain the specific volumetric power density or gravimetric power density, respectively),

$$P = \frac{V^2}{4* ESR}$$  \hspace{1cm} (3-4)
We note that the active material density of the electrodes in many recently developed nanoporous electrodes, such as the A-CNT electrodes described here, can vary over a broad range.[111, 113, 116] The traditional method of evaluating the supercapacitor performance in terms of the gravimetric energy and power densities, in which the only weight of the conductive
electrode material is included, will not accurately reflect the device performance when the active material density is very low.[113] For example, due to a very large “empty space” in the ion pathway, a very high power density of 100 kW kg\(^{-1}\) was obtained in the supercapacitor with 1\% Vf A-CNT electrodes, compared with 50 kW kg\(^{-1}\) in the supercapacitor with 40\% Vf A-CNT electrodes, because only the weight of the active materials was used here in the calculations. However, if the total electrode weight including both the active materials and the electrolytes, is used to determine the device gravimetric energy and power densities, the supercapacitor with 1\% Vf A-CNTs shows a very low gravimetric energy and power density compared with that of the supercapacitor with 40\% Vf A-CNTs.

For the supercapacitors with 1\% Vf of A-CNTs, the specific gravimetric capacitance will become 4.3 F/g when the total electrode weight, including both the active material (1\% Vf) and electrolyte (99\% Vf), is used in the calculation. This is much smaller than 270 F/g deduced when only the weight of the A-CNTs is included. In contrast, for the 40\% Vf A-CNTs, a gravimetric capacitance of 270 F/g for the active material alone is equivalent to a 139.8 F/g when all the electrode weight is included. In order to make correction when comparing the electrochemical performance of electrodes with large differences in the active material densities, the gravimetric efficiency (\(\eta\)) is introduced here,

\[
\eta = \frac{M_{act}}{M_{eld}}
\]  

(3-5)

where \(M_{act}\) and \(M_{eld}\) are the weight of the active material and the total weight of the electrode (including both the electrolyte and active material), respectively. Hence, the gravimetric efficiency of the as-grown 1\% Vf A-CNTs electrode is only 1.6 \%, while that of 40\% Vf A-CNTs is 51.8\%, when EMI-BF\(_4\)/PC is used as the electrolyte in both cases. This is consistent with the data in Figure
3e which shows that the electrodes with 40% Vf A-CNTs exhibit a much higher volumetric energy density (75 Wh L\(^{-1}\)) and power density (> 25 kW L\(^{-1}\)), compared with that with 1% Vf of A-CNTs.

### 3.3.4 Cycle life

The 40% Vf A-CNTs supercapacitors also exhibit an excellent cycling life as shown in Figure 3-11.

![Figure 3-11. Cycle performance of 40% Vf A-CNTs supercapacitor with a voltage of 4 V at charge and discharge current density of 5 A g\(^{-1}\).](image)

The data was acquired over 5000 cycles by repeating the galvanostatic charge/discharge process between 0 and 4 V at a current density of 5 A g\(^{-1}\), which shows an excellent electrochemical stability of the supercapacitors of the ultra-high density A-CNTs with the retention of 98% after 5000 cycles.

### 3.3.5 Nyquist plots

To further examine the possible effect of the ultra-high density A-CNTs on the performance of supercapacitor electrodes, the electrochemical impedance spectroscopy (EIS) analysis was performed in the frequency range of 100 kHz to 10 mHz as presented in Figure 3-12.
Nyquist plots of 1% Vf and 40% Vf A-CNTs supercapacitors in the range of 100 kHz to 10 mHz.

Nyquist plots of the electrodes with 1% and 40% Vf A-CNTs show sharp rises at low frequencies and semicircles in the high frequencies. The semicircle behavior is attributed to the charge transfer resistance of the electrodes, while the sharp increase of the imaginary part at low frequencies is due to the capacitive behavior of the electrode. The electrodes with 40% Vf A-CNTs also show much smaller resistance ($Z'$) when normalized with the area of the current collector of the capacitors ($\Omega \text{cm}^{-2}$) compared with that of 1% Vf A-CNTs.

### 3.3.6 Comparison with activated carbon supercapacitor

For the comparison, the power and energy densities of the electrodes fabricated from the activated carbon with 0.8 mm electrode thickness were characterized, and the electrochemical performances are presented in Figure 3-13a and Figure 3-13b.
Figure 3-13. a) Gravimetric and b) volumetric Ragone plots of supercapacitors with electrodes of 40% Vf A-CNTs and with electrodes of activated carbon.

The activated carbon electrodes of 0.8 mm thick exhibit a much lower volumetric energy density and power density (20 Wh L$^{-1}$ and 1.1 kW L$^{-1}$, under 4 V) compared with that of the electrodes with 40% Vf of A-CNTs (75 Wh L$^{-1}$ and > 25 kW L$^{-1}$ under 4 V). The results indicate superior electrochemical performance of the ultra-high density A-CNTs electrodes fabricated from
the mechanical densification method developed here, which possess the nanomorphology of the aligned ion pathways to achieve fast charge/discharge rate and high power and energy densities.

Figure 3-13a and Figure 3-13b reveal that, while increasing the voltage from 3 V to 4 V leads to a large increase in the energy density, from 15 Wh L\(^{-1}\) to 75 Wh L\(^{-1}\) (30 Wh kg\(^{-1}\) 150 Wh kg\(^{-1}\)), there is very little increase in the power density. The large increase in the energy density is due to the increase in the specific capacitance of the electrodes with increasing voltage, as shown in Figure 3-14.

![Figure 3-14](image.png)

**Figure 3-14.** The specific capacitance of supercapacitors with 40% Vf A-CNTs under different discharge current densities.

The specific capacitance is 260 F g\(^{-1}\) (135 F cm\(^{-3}\)) at 4 V. These values are much higher than those reported earlier for the supercapacitors using A-CNTs densified by the liquid collapsing method.[22] On the other hand, the power density also depends on the ESR (see Equation (3-4)), besides the applied voltage. The results indicate that there is a large increase in the ESR as the peak voltage is increased from 3 V to 4 V, which is consistent with the results of an earlier study.[117]
The transport of mobile ion in ionic devices such as supercapacitors is through diffusion process and drifting process. Diffusion is slower and hence exhibits much higher ESR than drifting process. For supercapacitors with IL and IL/ML electrolytes, an earlier study shows that the capacitance increase at high voltages is caused mainly by the capacitance associated with the diffusion process, which also causes a large increase in ESR at high voltages.

**3.4 Conclusions**

This work demonstrates a unique method for densifying A-CNTs to extra high volume fraction while maintaining the nanomorphology of the aligned ion pathways which significantly reduce the resistance to the mobile ion transport in the electrodes. Consequently, supercapacitor cells with 40% Vf A-CNTs of 0.8 mm electrode thickness exhibits excellent electrochemical performance, including a volumetric power density and energy density of 25 kW L$^{-1}$ (50 kW kg$^{-1}$) and 75 Wh L$^{-1}$ (150 Wh kg$^{-1}$), respectively, which are much higher than that of supercapacitors with activated carbon electrodes and A-CNTs densified by liquid collapsing method. Moreover, the cell with high volume fraction A-CNTs electrodes also exhibits an excellent electrochemical stability with the capacitance retention of 98% after 5000 cycles.
Chapter 4

Conducting Polymer coated A-CNTs Composites for High Performance Supercapacitor

In the last chapter, electrodes based on A-CNTs have exhibited high electrochemical performance including high specific capacitance, energy density, power density and long cycle life. As we mentioned in Chapter 1, the specific capacitance can be improved further by introducing pseudocapacitive elements. Hence, in this chapter, conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) were employed as the electrodes of pseudocapacitor. A symmetric supercapacitors using the compacted vertically aligned CNTs coated with different thickness PEDOT as electrodes, as well as using a mixture of BMI-BF4/PC as electrolyte, was used to investigate the supercapacitor performance and configurations to achieve the highest possible specific capacitance and the volumetric energy storage density of the cell. In order to establish optimum capacitive characteristics of the composites, the capacitive characteristics of cell is investigated by means of cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge/discharge cycling. A new method was used to evaluate the cell energy loss and coulombic efficiency. The capacitive, power energy density and impedance characteristics of the composites were studied in details. Results show that supercapacitor electrodes incorporating PEDOT on A-CNTs surface exhibits excellent electrochemical properties with higher specific capacitance, better rate capability and higher energy and power densities compared with pure A-CNTs electrodes.
4.1 Introduction

Conducting polymers for the supercapacitor electrodes have been developed fast in the last decade due to the high charge/energy density and low cost. The pseudocapacitors based on conducting polymer can typically store larger amount of charges per gram/volume compared with EDLC supercapacitor cells do as the whole bulk (not only the surface) of conducting polymer has involved the electrochemical reactions. The conductive property of conducting polymers comes from a conjugated strong bond system along the backbone of polymer. Basically they can be formed either from chemical oxidation of the monomer (e.g. iron chloride) or electrochemical oxidation of the polymer. Two oxidation reactions can occur at the same time. The oxidations of the monomer and the polymer are coincident with the insertion of a dopant/counter ion (for example, Cl\(^-\)). The doping level is usually below 1 dopant per polymer unit in the p-type conducting polymer: approximately 0.3–0.5, which means 2–3 monomer units per dopant. This depends on how closely the positive charges can be separated along the polymer chain. The conducting polymers that are widely studied for the electrodes in supercapacitor cells are polypyrrole, polyaniline, and PEDOT.

Conducting polymers can be classified into p-doped with counter anions for oxidation and n-doped with counter cations for reduction. The equations for these charging processes of the two kinds are expressed as:

\[
CP + nA^- \rightarrow CP^{n+}(A^-)_n + ne^- \quad \text{(p-doping) } (4-1)
\]

\[
CP + nC^+ + ne^- \rightarrow CP^{n-}(C^+)_n \quad \text{(n-doping) } (4-2)
\]

where A\(^-\) and C\(^+\) are the anion and cation respectively. The discharge processes of the two kinds are the reverse of the above equations.
The doping process of p-doping type of conducting polymer can be described in Figure 4-1. Briefly, the conductive polymer loses electrons during the charge process and becomes polycations with anion deficiency, which causes the anions in the solution (for example, Cl\textsuperscript{-} anions) to migrate on the surface and intercalate into the bulk of conducting polymer in order to maintain the electrical neutrality.

![Figure 4-1. Doping process in a conducting polymer.](image)

Supercapacitor cells based on conducting polymer electrodes have three main configurations. The first one is the symmetric configuration using the same p-doping polymer for the two electrodes. The second one deploys asymmetric configuration using two different p-doping polymers with different ranges of electrochemical reaction potentials. The last one is also symmetric configuration using the same polymer for the two electrodes with the p-doped polymer used as the positive electrode and the n-doped polymer used as the negative electrode. Moreover, the asymmetric cell using conducting polymer as the positive electrode and carbon
materials (graphene, CNTs and activated carbon) as the negative electrode can also be constructed.

It should be noted that conducting polymer electrodes typically have poor mechanical stability because of volume changes during the doping/dedoping process, which cause failure of the electrode during long cycling.[74, 118, 119] Recent experiments have demonstrated that the composite approach, in which conducting polymer layers are deposited on conductive porous networks such as CNTs, can lead to supercapacitors with significantly improved cycling stability.[86, 120] In such a conductive composite approach, the CNT networks provide electron transport pathways as well as mechanical support to the conducting polymer while the deposited conducting polymer layers enhance the charge storage capacity of the electrodes. The high density (via packing) of A-CNT forests are distinctively advantageous as the conductive networks to support the conducting polymer coating layer in supercapacitors, relative to randomly packed morphologies. Apart from the direct (and thereby fast) ion transport to reduce resistance to the ion transport, as illustrated in Figure 4-2, the conducting polymer/A-CNTs also provide better mechanical stability and hence higher retention of the capacitance after long charge/discharge cycles, compared with the electrodes of the PEDOT/randomly packed CNT networks.
Figure 4-2. Microstructures of the electrode materials. (a) SEM image of as-grown aligned carbon nanotubes. (b) SEM image of PEDOT/A-CNTs with 10 nm coating thickness.

In the extant literature, electrodes of conducting polymer/CNTs were fabricated by electrochemical methods, which will result in non-uniform conducting polymer layers on the CNTs.[82, 83, 121] In this work, an oxidative chemical vapor deposition (oCVD) was employed to fabricate CP/A-CNTs electrodes in which a conducting polymer, PEDOT, layer forms a conformal coating on very high aspect ratio A-CNTs (0.2 mm long). The oCVD allows precise control of the PEDOT layer thickness from sub-nanometer to tens of nanometers.

In this work, we assembled supercapacitors using compacted vertically aligned CNTs (A-CNTs) coated with different thickness PEDOT as electrodes (PEDOT/A-CNTs). An ionic liquid/molecular liquid mixture (IL/ML), 2 M BMI-BF₄ (1-butyl-3-methylimidazolium tetrafluoroborate) in PC (propylene carbonate), was used as the electrolyte. The IL/ML mixture has a wider electrochemical window compared to aqueous liquids and higher ionic conductivity compared to the pure BMI-BF₄.[115] A-CNTs forests are grown using chemical vapor deposition (CVD) from iron catalysts sputtered on silicon wafers using ethylene as the carbon source and processes developed at MIT. [122, 123] PEDOT were deposited uniformly on A-CNTs by modified CVD method and the composites were densified to 5 % volume fraction
using a unique mechanical densification process to achieve the full potential and a higher volumetric performance of electrodes.\cite{112} The symmetric supercapacitors showed stable electrochemical properties at an operation voltage of 2 V in 2 M BMI-BF$_4$/PC electrolyte. The results show that the combination of PEDOT with A-CNTs is an effective way to increase the SC than pure A-CNTs, and the SC increases with increasing thickness of PEDOT from 3 nm, 6nm to 10 nm on surface of A-CNTs. The larger SC and higher operation voltage result in high volumetric and gravimetric energy and power densities.

4.2 Preparation of PEDOT/A-CNTs supercapacitor cell

4.2.1 Preparation of PEDOT/A-CNTs

The fabrication process of A-CNTs by modified chemical vapor deposition on silicon wafers have been described in details in the last chapter. This experiment was carried in our collaborate Prof. Brian L. Wardle’s lab. As grown A-CNT forests have 1% Vf with the density of 10$^9$ to 10$^{10}$ CNTs cm$^{-2}$. PEDOT depositions were performed in a custom-built vacuum chamber as depicted in Figure 4-3. \cite{124}
Figure 4-3. Schematic figure of modified oCVD process chamber.[124]

The A-CNT forests as the substrate were held face down to the oxidizing agents. EDOT was polymerized by Iron (III) chloride as the oxidant. Liquid EDOT monomers were heated to 150 °C outside the vacuum chamber and flowed into the chamber simultaneously. The process involved sublimation of the oxidant onto the A-CNTs followed by exposure to a vapor of the EDOT monomer. All PEDOT deposition experiments were performed at a substrate temperature of 70 °C and at a pressure of 50 mTorr. A uniform coating of PEDOT on CNTs can be obtained and the thickness of PEDOT coating layer on CNTs can be controlled precisely within nanometer by controlling the deposition time. Figure 4-4 exhibits the A-CNTs and PEDOT conformal coated on A-CNTs.
Figure 4-4. Schematic illustration of A-CNTs (a) before and (b) after PEDOT coating.[112]

4.2.2 Supercapacitor assembly

Pure A-CNTs forests and PEDOT/A-CNTs with different coating layer thickness of 3 nm, 6 nm and 10 nm PEDOT on A-CNTS, respectively, were used as the electrodes. The electrodes are labeled as PA3, PA6 and PA10 and the thickness of the electrodes is 0.2 mm (the height of A-CNTs).
In order to achieve high energy and power density, especially high volumetric performance of the device, the electrode materials were densified to 5% volume fraction using a unique mechanical densification process developed in this thesis study. The pure A-CNTs or PEDOT/A-CNTs arrays were released from the silicon substrate and then subjected to a mechanical biaxial densification process in two orthogonal directions. By inducing the inter-tube distance via densification in the two directions, A-CNTs and PEDOT/A-CNTs arrays with 5% volume fraction density were obtained.

Two-electrode symmetric supercapacitors with PEDOT/A-CNTs at different thickness of PEDOT were assembled in a teflon system with stainless steel cylindrical collectors and gold-plated steel plates as the current collector. The two electrodes were sandwiched with a 20 μm thick porous paper as the separator. 2 M BMI-BF₄/PC mixture was used as the electrolyte due to improved ionic conductivity compared with that of pure BMI-BF₄.

Morphological and compositional characterization of the PEDOT-coated CNT arrays was performed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The single electrodes and symmetric supercapacitor cells were tested by voltammetry cycling (CV) at scan rates from 10 to 100 mV s⁻¹, electrochemical impedance spectroscopy (EIS) in a wide frequency range 1 MHz to 0.01 Hz and galvanostatic charge-discharge with a current load from 0.2 to 10 A g⁻¹.

The electrochemical performance of the symmetric supercapacitor cells using a two-electrode system. The CV and EIS measurements were performed at a potentiostat/frequency analyzer (Parstat 2273) and Versat 4 (Princeton Applied Research) was used for the galvanostatic charge/discharge test.
4.3 Characterizations of supercapacitor cells

4.3.1 Morphology characterizations

Figure 4-2(a) and (b) are SEM images of the pure A-CNTs and A-CNTs coated with 10 nm PEDOT composite, respectively. Figure 4-5 shows that the PEDOT layer forms a conformal coating on the A-CNTs.

Figure 4-5. TEM figure and scheme of composite, comprised of conformal PEDOT coating on A-CNTs. (The image was from our collaborator Prof. Wardle’s group in MIT)

The aligned nanomorphology of A-CNTs is remained after conformal coating PEDOT layers (Figure 4-2(b)). Figure 4-6 illustrates the difference in the ion storage and transport processes between the pure A-CNTs and the PEDOT/A-CNTs.
In the A-CNTs electrodes, the ions are stored on the surfaces of A-CNTs (EDLC) and the excess ions will travel through the ion pathways formed by the A-CNTs during the charge/discharge processes. While in the PEDOT/A-CNTs electrodes, besides transporting in the ion pathways formed by the PEDOT/A-CNTs, the ions will also travel into and out of the redox material (PEDOT films) to store the ions through the pseudocapacitor (in the bulk of the PEDOT films), which may affect the overall charge/discharge speed of the electrodes. This paper studies how the charge storage and transport processes evolve as the PEDOT/A-CNTs as the PEDOT film thickness is increased to 10 nm and develops understanding on the influences on the supercapacitor cell performance.

4.3.2 New method to investigate charge/discharge cycle

Supercapacitors as charge storage devices should have minimum energy loss, and which are reflected symmetric charge/discharge curves. We note that the degree of the rectangular shape of CV curves are often cited as an indication of a high efficiency supercapacitor. [125, 126] How to
define the rectangular shape is often subjective. To quantify the energy storage efficiency (how symmetric a CV curve between the charge/discharge cycles), we introduce the QV curves which are direct conversion of CV curves, where \( Q = \int I \, dt \), \( I \) is the current, as shown in Figure 4-7.

![Figure 4-7. Typical QV curve of supercapacitor cell.](image)

For an ideal supercapacitor (with very little loss), the QV curves for the charge/discharge processes should overlap. The area enclosed by the charge/discharge QV curves is the energy loss which shows clearly how well a supercapacitor perform as an energy storage device. As shown in Figure 4-7, the energy loss can be expressed as the area \( \text{area II} \) over area \( \text{area I} \) plus \( \text{area II} \).

The energy efficiency or the Coulombic efficiency, which is the ratio between the discharged energy versus the total input energy during the charge process.[127] The energy stored in the charge process and that released in the discharge process can be obtained by integrating potential with charge. Hence the coulombic efficiency can be represented as \((1 - \text{energy loss})\).
Figure 4-8. (a) Volumetric and (b) gravimetric QV curves of cells with different electrodes.

As shown in Figure 4-8 (a), with the increased PEDOT coating thickness, the coulombia efficiency decreases because more pseudocapacitive reactions are involved during the charge/discharge process. The electrode’s ability for storing charges is also represented in Figure 4-8 (a). It can be found in Figure 4-8 (b) that the cell with PA10 as electrode can store 50% more charges per weight than the cell with pure A-CNTs does at a scan rate of 10 mV s\(^{-1}\). If the
volumetric property is considered, 10 times more charges will be stored by PA10 capacitor than A-CNTs capacitor as shown in Figure 4-8 (a). The coulumbia efficiencies of cells with different electrodes, calculated from QV curves under the scan rates of 100 mV s\(^{-1}\) and 10 mV s\(^{-1}\), are revealed in Figure 4-9.

![Figure 4-9](image_url)

**Figure 4-9.** Coulombic efficiencies of cell with PA10 as electrode under the scan rates of 100 mV s\(^{-1}\) and 10 mV s\(^{-1}\).

When the scan rate decrease to 10 mV s\(^{-1}\), the coulumbia efficiencies of cells with A-CNTs, PA3, PA6 and PA10 increase to 86.9%, 85.6%, 84.1% and 82.1%, respectively, exhibiting ideal capacitive behavior. The increase of coulumbia efficiency is due to the lower charge/discharge process during which the cells will have enough time to store and release charges, especially for the pseudocapacitor. It should be noted that the coulumbia efficiency of PA10 capacitor is smaller than the pure A-CNTs capacitor because of the slow diffusion of ions in the bulk of PEDOT. However, the difference of the coulumbic efficiencies will reduce when the scan rate is decreased from 100 mV s\(^{-1}\) to 10 mV s\(^{-1}\).
Figure 4-10. (a) Volumetric and (b) gravimetric specific capacitances of cell with PA10 as electrode under the scan rates of 100 mV s\(^{-1}\) and 10 mV s\(^{-1}\).

The volumetric and gravimetric specific capacitances of all cells under the scan rates of 100 mV s\(^{-1}\) to 10 mV s\(^{-1}\) are revealed in Figure 4-10(a) and Figure 4-10(b). In the four supercapacitor cells, a general trend can be seen in Figure 4-10(a) that the specific capacitance increases with the increase of PEDOT coating thickness on A-CNTs, and PA10 cell has the highest specific capacitance. The result of higher capacitances with lower scan rate is consistent with that of
coulombia efficiency because of the slower charge/discharge process. Meanwhile, the specific capacitances ratio of all cells is also consistent with the electrodes’ abilities for storing charges.

4.3.3 Nyquist plot

Figure 4-11 presents the Nyquist plot obtained in the frequency range of 100 kHz to 10 mHz of 5 mV applied voltage, showing a semicircle in the high frequency region and a sharp rise of the imaginary impedance part, revealing the dominance of the cell capacitance in the low frequency region.

![Nyquist plot](image)

**Figure 4-11.** Nyquist plot for symmetric supercapacitors with A-CNTs, PA3, PA6, PA10 at 5% volume fraction in 2 M BMI-BF₄/PC.
Figure 4-12. (a) Real part capacitance versus frequencies of cells with different electrodes. (b) The ratio of real and imaginary capacitance versus frequencies of cells with different electrodes.

The intersection of the real impedance part in the high frequency region on the real axis of Nyquist plot is related to the internal resistance including electrolyte resistance, buck materials resistance and contact resistance. All cells show an internal resistance of 0.1 Ω cm², representing a high electrical conductivity of the cells. Figure 4-12(a) presents the real part of the capacitance
$C'$ of different cells as a function of frequency. It can be found that $C'$ decreases sharply when the frequency decreases, then $C'$ will be less frequency dependent. $C'$ represents the cell capacitance. As shown in Figure 4-12(a), the capacitances of cells increase when more PEDOT is coated on the A-CNTs. The capacitances ratio of all cells is also consistent with the results of QV curve and specific capacitances ratio derived from CV curves, showing an excellent electrochemical stability. The energy loss can be expressed by the ratio of $C''$ and $C'$ as shown in Figure 4-12(b).

The typical supercapacitor charge/discharge time is > 50 seconds, corresponding to 0.02 Hz or lower frequencies. As can be seen from Figure 4-12(b), there is only a small increase in the loss at below 0.02 Hz when the PEDOT layer thickness in the PEDOT/A-CNT cells increases from 0 to 10 nm. Figure 4-13 presents the Comolmbic efficiency calculated from the loss tangent data (from the impedance spectra, efficiency = 1 - loss) at 0.025 Hz, which can be compared with that in Figure 4-9 acquired at 100 mV/s (40 seconds per charge/discharge cycle).

![Graph](image)

**Figure 4-13.** Coulombic efficiencies and specific capacitances of cell with PA10 as electrode from CV and Nyquist measurements (one is for high voltage and one is obtained at low voltage).
It can be seen that the two sets of data are consistent, except that the efficiency acquired at low voltage (5 mV, Figure 4-13) is slightly higher than that acquired at high voltage (2 V, Figure 4-8(a)). As has been shown in earlier studies, the mobile ion transport in ionic devices such as supercapacitors is through both drifting process which is fast and suffers much lower electric resistance, and diffusion process which is slower and exhibits higher equivalent electric resistance.[117] Compared with low operation voltage (5 mV), the higher operation voltage (>1V) will induce large change in the ion concentration and hence will involve the diffusion process, resulting in larger energy loss and lower coulombic efficiency. On the other hand, the specific capacitance will increase with more diffusion process. As shown in Figure 4-13 that combine the volumetric specific capacitances based on CV curve and Nyquist plot, the volumetric secific capacitances obtained in Nyquist plot measured at 5 mV are a little lower than those from CV measurement. Through comparing the two measurements, it could be found that the impedance method is quick and also over a broad frequency range to measure the specific capacitance and efficiency.

4.3.4 Galvanostatic charge/discharge cycles
The galavanostatic cycles of different cells at alternate charge/discharge current density of 5 A g⁻¹ and -5 A g⁻¹ are shown in Figure 4-14(a). The cycles exhibit symmetric linear charge/discharge performance showing a rapid I-V response, representing excellent capacitive characteristics. The discharge time increases with more PEDOT coating thickness, which leads to the increase of specific capacitance represented in Figure 4-14(a).
Figure 4-14. (a) Galvanostatic charge/discharge curves for cells with A-CNTs, PA3, PA6 and PA10 as electrodes under different discharge current densities in 2 M BMI-BF$_4$/PC. (b) Coulombic efficiencies of different cells with conventional and new methods.

The higher capacitance of the composites results obviously from the contribution of the embedded PEDOT on surface of A-CNTs which can exert some effects: (1) the synergy effect of pseudocapacitance for PEDOT and good conductivity for A-CNTs. The A-CNTs provide a
stable mechanical structure for the ions transfer in the channel and ions diffusion in the bulk of electrodes. (2) the provision of interconnected pathways ions through the pore network of the polymer due to the highly porous structure of PEDOT and enhanced ions transport during the charge/discharge process. (3) the thinness of the polymer layer on each A-CNT, minimizing barriers both for ion transfer across the polymer/electrolyte interface and ion transport within the polymer phase. As pointed out in our previous discussion, the Coulombic efficiency can be used to evaluate the capacitive performance of supercapacitor cells. In the current literature, the Coulombic efficiency based on galvanostatic charge/discharge is usually represented as the ratio between discharge time and charge time \( t_{\text{discharge}}/t_{\text{charge}} \)[128, 129] However, this method is not accurate to reflect the real energy ratio during charge/discharge process. Here, we will continue to plot the QV curve and obtain the efficiency shown in Figure 14(b). Although the higher value (around 95%) is calculated using old method, the new method should be used to investigate the real performance of cells. Meanwhile, it can be found that the Coulombic efficiency is lower than that from CV curve (100 mV s\(^{-1}\)) and Nyquist plot (0.025 Hz) because of the short charge/discharge time (higher frequency), which is also consistent with the previous comments. Figures 4-15(a) and 4-15(b) reveal the volumetric and gravimetric specific capacitances of the cells at current densities of 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 A g\(^{-1}\), respectively. It can be found that the volume specific capacitance is greatly improved by conformal coating PEDOT on surface of A-CNTs and it is obviously enhanced when the thickness of PEDOT increased because of the increase of volume density. The volume specific capacitance of devices with A-CNTs and the composites as electrodes are 6.54 F cm\(^{-3}\) (A-CNTs), 14.96 F cm\(^{-3}\) (PA3), 28.78 F cm\(^{-3}\) (PA6) and 63.45 F cm\(^{-3}\) (PA10) at 2 A g\(^{-1}\), respectively. The largest volume specific capacitance for the PA10 device reaches 92.79 F cm\(^{-3}\) at a current density of 0.2 A g\(^{-1}\). It should be noted that the
capacitance ratio of all cells is consistent with the results discussed previously, including QV curves, CV curves and Nyquist plot analysis. The retention life performance was investigated by galvanostatic charge/discharge tests for 1000 cycles with the discharge current density of 2 A g$^{-1}$ in two electrode system.

**Figure 4-15.** (a)Volumetric and (b) gravimetric specific capacitances of different cells versus discharge current densities.
As shown in Figure 4-16, the PA10 cell displays capacity retention of 89% after 1000 cycles. The decrease may be caused by some film swelling as the electrolyte ions intercalate in and out of the pores of the film, as well as some energy loss to irreversible processes that lead to hysteresis. The specific capacitance values are still well maintained, even at a high current density of 2 A g\(^{-1}\), representing an excellent rate capability.

![Figure 4-16. Capacitance retention property under 1000 cycles.](image)

The superior rate capability of the device can be attributed to the reduced diffusion paths of ions in aligned structure leading to faster kinetics (ion insertion/extraction) in the electrode film. In order to investigate the improvement of the A-CNTs on the cycle life retention of composite electrodes compared with random CNTs, supercapacitors with PEDOT/random CNTs electrodes were also fabricated and characterized. From Figure 16, symmetric supercapacitors made of the PEDOT/random CNTs had a retention of 73% after 1000 cycles of 2
Voltage cycle. In the randomly packed CNT networks, there are CP layers in the gaps between CNTs and after long charge/discharge cycles, the mechanical failure of CP layers in these gaps will cause disruption of the electric conduction paths between CNTs and reduce the conductivity of CNT networks. As a result, the capacitance is reduced. In contrast, the electric conduction path of the continuous aligned CNTs would not be disrupted by the mechanical failure of the CP coating layers due to the A-CNT/CP morphology. Hence, the A-PEDOT/A-CNTs electrodes exhibit more robust mechanical stability and high retention of the capacitance, compared with the electrodes of the CP deposited on randomly packed CNT networks.

4.3.5 Energy and power densities

The energy density is proportional to the gravimetric or volumetric capacitance (F g⁻¹ or F cm⁻³) of the cell and square of the operation voltage (V). The power output capability of supercapacitor depends strongly on not only the rates of ionic mass transport but also the equivalent series resistance. As shown in the table 4-1, the energy densities of cells with pure A-CNTs, PA3, PA6 and PA10 are 1.12 Wh L⁻¹, 2.76 Wh L⁻¹, 6.11 Wh L⁻¹ and 11.22 Wh L⁻¹, respectively. The increase of energy density value is due to the increasing specific capacitance of electrode with more PEDOT was coated. Same trend is found in the power density performance. Although the gravimetric power densities of cells with composites electrode are similar or a little lower than that of cell with pure A-CNTs electrode. The volumetric power densities of composites electrodes capacitors are much larger because of the higher composites electrodes packing density. For the cell with PA10 as electrode, the volumetric energy and power densities are 11.22 Wh L⁻¹ and 35.24 kW L⁻¹, which are larger than the results of symmetric conducting polymer supercapacitors reported earlier.

Table 4-1. The volumetric energy density and power density of all cells in 2 M BMI-BF₄/PC.
### 4.4 Conclusion

Composites of polymerizing conductive polymer PEDOT on surface of aligned CNTs exhibit higher electronic and ionic conductivity and larger electrode specific capacitance, most importantly, larger volumetric specific capacitance and greater stability in charge/discharge cycling compared with the pure A-CNTs electrodes. Meanwhile the interactions were strongly depends on the coating thickness of PEDOT on A-CNTs surface. Microstructures of the composites suggests that PEDOT was tightly wrapped around A-CNTs. The porous morphology of the composite provides a larger surface area and enables the rapid diffusion of ions into the bulk of the material. The vertical directional growth of carbon nanotubes provides the straight pathways for ions to transport fast and mechanical structure to enhance the cell electrochemical stability. Symmetric supercapacitors using the 5% compacted A-CNTs coated with 10nm thickness PEDOT as electrodes, as well as using the ionic liquid as electrolyte can achieve the highest volumetric SC (92.79 F cm⁻³) and enhance the volumetric energy storage density (11.22 Wh L⁻¹ and 35.24 kW L⁻¹) further of the cell. The distribution of capacitance in this way suggest that at PA10 electrode coating thickness on A-CNTs is the ideal amount of allowing the right balance between contact of nanotubes, amount of conductive polymer and porosity size. The obtained results can be employed to get a desired value of energy and power density by controlling the microstructure of the PEDOT/A-CNTs composites. Especially because of its bulk

<table>
<thead>
<tr>
<th>Sample</th>
<th>Energy Density (Wh L⁻¹)</th>
<th>Power Density (kW L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-CNTs</td>
<td>1.12</td>
<td>4.03</td>
</tr>
<tr>
<td>PA3</td>
<td>2.76</td>
<td>8.76</td>
</tr>
<tr>
<td>PA6</td>
<td>6.11</td>
<td>18.47</td>
</tr>
<tr>
<td>PA10</td>
<td>11.22</td>
<td>35.24</td>
</tr>
</tbody>
</table>
density is higher, it can provide a possible method for the future of preparing small size and portable energy storage devices.
Chapter 5

Asymmetric Supercapacitor Based on Conducting Polymer and Aligned Carbon Nanotubes

In the Chapter 4, pseudocapacitor based on conducting polymer (CP) coated on A-CNTs was developed and investigated. The specific capacitor has been improved significantly compared with that of A-CNTs electrode. However, as revealed in Chapter 4, the pseudocapacitor leaded to the narrow operation voltage (2V), which resulted in much lower energy density and maximum power density. To expand the operation voltage while maintaining the high specific capacitance, an asymmetric supercapacitor, exploiting nm-scale conformal coating of CP on aligned carbon nanotubes (A-CNTs) as the negative electrode and an ultra-high density A-CNTs as the positive electrode, has been developed in this chapter. The conformal CP coating on the A-CNTs enhances charge storage while the aligned nanotube morphology provides straight and fast ion transport pathways. The A-CNTs electrode, densified from a unique mechanical method, possessing high volumetric capacitance while preserving the aligned morphology to maintain the high power, provides an ideal positive electrode for the asymmetric supercapacitor. By complementary tailoring of the asymmetric electrodes, the device exhibits a wide operation voltage of 4 V with the high power and energy densities as 130.6 kW L$^{-1}$ and 82.8 Wh L$^{-1}$ in volumetric performance. Moreover, the new method of investigating the energy storage efficiency was continued to be deployed to evaluate the efficiency of a supercapacitor cell. An equivalent circuit was developed to model the performance of each electrode and investigate the asymmetric design of the cell.
5.1 Introduction

As we mentioned in Chapter 1, the energy density (E) of supercapacitor depends on the gravimetric or volumetric cell capacitance (C) and operation potential (V), i.e.,

\[ E = \frac{1}{2} CV^2 \]  \hspace{1cm} (5-1)

And the maximum power density \( P \) is determined by

\[ P = \frac{V^2}{4 \cdot ESR} \] \hspace{1cm} (5-2)

where ESR is the gravimetric or volumetric equivalent series resistance of the supercapacitor cell. The cell capacitance is determined mainly by the electrode materials and the operation potential is related to the electrochemical window (EW) of the electrolyte and electrodes. Equations (5-1) and (5-2) indicate that one of effective ways to increase the power and energy densities is to raise the cell voltage. One promising approach to increase the operation voltage and hence the energy and power densities is to assemble asymmetric supercapacitors which combines the battery-like pseudocapacitive electrode, such as the redox active materials of transition metal oxides or CP which has high energy density, and the EDLC electrode which provides high power density.[130, 131] The asymmetric configuration will take the advantage of different electrochemical windows in both electrodes to increase the cell operation voltage, resulting in an improved specific capacitance, energy and power densities. [132, 133]

As we discussed in the last chapter, compared with EDLC whose working mechanism is based on the charges storing on the surface of the porous electrode, CP provides the entire volume for the redox reaction and energy storage, resulting in a superior specific energy density.[89, 134] However, CP electrodes are well known for very poor cycle life attributing to the large volume change and consequent polymer breakage during the charge/discharge process.
and hence not suitable for supercapacitor electrodes when used alone.\cite{73} Hence, in this work, composite electrodes combining PEDOT and A-CNTs were fabricated. As shown in Figure 5-1(a), the A-CNTs provide the parallel pathways to enhance the ion transfer speed, reduce the electric resistance and improve the ion accessibility under the higher current density.

**Figure 5-1.** SEM images of (a) as grown A-CNTs with 1\% Vf and (b) densified A-CNTs with 40\% Vf.
Here, a modified chemical vapor deposition (o-CVD) was employed to deposit PEDOT (which has higher conductivity and wider potential window compared with other conducting polymer) on the A-CNTs.\cite{32, 135} As shown in Figures 5-2(a) and (b), nanometer thin PEDOT layer is deposited as the conformal coating on the A-CNTs, preserving the nanomorphology of aligned ion transport pathways of the A-CNTs.

**Figure 5-2.** (a) SEM images of PEDOT/A-CNTs composite. (b) Scheme and high magnification TEM images of the composite. (The images were from our collaborator Prof. Wardle’s group in MIT)
The composite electrodes thus fabricated possess high mechanical stability and hence a long cycling life compared with that of CP deposited on randomly packed CNTs. Based on the EW as shown in Figure 5-3, the PEDOT/A-CNTs was used as one electrode (see illustration in Figure 5-2(b)).

**Figure 5-3.** CV curves of both electrodes at 100 mV s\(^{-1}\) in 2 M BMIBF\(_4\)/PC.

The A-CNTs are utilized as the other electrode, and this combination provides the asymmetric supercapacitor with 4 V operation voltage, much higher than each individually electrode. In order to achieve both high gravimetric and volumetric performance of the cell, the PEDOT/A-CNTs electrode was densified via a mechanical compression process to 5% volume fraction (Vf) of A-CNTs and the A-CNTs electrode was densified to 40% Vf shown in Figure 5-2(b).

To better understand the working mechanism of the asymmetric pseudocapacitances, an equivalent circuit was developed based on the electrochemical impedance spectroscopies (EIS) of individual electrodes and the asymmetric supercapacitor cell over a broad frequency range. It
is noted that in the extant literature, there is few work concerning about the fitting for both pseudocapacitive and EDLC type electrodes, as well as the asymmetric cell [8,22-24]. The asymmetric electrochemical cell here provides an opportunity to study these two types of electrodes because both electrode materials are A-CNTs based. The complicated charge/discharge process will be represented as different circuit elements to investigate the equivalent capacitance, ion diffusion coefficient and other parameters. The modeling of the asymmetric cell will also provide vital information for the data from three-electrode and two-electrode measurements and studying whether each electrode is optimized for the asymmetric cell.

In this chapter, an asymmetric supercapacitor exploiting nm-scale conformal coating of PEDOT on A-CNTs as the negative electrode and the ultrahigh density A-CNTs as the positive electrode was developed. Both electrodes were tailored separately to extend the cell operation potential to 4 V in 2 M 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIBF4)/propylene carbonate (PC) electrolyte, leading to 130.6 kW L⁻¹ and 82.8 Wh L⁻¹ in volumetric performance and 269.4 kW kg⁻¹ and 170.7 Wh kg⁻¹ in gravimetric performance, respectively. In addition, a new and accurate method (QV curve) was introduced to measure the energy storage efficiency of the asymmetric cell. An equivalent circuit model was developed based on the EIS, revealing the difference in working mechanisms between EDLC and pseudocapacitor and demonstrating the optimized asymmetric design, which leads to the high cell performance.

5.2 Supercapacitor fitting based on equivalent circuit

Compared with the conventional capacitor, the electric characteristics of a supercapacitor cell are more complicated due to the usage of porous electrodes in nature. This usage of porous electrodes leading to the high specific capacitance makes the behavior of the supercapacitor cells
complicated. The electrochemical performance of porous electrode has a strong relationship with the frequency of operation. Many models have been used to simulate the complex behavior of supercapacitor cells and the most widely used models were deployed from porous electrode theory. Models based on this theory precisely simulate the performance of supercapacitors by solving related governing equations. There are also some other equivalent circuit models that can be used to accurately simulate the dependence of supercapacitor cell on frequency by performing multiple time constants. Time constants in electrical circuits can be generated through connecting resistor/capacitor branch. And the values can be determined from electrochemical Nyquist plot measurements. The simplest model of this type is called as Classical Equivalent Circuit Model.

![Figure 5-4. Classical equivalent Circuit Model.](image)

As shown in Figure 5-4, the Classical Equivalent Circuit model is composed of three electrical components, the capacitor \( C \), the ESR and the resistance EPR parallel with \( C \). \( C \) is the charge storage capacity of the supercapacitor cell, ESR is the internal equivalent series resistance and EPR can be used to model the loss due to the leakage current which also have an influence on charge/discharge cycle life of supercapacitor cell. It is essential to expand the simple model shown in the figure to precisely simulate the performance of supercapacitor with complicated
physics and materials system. Different models with various electrical elements have been used in the current literature.

One of the commonly used equivalent circuit models is called transmission line network model. In this model, the non-linear capacitances and the resistances represent the electrostatic double layer capacitance and the distributed ESRs related to each pore in the electrode material. The frequency of application and other electrochemical performance can be determined based on these RC elements. There are also additional resistances in the electrode and the mobile ions diffusion resistances in the membrane. Figure 5-5 represents the equivalent circuit of this model.

There is a special model called ladder model in the transmission network models group. Here the pores in the electrodes are assumed to be cylindrical and filled with homogeneous electrolyte solution. Each single pore with cylindrical configuration can be simulated by a homogeneously
distributed electrolyte solution resistance and a double layer capacitance. Figure 5-6 shows the simplified equivalent circuit when the number of pores on either electrode is assumed to be same and grouped together.

However, due to the large amount of resistor/capacitor branches in the equivalent, the complicated equivalent will lead to long simulation time and low efficient. It is essential to develop simple and accurate equivalent circuit to describe the electrochemical performance of supercapacitor cell.

5.3 Experimental

The synthesis process of A-CNTs has been described in the section 3.2.1 (Chapter 3). The process of conformal coating on A-CNTs has been introduced in the section 4.2.1 (Chapter 4).

PEDOT/A-CNTs and A-CNTs electrodes were attached on Au sheets that serve as the current collectors. The asymmetric supercapacitors were prepared by assembling PEDOT/A-CNTs as the negative electrode and densified A-CNTs as the positive electrode, which were separated by a porous paper with the thickness of 25 μm. A 2 M BMIBF₄/PC mixed electrolyte was used for the asymmetric supercapacitor. (1-Butyl-3-methylimidazolium tetrafluoroborate (BMI, > 97%) and propylene carnoate (PC, 99%) were purchased from Sigma-Aldrich). Each
electrode was characterized using screen-printed electrodes system (Dropsens) where the PEDOT/A-CNTs or A-CNTs on the platinum current collector for the working electrode, while the silver and platinum were used as the reference and counter electrodes, respectively. For supercapacitor devices, the electrical impedance and CV curves were characterized using a potentiostat/frequency analyzer (Parstat2273). Galvanostatic cycling was measured at different discharge current densities with Versastat 4 (Princeton Applied Research).

5.4 Results and discussion

5.4.1 Electrochemical performance of each electrode based on three-electrode system

As shown in Figure 5-3, a potential window of -2.2 V to 1.3 V was obtained at a scan rate of 100 mV s\(^{-1}\) for the A-CNTs electrode. In contrast, the PEDOT/A-CNTs composite electrode shows an electrochemical window from -1 V to 1.8 V at the same scan rate. The quasi-rectangular CV curve for the PEDOT/A-CNTs composite electrode reveals that the electrode preserves the nanomorphology of aligned ion transport pathways (due to the A-CNTs) that enable fast ion transport in and out of the electrode and a reversible doping/dedoping process of the PEDOT coating layer. The doping process of PEDOT is presented as

\[
\text{Cp} \rightarrow \text{Cp}^{n+} + n\text{e}^{-} \quad (5-3)
\]

In the cathode, the negative ions will screen the positive charges of \(\text{Cp}^{n+}\) as \(\text{Cp}^{n+} + (A^-)_n\), where \(\text{Cp}\) is the conducting polymer, \(A^-\) is the negative ion of the electrolyte, in the bulk of the conducting polymer. Compared with EDLCs based on carbon in which ions’ sorption and desorption determine cell performance, supercapacitor based on conducting polymer stores charges in the bulk of the active materials, i.e., the conducting polymer. The specific capacitance can be calculated through integrating the discharge part of CV curve. The data show that the volumetric specific capacitance of PEDOT/A-CNTs is larger than that of A-CNTs, because of
the higher volumetric capacitance of the pseudocapacitance of the composite electrode, as expected.

The galvanostatic cycle measurements were performed to quantify the specific capacitance and investigate the electrochemical behavior of the electrodes. The charge/discharge curve for the PEDOT/A-CNTs electrode at alternate current density of 1 A g\(^{-1}\) and -1 A g\(^{-1}\) based on the three electrode system in 2 M BMIBF\(_4\)/PC is presented in Figure 5-7.

![Graph showing charge/discharge curves](image)

**Figure 5-7.** Galvanostatic charge/discharge curves of both electrodes at 1A g\(^{-1}\) 2 M BMIBF\(_4\)/PC.

From the slope of the galvanostatic curves, \(\frac{dV}{dt}\), the capacitance of the electrode can be determined by

\[
C = \frac{I}{\frac{dV}{dt}}
\]

(5-4)

where \(I\) is the constant current density, \(V\) is the potential, and \(t\) is discharge time. From the data in Figure 5-7, a specific capacitance of 205 F g\(^{-1}\) for PEDOT/A-CNTs electrode is deduced for
the current density of 1 A g\(^{-1}\). A specific capacitance of 121 F g\(^{-1}\) is obtained for the densified A-CNTs electrode at 1 A g\(^{-1}\) from the discharge curve.

![Graph showing specific capacitance vs. discharge current density](image)

**Figure 5-8.** Specific (a) volumetric and (b) gravimetric capacitances at different discharge densities of both electrodes.

Figure 5-8(a) and Figure 5-8(b) present the volumetric and gravimetric specific capacitances of both electrodes versus discharge current density, from 0.5 A g\(^{-1}\) to 10 A g\(^{-1}\). The data show that the PEDOT/A-CNTs pseudocapacitor electrodes show a high capacitance retention of 71\% (from 110.5 F cm\(^{-3}\)/245.6 F g\(^{-1}\) at 0.5 A g\(^{-1}\) to 78.4 F cm\(^{-3}\)/174.3 F g\(^{-1}\) at 10 A g\(^{-1}\)). This high capacitance retention arises from the uniformly coating of PEDOT on A-CNTs, as shown in Figure 5-2 (b), which preserve the nanomorphology of parallel ion transport pathways.
formed from the PEDOT/A-CNTs and high electronic conductivity of the CNTs which improve the ions transport and result in high power density.

5.4.2 Asymmetric cell assembly

The results in Figure 5-3 show the stable potential windows of -2.2 V to 1.3 V for the A-CNTs electrode and of -1 V to 1.8 V to the PEDOT/A-CNTs electrode obtained in the 2 M BMIBF$_4$/PC using Ag as the reference electrode. Thus, the operation window of asymmetric supercapacitor can be extended up to 4 V (2.2 V for A-CNTs plus 1.8 V for PEDOT/A-CNTs) by tuning the mass (volume) ratio of the two electrodes. Since the charges stored in the two capacitor electrodes should be equal in magnitude with opposite signs ($|q_+| = |q_-|$), the mass ratio between the two electrodes can be determined from the electrochemical windows of the two electrodes. For a capacitor electrode, the stored charge $q$ is:

$$q = C \Delta V m$$

(5-5)

where $C$ is the specific gravimetric capacitance, $\Delta V$ is the maximum potential range allowed by the electrochemical window, and $m$ is the mass of the electrode. From ($|q_+| = |q_-|$), the mass ratio between the two electrodes is determined by,

$$\frac{m_+}{m_-} = \frac{C_- \Delta V_-}{C_+ \Delta V_+}$$

(5-6)

For the asymmetric capacitor developed here, the specific capacitances of the PEDOT/A-CNTs and A-CNTs electrodes are 205 F/g and 121 F/g, respectively, at a constant discharge current of 1 A/g. The optimal mass ratio of the two electrodes can be deduced to be 0.72. Thus, the asymmetric supercapacitors were assembled with the mass ratio of 0.72 between the PEDOT/A-CNTs and A-CNTs electrodes, separated by a 25 μm thick porous membrane (Celgard 3501, Celgard LLC) while 2 M BMIBF$_4$/PC was used as the electrolyte.
5.4.3 CV and QV curves

Figure 5-9 presents the CV curves of the asymmetric capacitor thus fabricated at different scan rates of 10, 20, 50, 100, 200 mV s\(^{-1}\) between 0 and 4 V for a two-electrode measurement system.

**Figure 5-9.** CV curves of asymmetric cell at different scan rates of 10, 20, 50, 100 and 200 mV s\(^{-1}\) between 0 and 4 V in 2 M BMIBF\(_4\)/PC electrolyte.

**Figure 5-10.** QV curve of cell at different scan rates between 0 and 4 V.

**Figure 5-10.** QV curve of cell at different scan rates between 0 and 4 V.
Figure 5-11. Coulombic efficiency of asymmetric cell with different scan rates.

The cell shows a near rectangular shape CV curve especially under small scan rate, indicating an ideal capacitive behavior under 4 volts operation. Besides the energy and power densities, the energy storage efficiency, which is directly related to the loss of a supercapacitor in the charge/discharge process, can be used to describe how ideal the capacitive behavior of the cell is. We note that the coulombic efficiency which is the ratio of total charges between discharging and charging process deduced from the CV curves in Figure 5-9 was used to describe the performance of a supercapacitor.[136, 137] Here, we show that although the coulombic efficiency can provide an approximate estimation of the energy storage efficiency (and hence the loss), one can evaluate from the CV curves in Figure 5-9 exactly the energy storage efficiency and loss of a supercapacitor during a charge/discharge cycle using a QV curve. The calculation method has been introduced in the last chapter. Here, the QV curves of Figures 10 and 11 are direct conversion of data in Figure 5-9, where \( Q = \int I dt \) and I is the current. For an
ideal capacitor (with very little loss), the QV curves for the charge/discharge processes should overlap. Figure 5-10 presents the QV curves of the asymmetric cell with different scan rates. Figure 5-11 shows the energy storage efficiency derived from Figure 5-10 which shows a near 90% efficiency at 10 mV s\(^{-1}\) scan rate, indicating a near ideal capacitor behavior of the asymmetric supercapacitor. As the scan rate increases, the loss is also increased, as reflected by the decrease of energy efficiency with scan rate. For the comparison, the coulombic efficiency is also presented in Figure 5-11, which stays nearly a constant in the same scan rate range.

### 5.4.4 Galvanostatic charge/discharge curve

To evaluate the capacitive performance of the asymmetric capacitor further, galvanostatic charge/discharge curves at different current densities were also characterized. The galvanostatic cycles at alternate charge/discharge current densities of 2 A g\(^{-1}\) and –2 A g\(^{-1}\) were presented in Figure 5-12.

![Galvanostatic charge/discharge curve](image)

**Figure 5-12.** Galvanostatic charge/discharge curves of device at a current density of 2 A g\(^{-1}\).

It should be noted that the current densities are based on the total mass of both electrodes. The symmetric charge/discharge processes indicate the high energy storage efficiency. Figure 5-
13(a) and Figure 5-13 (b) presents the cell volumetric and gravimetric capacitance at different discharge current densities. It should be pointed out that the calculated cell capacitance was based on the total volume of the active materials (including two electrodes and separator) or total mass because it is not meaningful to deduce the specific capacitance of a single electrode for the asymmetric supercapacitor. The cell capacitance decreased from 37.2 F cm$^{-3}$ to 27.7 F cm$^{-3}$ as the discharge current density increases from 0.5 A g$^{-1}$ to 10 A g$^{-1}$, indicating a good capacitance retention. The cycling stability of A-PEODT/CNTs//A-CNTs asymmetric supercapacitor was investigated by continuously cycling the galvanostatic charge/discharge process between 0 and 4 V at a current density of 5 A g$^{-1}$. As shown in Figure 5-14, the asymmetric cell shows a 91% capacitance retention after 5000 cycles. The small capacitance loss (~ 9%) is probably caused by the volume change during the charge/discharge process of PEDOT/A-CNTs electrode.
Figure 5-13. Cell (a) volumetric and (b) gravimetric capacitances of cell at different discharge current densities.
Figure 5-14. Cycle life vs number of cycles.

5.4.5 Energy and power densities
Figure 5-15. (a) Volumetric and (b) gravimetric Ragone plot of asymmetric cell.

The volumetric energy and maximum power densities are also evaluated for the asymmetric supercapacitors, based on Equation (5-1) and Equation (5-2). The asymmetric cells exhibit both high volumetric and gravimetric maximum power density and energy density, which are 130.6 kW L\(^{-1}\) (269.4 kW kg\(^{-1}\)) and 82.8 Wh L\(^{-1}\) (170.7 Wh kg\(^{-1}\)), respectively, and are higher
compared with symmetric supercapacitors with the A-CNTs, or CP-ACNTs, mainly due to the higher operation voltage in the asymmetric configuration.[32, 59, 107, 138] The volumetric and gravimetric Ragone plots (energy density versus average power density) of asymmetric cell are exhibited in Figure 5-15(a) and Figure 5-15(b), respectively. It should be mentioned that the average power density in the Ragone plot is different from the maximum power density. The average power density can be obtained by

\[ P = \frac{E}{\Delta t} \]  \hspace{1cm} (5-7)

where \( \Delta t \) is discharge time.[139]

5.4.6 Equivalent circuit fitting

In order to investigate the influence of PEDOT coating on the A-CNTs and develop understanding of the working mechanisms of pseudocapacitor and EDLC type electrodes, an equivalent circuit model shown in Figure 5-16 is utilized to simulate the electrochemical impedance spectroscopies (EIS) of the two electrodes and the asymmetric cell. [97, 140, 141]

**Figure 5-16.** Equivalent impedance circuit of each electrode.
In this model, $R_1$ is the internal resistance of electrode related to the conductivity of electrolyte, the Ohmic resistance of the electrode materials, and resistance in the separator, and the contact resistances between active materials and current collector. $C_1$ is the interface contact capacitance between the active material and gold current collector. $A_w$ is the Warburg diffusion element attributed to diffuse ion storage at low frequency in the interface between electrode and electrolyte. The Warburg diffusion impedance can be expressed as $Z_w = A_w/(j\omega)^{0.5}$, where $A_w$ is the Warburg coefficient, $\omega$ is the angular frequency. When the applied voltage is small ($-k_BT/e$), the Warburg coefficient is inversely proportional to the electrode area.

$$A_w = \frac{\alpha}{nA\sqrt{D}} \quad (5-8)$$

where $n$ is the valence of the mobile ions, $A$ is the electrode area, $\alpha$ is a coefficient, and $D$ is the diffusion coefficient. $R_2$ is the interface resistance between electrode and electrolyte. $R_3$ is the charge transfer resistance. $C_2$ represents the double layer capacitance related to the porous electrode. $C_3$ is the pseudocapacitance attributed the conformal coating of PEDOT. The total capacitance of PEDOT/A-CNTs electrode should be expressed as $C_2+C_3$. Due to the porous surface of two electrodes, constant phase element (CPE) is used for $C_2$ in the model. The impedance of CPE is defined as $Z_{cpe} = 1/T(j\omega)^n$, where $T$ is the frequency independent constant with dimensions of $(F \text{cm}^{-2})^n$ related to the roughness and pseudocapacitive kinetics of electrode, $n$ can be calculated from the slope of log $Z$ vs. log $f$ whose value range from -1 to 1. If $n=0$, the CPE is a pure resistor, $n=1$, CPE is a pure capacitor, $n=-1$, CPE behaves as an inductor.[142] $R_4$ represents the faradaic resistance. Nyquist plots of two electrodes in the frequency range of 100 kHz to 10 mHz at open circuit potential with a 5 mV perturbation signal are shown in Figure 5-17(a) and Figure 5-17(b), respectively.
Figure 5.17. Nyquist plot and fitting curve for (a) PEDOT/A-CNTs electrode, (b) densified A-CNTs electrode.

Both plots show a sharp increase of the imaginary part in the low frequency region and a semicircle in the high frequency region. The semicircle behavior is attributed to charge transfer.
resistance of the electrodes, while the sharp increase of the imaginary part is due to the capacitive behavior of the electrode. The fittings to the EIS of both electrodes are also represented in Figure 5-17(a) and Figure 5-17(b) as the solid curves, showing that the equivalent circuit of Figure 5-16 can fit the impedance spectroscopy of both electrodes very well. The fitting parameters are listed in Table 5-1 for comparison.

As shown in the Table 5-1, in the high frequency range, the internal resistances of two electrodes show similar small R1. R1 for the PEDOT/A-CNTs electrode is a little larger because of the higher resistance of PEDOT compared with that of pure densified A-CNTs. In the medium frequency region, the larger Warburg coefficient, interface resistance and charge transfer resistance for the PEDOT/A-CNTs electrode compared with those for the A-CNTs electrode indicate the pseudocapacitor redox process. At the low frequency, the double layer capacitance and pseudocapacitance for PEDOT/A-CNTs electrode are 0.19 and 0.70 F cm\(^{-2}\), indicating that the faradaic charge/discharge of PEDOT coating layer plays an important role in contributing to the total capacitance. For the A-CNTs electrode, the double layer capacitance is 0.36 F cm\(^{-2}\). It is noted that the small “psedudocapacitance” of 0.11 F cm\(^{-2}\) for the A-CNTs electrode may come from the slow diffusion process in the small pore size of the electrode. It can be found that the fitting capacitance values are consistent with those calculated from galvanostatic measurements (the values in F/cm\(^2\) can be converted to that in F/cm\(^3\) by dividing them with the electrode thickness of 210 \(\mu\)m for PEDOT/A-CNTs electrode and 250 \(\mu\)m for A-CNTs electrode). The large value of n (larger than 0.9) also indicates the porous structure of densified A-CNTs and composite electrode. By combining the two sets of fitting parameters (Table I) for the two individual electrodes electrically in series, the data for the asymmetric cell can be fitted very well
without adjustable parameters, as shown in Figure 5-18 in the whole frequency range, indicating the optimized design of the asymmetric cell.

Table 5-1. Fitting parameters for the EISs of two electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>( R_1 ) (( \Omega ) cm(^2))</th>
<th>( C_1 ) (F cm(^{-1}))</th>
<th>( A_{sw} ) (( \Omega ) s(^{0.5}) cm(^{1/2}))</th>
<th>( R_2 ) (( \Omega ) cm(^2))</th>
<th>( R_3 ) (( \Omega ) cm(^2))</th>
<th>( C_2 ) (F cm(^{-1}))</th>
<th>( n )</th>
<th>( C_3 ) (F cm(^{-1}))</th>
<th>( R_4 ) (( \Omega ) cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT/A-CNTs</td>
<td>0.15</td>
<td>0.001</td>
<td>43.33</td>
<td>14.5</td>
<td>1.91</td>
<td>0.19</td>
<td>0.90</td>
<td>0.70</td>
<td>0.74</td>
</tr>
<tr>
<td>A-CNTs</td>
<td>0.14</td>
<td>0.001</td>
<td>28.73</td>
<td>6.57</td>
<td>1.39</td>
<td>0.36</td>
<td>0.95</td>
<td>0.11</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Figure 5-18. Nyquist plot and fitting curve for asymmetric cell.

5.5 Conclusions

In this Chapter, an asymmetric supercapacitor with high electrochemical performance has been developed with conformal coating of PEDOT on A-CNTs as the negative and the ultra-high density A-CNTs as the positive in 2 M BMIBF\(_4\)/ PC electrolyte. The positive and negative electrodes materials are individually tailored and work synergistically together in the asymmetric
cell configuration so that the cell can be operated under the high operation voltage of 4 V to achieve energy and power densities with a long cycle life. Moreover, the EIS of each electrode is modeled by equivalent circuit elements to describe quantitatively the functions of pseudocapacitor and EDLC directly. The EIS of the asymmetric cell is also simulated based on the parameters from two electrodes which demonstrate the optimized asymmetric design.
Chapter 6

Hybrid Asymmetric Supercapacitor via Nano-scale Morphology Control of Graphene, Conducting Polymer, and Carbon Nanotube Electrodes

In the Chapter 5, asymmetric supercapacitor based on PEDOT/A-CNTs//A-CNTs was introduced. The asymmetric configuration makes full use of the two electrodes to expand the operation voltage, hence the energy density and maximum power density have been improved. It should be noted that although A-CNTs as the EDLC high power electrodes provide the aligned channel to enhance ions transfer, the specific capacitor is still relatively low due to the low specific surface area, which influence the electrochemical performance of the entire cell. In this chapter, we tried to use activated graphene flakes with the higher specific area (more than 3000 m²/g) as the high power electrode in the asymmetric cell to improve the performance of asymmetric cell further. Here, an asymmetric supercapacitor, exploiting an ultra-high density nano-porous aligned microwave exfoliated graphite oxide (MEGO) as one electrode, and nm-scale conformal coating of a conducting polymer, PEDOT on A-CNTs as the other electrode, is introduced. The asymmetric configuration of the supercapacitor allows both electrodes to be separately tailored, increasing the device operation voltage and capacitance, leading to power and energy densities beyond all other such carbon-based supercapacitor architectures to date. The aligned MEGO electrode, fabricated via a self-assembly process, shows high specific gravimetric and volumetric capacitance for the high power electrode. As a result of complementary tailoring of the asymmetric electrodes, the layered device exhibits a wide 4V electrochemical window, and the highest power and energy densities reported thus far for
carbon-based supercapacitors, 149 kW L\(^{-1}\) and 113 Wh L\(^{-1}\) in volumetric performance and 233 kW kg\(^{-1}\) and 177 Wh kg\(^{-1}\) in gravimetric performance, respectively.

6.1 Introduction

As we introduced in the Chapter 1, different carbon materials can be used or investigated for the supercapacitor electrodes including but not limited to activated carbon, carbon onions, carbon black, carbon nanotubes, carbide-derived carbon and graphene. However, all these electrode materials have the same drawback that is the relatively low density (usually smaller than 0.5 g/cm\(^3\)). Hence, the outstanding high surface area may not lead to high volumetric performance for supercapacitor cells. In other words, although the electrodes with high surface area may have high gravimetric specific capacitance, and thus high gravimetric energy density, their volumetric performance is not necessary to be improved with the high gravimetric one. It is highly desired to fabricate the electrode materials with high density while maintaining the high specific surface area.

Graphene has been investigated widely to be used as electrode material for supercapacitor cells due to the remarkably high surface area (> 2,600 m\(^2\)/g), leading to the tremendous amount of charges stored and hence very high capacitance and energy density.[47] Activation of carbon materials is a common process to increase the surface area of the electrode. The highly porous electrode material with controlled pore size can be achieved if this activation is controlled carefully. Recently, Zhu et al. reported a new type of supercapacitor electrode with microwave treatment of graphene oxide (GO).[47] Then Microwave Exfoliated Graphite Oxide (MEGO) was active with KOH. The whole process was shown in Figure 6-1.
A large Brunauer-Emmett-Teller (BET) specific surface area with 3100 m$^2$/g has been obtained in this material, which is even higher than the theoretical specific surface area for graphene (2630 m$^2$/g). This activation process can be expressed as the reaction $6\text{KOH} + 2\text{C} \leftrightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3$. The activated MEGO (aMEGO) exhibited superior gravimetric electrochemical performance compared to the other carbon materials and graphene-based electrodes reported in other literatures. The supercapacitor cell with aMEGO as electrodes exhibit specific capacitance of 166 F/g, very high gravimetric energy density of around 70 Wh/kg and high maximum power density of 250 kW/kg under 3.5 V with BMIBF4/AN as the electrolyte. However, the volumetric electrochemical performance such as volumetric specific capacitance and energy density has been hindered due to the relatively low package density of less than 0.5 g/cm$^3$.

One method to increase the package density of the carbon material electrodes is to compress porous carbon electrode with mechanical pressure.[33, 143-145] During this mechanical densification process, the pores less than 1 nm and inhomogeneous pore size will be inevitably created. The aMEGO electrodes based on the normal mechanical packing method have a low density of 0.34 g/cm$^3$ which is much below the crystallographic density of the nature graphite (2.2 g/cm3). And the relatively low volumetric capacitance of 60 F/cm$^3$ is obtained. Murali et al. reported the aMEGO with high package density using high pressure
compressed method to achieve high volumetric specific capacitance and energy density.[145] By applying 25 tons of compression force, the bulk density of 0.75 g/cm³ could be obtained. Hence, a high volumetric capacitance of 110 F/cm³ by using BMIBF4/AN as the electrolyte was obtained at 3.5 V. The volumetric energy density was also got improved from 23 Wh/l for the uncompressed electrodes to 48 Wh/l for the compressed electrodes.

![Figure 6-2. VASAA of nano-porous aMEGO sheets to produce high density highly aligned aMEGO sheets.][146]

In this chapter we will adopt Vacuum-Assisted Self-Assembly Alignment (VASAA) method to fabricate aligned aMEGO electrodes with high density as high volumetric performance electrodes for supercapacitor cells. VASSAA is commonly used technique for the chemical materials synthesis but is fairly new one for the fabrication of carbon based materials such as CNTs and reduced graphene oxide.[147, 148] In this technique, carbon material is dissolved in the selected solvent to form the homogenous dispersion and then the dispersion is filtered through membrane which can be chosen depending the particle size of materials. Due to the 2D morphology of graphene material, this method can be optimized to fabricate aMEGO with high density and unique morphology. The widely accepted mechanism of this technique can be described as follows. During the solvent filtered stage, neighboring graphene sheets contact with each other by the vacuum force through the filter pores to increase the package density of the sheets. The filtration process is illustrated in Figure 6-2. For instance, Liang et al.
reported a multilayer graphene paper with this unique vacuum method leading to density as high as 1.6 g/cm$^3$.[149] We will describe the fabrication details in the following section.

**Figure 6-3.** Nanostructured electrodes in asymmetric supercapacitors. (left) Low and high magnification TEM micrographs of the negative electrode (negative ions are shown schematically in the PEDOT layer), comprised of conformal oCVD PEDOT on A-CNTs, and (right) SEM images of a-graphene flakes electrode.

In this chapter, an asymmetric supercapacitor, exploiting an ultra-high density nanoporous A-aMEGO flakes as one electrode, and nm-scale conformal coating of a conducting polymer, PEDOT on A-CNTs as the other electrode, is introduced (See Figure 6-3). The asymmetric configuration of the supercapacitor allows both electrodes to be separately tailored, increasing the device operation voltage and capacitance, leading to power and energy densities beyond all other such carbon-based supercapacitor architectures to date. The A-MEGO flakes electrode, fabricated via a self-assembly process, shows high specific gravimetric and volumetric capacitance for the positive electrode. The conformal vapor deposited conducting polymer coating enhances the charge storage of the negative electrode, while the underlying aligned nanowire morphology provides direct non-tortuous fast ion transport pathways to enhance power. As a result of complementary tailoring of the asymmetric electrodes, the layered device exhibits a wide 4V electrochemical window, higher than the individual electrodes, i.e., 2.8 V for
PEDOT/A-CNT and 3.2 V for A-MEGO. The highest power and energy densities are reported thus far for carbon-based supercapacitors, 149 kW L\(^{-1}\) and 113 Wh L\(^{-1}\) in volumetric performance and 233 kW kg\(^{-1}\) and 177 Wh kg\(^{-1}\) in gravimetric performance, respectively.

6.2 Experimental

6.2.1 Fabrication of aligned aMEGO film

The aMEGO materials were prepared by activation of MEGO which is reported in Ref. 46. Briefly, MEGO powder (200 mg) was mixed with 7 M KOH solution (10 ml) for 24 h. After filtration and drying of the mixture, the materials were activated at 800 °C in a tube furnace under the atmosphere of argon flow for 1 h. Then the mixture was washed with de-ionized water for several times until a neutral pH. Finally the solid materials were annealed at 1100 °C to remove any residual functional groups. This annealing process is essential for the better electrochemical performance through eliminating the possible electrochemical reactions involved by the remaining functional groups.

We developed this VASAA method in order to fabricate nano-porous aMEGO sheets with highly ordered nanostructure. To fabricate highly A-aMEGO, nano-porous aMEGO powder was dispersed in N, N-dimethylformamide (DMF) with the help of stirrer for 24 hours and an extra sonication process for 3 hours. Next, this solution was immediately vacuum filtered through Anodisc filter membrane (Whatman, with 0.02 μm pore size). The filtration set-up is illustrated in Figure 6-4.
As shown in Figure 6-5, Anodisc is an alumina matrix with high purity and has very precise and honeycomb-like pores. This membrane has high efficiency in stacking aMEGO sheet due to this unique pore structure and the small pore size. There are several parameters that influence the quality and density of the A-aMEGO films based on the VASAA method. The first one is the vacuum level. It could be found that the A-aMEGO film will become more compact and the high density will be obtained by increasing the vacuum strength. Hence the vacuum level can be used to adjust the density of as-filtered sheets. There are some other important factors that can influence the properties of sheets, including the dispersion concentration, solvent type, speed of solvent removal, and the film transfer method. The
thickness of these as-filtered films can be ranged from 7-18 micron which is dependent on the amount of aMEGO and the film density can reach up to 1.25 g/cm³. These thin sheets then will be stacked to reach different thicknesses (50 to 100 μm) for the usage of supercapacitor electrodes.

![Unique pore structure of Anodisc filter.](Image)

**Figure 6-5.** Unique pore structure of Anodisc filter.

We usually deploy two methods to transfer A-aMEGO thin films from Anodisc to other substrates such as current collectors, which are peeling off method as well as the floating method. A razor blade is used to carefully peel the film off the substrate for the first method. This method is fast. However, the size of final obtained film size is usually less than 2-3 mm in lateral dimensions due to the lateral force applied by the blade to the film. For the other method that is floating method, it is much more effective to make samples with large size since there is no lateral force applied on the samples. This method is based on the fact that alumina membrane can be dissolved in KOH solutions. During the floating method process, the as-filtered A-MEGO films with Anodisc membrane is placed on the surface of a 4 M KOH aqueous
solution for 2 hours until the alumina membrane is dissolved in this KOH solution. Then A-aMEGO film will float on the surface of this solution. For the next step, this solution is replaced with DI-water for 5-6 times until a neutral pH is obtained. Finally, the remaining water is removed gradually and the A-aMEGO film is transferred to other various substrates such as gold leaf, polymer, silicon wafer, etc. Figure 6-6(a) and Figure 6-6(b) exhibit the A-aMEGO film before and after applying the floating method to the Anodisc membrane in KOH solution, respectively.

![Image](image_url)

**Figure 6-6.** (a) As-filtered aMEGO film, (b) aMEGO film after applying the floating method.[42]

### 6.2.2 Fabrication of PEDOT/random CNTs composite

In order to investigate the improvement of the A-CNTs on the cycle life retention of composite electrodes compared with randomly packed CNT networks, supercapacitors with random PEDOT/CNTs electrodes were also fabricated. The random CNTs electrodes were prepared by mixing 90 wt% active materials and 10wt% polytetrafluoroethylene(PTEF) to form slurry. The slurry was pressed gold current collector, then dried at 80 °C for 24 h. 3,4-Ethylenedioxythiophene (EDOT) with molecular weight 142.17 g mol⁻¹ was received from Sigma-Aldrich. Sodium poly(styrene sulfonate) (PSS) with molecular weight 70,000 was
purchased from Sigma Aldrich. Electrochemical polymerization of PEDOT was performed using the Autolab PGSTAT 302N (Metrohm, USA) at current density 0.5 mA cm\(^{-2}\) in room temperature. PEDOT was grown on the electrodes and around the CNTs in an aqueous solution of EDOT (0.01 M in deionized water) and PSS (0.1 M in deionized eater) with a conventional four-electrode configuration. The amount of polymer coated on the electrode site was controlled by the total charge density passed during polymerization process (750 mC cm\(^{-2}\), 1500 mC cm\(^{-2}\), and 2250 mC cm\(^{-2}\)). The working and sensing electrodes were connected to the electrodes. The reference and counter electrode were connected to a platinum wire within the EDOT/PSS. The capacitance stability of PEDOT/A-CNTs and PEDOT/random CNTs symmetric supercapacitors was measured under driving voltages of 1 V and 2 V, respectively, at a current density of 5 A g\(^{-1}\) for 1,000 cycles.

6.2.3 Preparation of the asymmetric cell

The fabrication process of PEDOT/A-CNTs composite electrode has been described in Chapter 4. For the cell assembly, PEDOT/A-CNTs and a-graphene flakes electrodes were attached on Au sheets that serve as the current collectors. The asymmetric supercapacitors were prepared by assembling PEDOT/A-CNTs as the negative electrode and self-assembled a-graphene flakes as the positive electrode, which were separated by a porous paper with the thickness of 40 \(\mu\)m. A 2 M BMIBF\(_4\)/propylene carbonate (PC) mixed electrolyte was used for the asymmetric supercapacitor. For the BMIBF\(_4\)/PC mixture, 2M BMIBF4/PC exhibits the highest ionic conductivity and hence was chosen for this study.

Each electrode was characterized using screen-printed electrodes system (Dropsens) where the PEDOT/A-CNTs or graphene flakes on the platinum current collector for the working electrode, while the silver and platinum were used as the reference and counter electrodes,
respectively. For supercapacitor devices, the electrical impedance and CV curves were characterized using a potentiostat/frequency analyzer (Parstat2273). Galvanostatic cycling was measured at different discharge current densities with Versastat 4 (Princeton Applied Research).

6.3 Results and discussion

6.3.1 Electrochemical performance of each electrode

**Figure 6-7.** (a) CV curves of PEDOT/A-CNTs and (b) CV curves of a-graphene flakes at 5 mV s\(^{-1}\) in 2 M BMIBF\(_4\)/PC.

Figure 6-7(a) presents a CV curve of the A-MEGO electrode with 2 M BMIBF\(_4\)/PC as the electrolyte at a scan rate of 5 mV s\(^{-1}\) showing an ECW of -2.2 V to +1 V. Figure 6-7(b) presents a CV curve of the PEDOT/A-CNTs electrode in the same electrolyte system under the same scan rate, which shows an ECW of -1 V to +1.8 V.
Figure 6-8. Galvanostatic charge/discharge curves of A-MEGO electrode.

The galvanostatic cycles for A-MEGO at 2 A g⁻¹ are presented in Figure 6-8. The symmetric and linear charge and discharge characteristics reveal a rapid I-V response and reversible electrochemical reaction, resulting in an excellent capacitive behavior. The capacitance of the electrode was determined from the constant current divided by the slope of discharge curve. A high specific volumetric capacitance of 189.7 F cm⁻³ (165 F g⁻¹ for gravimetric capacitance) was obtained at 2 A g⁻¹. The high volumetric capacitance performance results from the stacked graphene flakes at a density of 1.15 g cm⁻³. The a-graphene flakes electrode exhibits high specific capacitance shown in Figure 6-9(a), ranging from 214.3 F cm⁻³ to 170.4 F cm⁻³ (186.4 F g⁻¹ to 148.2 F g⁻¹, Figure 6-9(b)) as the discharge current increases from 0.5 A g⁻¹ to 10 A g⁻¹.
As we discussed in the last chapter, the CNT networks provide electron transport pathways as well as mechanical support to the CP while the deposited CP layers enhance the charge storage capacity of the electrodes.[82] The density of A-CNTs is raised by 5 times via a mechanical densification process to form the scaffold support for the CP coating layer in supercapacitors,
and is distinctly advantageous relative to randomly packed morphologies.[90] Apart from the direct ion transport to reduce ESR, as illustrated in Figure 6-3, the PEDOT/A-CNTs also provide better mechanical stability and hence higher retention of the capacitance after long charge/discharge cycles, compared with the electrodes of the PEDOT/randomly packed CNT networks. In Figure 6-3, the thin (~10 nm) PEDOT layers are deposited as a conformal coating on the very high aspect ratio (~ 10,000) A-CNTs.

For the PEDOT/A-CNTs electrode, the slope of the discharge curve in Figure 6-10 yields a specific volumetric capacitance of 92 F cm\(^{-3}\) at 2 A g\(^{-1}\) (230 F g\(^{-1}\) for gravimetric capacitance).

![Figure 6-10. Galvanostatic charge/discharge curves of PEDOT/A-CNTs composite a current density of 2 A g\(^{-1}\).]
Figure 6-11. (a) Volumetric and (b) gravimetric specific capacitance at different discharge densities of PEDOT/A-CNTs electrode.

Figure 6-11(a) presents the specific volumetric capacitance at different discharge current density, from 0.5 A g\(^{-1}\) to 10 A g\(^{-1}\). Capacitance retention of 74.2% was obtained from 104.3 F cm\(^{-3}\) at 0.5 A g\(^{-1}\) to 77.4 F cm\(^{-3}\) at 10 A g\(^{-1}\) (260.8 F g\(^{-1}\) to 193.5 F g\(^{-1}\), Figure 6-11(b)), indicating that the PEDOT/A-CNTs electrode provides reliable capacitive performance for high-power applications. This relatively high retention mechanistically arises from the conformal coating of oxidative chemical vapor deposition (oCVD) PEDOT on A-CNTs. The cycling stability of the
PEDOT/A-CNTs electrodes was characterized and compared with that of the electrodes of PEDOT deposited on randomly packed CNT networks.

![Graph showing cycle performances of symmetric supercapacitors](image)

**Figure 6-12.** Cycle performances of symmetric supercapacitors with the PEDOT/A-CNTs electrodes and the PEDOT deposited on randomly packed CNT networks under driving voltages of 1 V and 2 V, respectively, at current density of 5 A g⁻¹.

As shown in Figure 6-12, symmetric supercapacitors made of the PEDOT/A-CNTs had a retention of 89% after 1000 cycles of 2 V voltage cycle, compared with a retention of 73% after 1000 cycles from PEDOT on random CNT morphologies. At lower voltage of 1 V, the retention of the PEDOT/A-CNTs was increased to 94% while that of the PEDOT on random CNT networks was at 88%. In the randomly packed CNT networks, there are CP layers in the gaps between CNTs and after long charge/discharge cycles, the mechanical failure of CP layers in these gaps will cause disruption of the electric conduction paths between CNTs and reduce the conductivity of CNT networks. As a result, the capacitance is reduced. By contrast, the electric conduction path of the continuous aligned CNTs would not be disrupted by the mechanical
failure of the CP coating layers due to the A-CNT/CP foam-like morphology of nm-scale conformal coatings on A-CNTs separated by ~10 nm gaps where ions can move in and out of the CP film. Hence, the A-PEDOT/A-CNTs electrodes exhibit more robust mechanical stability and high retention of the capacitance, compared with the electrodes of the CP deposited on randomly packed CNT networks.

6.3.2 Asymmetric cell assembly and characterizations

Both electrodes are independently tailored in asymmetric supercapacitors to operate under more optimal conditions. Here, the PEDOT/A-CNTs electrode and A-MEGO electrode were assembled, separated by a 40 μm thick porous paper. 2 M BMIBF₄/PC was used as the electrolyte due to its high ionic conductivity. By properly tuning the mass ratio of the two electrodes, the asymmetric capacitor can be operated at the full 4 V cell operation voltage (1.8 V for the negative electrode plus 2.2 V for the positive electrode).[125, 150, 151] From the consideration that charge stored at the two capacitor electrodes should be equal in magnitude with opposite sign and the stored charge q at the electrode is, \( q = C \Delta V m \), where C is the specific gravimetric capacitance, \( \Delta V \) is the maximum potential range allowed by the ECW, and m is the mass of the electrode, the mass ratio between the two electrodes can be determined by the equations in the last chapter. From the specific capacitances of the positive and negative electrodes, 230 F g⁻¹ and 165 F g⁻¹, respectively, at a constant discharge current of 2 A g⁻¹, and \( \Delta V_+ = 1.8 \) V and \( \Delta V_- = -2.2 \) V, the mass ratio \( (m_+ / m_-) \) can be calculated as 0.88.

Figure 6-13(a) presents the CV curves of the fabricated asymmetric supercapacitors at scan rates from 5 to 100 mV s⁻¹ using the 2 M BMIBF₄/PC as electrolyte. The capacitors display near rectangular CV curves, especially for the lower scan rates. The galvanostatic cycles at alternate charge/discharge current densities of 2 A g⁻¹ and –2 A g⁻¹ were presented in Figure 6-13(b).
Figure 6-13. (a) CV curves of PEDOT/A-CNTs//a-graphene asymmetric supercapacitor at different scan rates between 0 and 4 V in 2 M BMIBF$_4$/PC electrolyte. (b) Galvanostatic charge/discharge curves of asymmetric device at different current densities.
Figure 6-14. (a) Volumetric and (b) gravimetric cell capacitances of asymmetric cell at different discharge current densities.

Figure 6-14(a) and 6-14(b) presents the cell volumetric and gravimetric capacitances at different discharge currents. It should be noted that the calculated cell capacitance was based on the total volume or mass of positive and negative electrodes because it is not meaningful to deduce the specific capacitance of a single electrode for the asymmetric supercapacitor. Cell volumetric capacitance is obtained as 52.3 F cm$^{-3}$ (81.6 F g$^{-1}$ for gravimetric capacitance) at 0.2 A g$^{-1}$ which is higher than that of a-graphene based symmetric supercapacitors and other conducting polymer based asymmetric supercapacitors.[152] Cycling stability of the asymmetric
supercapacitors was demonstrated by continuously cycling the galvanostatic charge/discharge process between 0 and 4 V at a current density of 5 A g\(^{-1}\) for more than 5,000 cycles. As shown in Figure 6-15, the asymmetric supercapacitor maintains electrochemical retention of 92% after 5,000 cycles. The small cell capacitance loss is attributable to the PEDOT/A-CNTs electrode as presented in Figure 6-12.

![Cycle capacitance retention](image)

**Figure 6-15.** Cycle capacitance retention of the asymmetric supercapacitor under a voltage of 4 V at a current density of 5 A g\(^{-1}\) in 2 M BMIBF\(_4\)/PC electrolyte.

The electrochemical performance of the asymmetric supercapacitor cell was further characterized by electrochemical impedance spectroscopy (EIS). Figure 6-16 shows the Nyquist plot obtained in the frequency range of 100 kHz to 10 mHz of 5 mV applied voltage, which shows a semicircle in the high frequency region and a sharp rise of the imaginary part of the electric impedance, reflecting the dominance of the cell capacitance in the low frequency region. The semicircle in the Nyquist is attributed to the charge transfer resistance of the porous electrodes. The high frequency intersection of the semicircle on the real axis of the Nyquist plot represents the internal resistances including Ohmic resistance of the electrolyte, the resistance of
the electrode materials, and resistance in the separator, and the contact resistances between active materials and current collector. The cell shows an internal resistance of 0.1 Ω cm² when normalized with the area of the current collector of the capacitors, indicating a high electrical conductivity and low ESR of the cells.

Figure 6-16. Nyquist plot of the asymmetric cell using 1 M BMIBF₄/PC as electrolyte.

Figure 6-17(a) and 6-17(b) present comparative Ragone plots of asymmetric cells in terms of the gravimetric and volumetric performance derived from the galvanostatic discharge curves measured at different charge/discharge current densities. The cells exhibit both high volumetric and gravimetric power and energy densities at 149 kW L⁻¹ (233 kW kg⁻¹) and 113.2 Wh L⁻¹ (176.6 Wh kg⁻¹), respectively. The values under 4V are significantly higher than those of other reported carbon based symmetric supercapacitors, conducting polymer based supercapacitors and other devices reported previously as compared in Figure 6-17(a) and 6-17(b).[59, 89, 125, 130, 146, 149, 150, 153-156] All data presented in Figures, including the references cited, are derived based on the volume/mass of the electrode materials. When using the whole electrode volume/mass, which also include the mass of the electrolyte, the volumetric power and energy
densities do not change while the gravimetric power and energy densities become 122 kW kg\(^{-1}\) and 92.3 Wh kg\(^{-1}\), respectively, which are still very high due to the high density of the electrode materials.

![Figure 6-17. (a) Volumetric and (b) gravimetric Ragone plots of asymmetric cell.](image)


We also tried to use the electrolyte of 1 M Et\(_4\)NBF\(_4\)/PC which is widely used for the commercial products for this asymmetric cell as a comparison. The electrochemical performance is shown in Figure 6-18 and 6-19 respectively. Figure 6-18(a) exhibits the electrochemical window of each electrode. The operation window then can be deduced to the relatively narrow value of 3 V (still higher compared the symmetric 2.7V). From 6-18(b), it can be found the specific capacitance with 27.82 F cm\(^{-3}\) at 0.2 A g\(^{-1}\) which is lower than that of the cell with BMIBF\(_4\)/PC under 4 V. According our earlier study, the operation voltage will also influence capacitance because higher voltage will result in more diffusion which will increase the cell capacitance. The Ragone plot of the cell at an operating voltage of 3 V with 1 M Et\(_4\)NBF\(_4\)/PC is
shown in Figure 6-19(a) and 6-19(b) where the energy and power densities are reduced due to the lower EC window.

**Figure 6-18.** (a) CV curves of each electrode using 1 M Et₄NBF₄/PC as electrolyte. (b) Cell capacitance of asymmetric cell.
Figure 6-19. (a) Volumetric and (b) gravimetric Ragone plots of asymmetric cell using 1 M Et₄NBF₄/PC as electrolyte.

6.4 Conclusions

An asymmetric supercapacitor, exploiting the conformal coating of PEDOT on A-CNTs as the one electrode which combines fast ion transport pathways, enhances charge storage capability, and reduces ESR, and the A-MEGO as the other electrode fabricated from a self-assembly process which possesses exceedingly high specific gravimetric and volumetric capacitance, has been developed in this paper. The positive and negative electrodes materials are
individually tailored to control spacing and alignment of graphene and CNTs, and work synergistically together in the asymmetric cell configuration by expanding the ECW. The unique nanomorphology of the conformal coating of CP on A-CNTs also imparts mechanical stability and high cycle retention of the capacitors, compared with electrodes comprised of CP deposited on randomly packed CNT networks. Tailoring of the positive and negative electrode materials at a scale approaching that of the ions can allow asymmetric supercapacitor performance to be further expanded, e.g., utilizing other conducting polymers besides the PEDOT demonstrated here, and further optimizing A-CNT and A-MEGO packing densities to expand cell performance further and meet the requirement of a broad range of energy storage applications.
Chapter 7

**Energy harvesting devices based on supercapacitor electrodes**

Because of the high electric energy density and its correlation with the electrode nanostructures of supercapacitor cells as presented in previous chapters, they are also attractive in the area of energy harvesting devices, which have not been explored. In this chapter, as a background information, several conventional energy harvesting devices will be introduced in the section 7.1. The working principles and device circuit design of the new energy harvesting device system based on the porous electrodes will be analyzed and investigated in Chapters 7.2 and 7.3, respectively. High performance of mechanical energy harvesting device based on the nanoporous electrodes of supercapacitor structures will be presented in Chapter 7.4. In the Chapter 7.5, thermal energy harvesting devices based on the supercapacitor cells will be discussed.

**7.1 Introduction**

Energy harvesting, also called energy scavenging, is the process during which energy is captured from external sources, (such as thermal energy, solar power, mechanical pressure, salinity gradients, wind energy and kinetic energy), and stored for small, wireless autonomous devices and wearable electronic devices. Many materials can be used as the mediators to convert the external energy to the electrical energy, such as piezoelectric, electrostrictive, pyroelectric and photovoltaic materials.

A typical energy harvesting device system based on piezoelectric or electrostrictive materials from ambient mechanical motions is shown schematically in Figure 7-1. The system is
composed of mechanical front-end, piezoelectric or electrostrictive material, control circuit and the electric load. The piezoelectric or electroactive materials can be regarded as both the elastic springs and the temporary dielectric energy storage capacitors. The ambient vibration energy $U_{M0}$ is collected by the front-end mechanical transformer. The stress and strain in the active materials are created by the external force. Hence, the mechanical energy $U_{M1}$ is converted from $U_{M0}$ and stored in the piezoelectric or electrostrictive materials.

![Figure 7-1. Schematic energy flow in a mechanical energy harvesting system.](image)

The energy conversion efficiency can be expressed as

$$\alpha = \frac{U_{M1}}{U_{M0}}$$  \hspace{1cm} (7-1)

The electrical energy $U_{E0}$ is generated from the energy conversion of the mechanical energy by the active materials. This efficiency can be represented as the effective electromechanical coupling factor: $k^2 = \frac{U_{E0}}{U_{M1}}$.

This effective coupling factor is dependent not only on the active materials, but also to the electrical boundary conditions. Electric control circuits are designed to apply the harvested
electric energy to electric load or store it in rechargeable batteries. Meanwhile some of the electric energy will be dissipated as heat due to various resistive losses. This energy conversion efficiency can be represented as:

\[ \beta = \frac{U_{E1}}{U_{E0}} \]  

Hence, the total energy conversion efficient in the mechanical energy harvesting system can be expressed as

\[ c = \frac{U_{E1}}{U_{M0}} = \alpha \beta k^2 \]  

The frequency of ambient vibration should be added to the final equation when the output power is considered.

Pyroelectric materials, which have been investigated for the thermal energy harvesting device system, incorporate polarization dependence with temperature. In many ferroelectric materials, spontaneous polarization shows strong temperature dependence in some special temperature range, leading to the pyroelectric effect. At the steady state (\(dT/dt = 0\)), polarization is constant and there is no current flow. When the temperature increases (\(dT/dt > 0\)) or decreases (\(dT/dt < 0\)), the overall polarization is reduced via reduction of the dipole moments or increased, which will create the current flow.[157] The generated current, \(I_p\) can be expressed as:

\[ I_p = A_f \frac{dP_s}{dt} = A_f p \frac{dT}{dt} \]  

where \(A_f\) represents the surface area of the capacitor based on the pyroelectric film, \(P_s\) (C/m\(^2\)) is the polarization of pyroelectric thin film, \(T\) is the temperature and \(p\) is the pyroelectric coefficient (= d\(P_s/dT\)) with the unit of C/m\(^2\)K.[158]
In this chapter, we will explore the nanoporous electrodes of supercapacitor cell structure as the energy conversion mediators, replacing the piezoelectric and pyroelectric materials, for the mechanical and thermal energy harvesting. As will be shown in the chapter, due to the much higher specific capacitance and higher electric energy density compared with the that of the piezoelectric and pyroelectric materials, and strong dependence of the cell capacitance with the pressure or temperature, the nanoporous electrodes exhibit high performance in the energy harvesting cycles.

7.2 Energy harvesting based on variable capacitance – Mechanical energy harvesting as an example

![Figure 7-2](image)

**Figure 7-2.** (a) QV curve and (b)CF curve during the energy harvesting process.

Many studies have been conducted in the past decades to investigate the energy harvesting devices based on the capacitance change of the electroactive materials.[159-164] Liu *et al.* analyzed the energy harvesting using the electrostrictive polymers with the passive switch circuits.[159, 160] Koh *et al.* also conducted a detailed analysis on the maximum energy to be harvested from a dielectric elastomer using passive switch circuit.[162] The corresponding energy harvesting cycle in both charge/voltage plane and in capacitance/force plane is presented.
in Figure 7-2(a) and Figure 7-2(b). The simple circuit working principles can be shown in Figure 7-3.

![Figure 7-3](image)

**Figure 7-3.** A simple switch circuit energy harvesting devices based on variable capacitance.

The working principles can be described as follows. In the device system shown in Figure 7-3, there are two rechargeable batteries with low and high voltages labeled as $V_L$ and $V_H$. As shown in Figure 7-3, at step 1 of this energy harvesting cycle, the supercapacitor is at the lowest capacitance $C_L$ with charge stored $Q_L$ at voltage $V_H$, where $Q_L = C_L V_H$. In the process from step 1 to step 2, the capacitance is increased to $C_2$. Since the charge $Q_L$ does not change, the voltage in the capacitor is reduced to $V_L$, which yields $C_2 = Q_L/V_L = C_L V_H/V_L$ at step 2. Further increasing the capacitance from step 2 to step 3 due to further expansion of the nanoporous electrode or temperature change causes the charging of the capacitor by a battery at $V_L$ (now the switch on $V_L$ side is turned on). This raises the charge in the capacitor to $Q_H$ at step 3 and a capacitance $C_H$, $Q_H = C_H V_L$. In the process from step 3 to step 4, the capacitor is under a constant charge $Q_H$ and capacitance is reduced, which raises the voltage to $V_H$ at step 4. The capacitance at step 4 is $C_4$ and $C_4 = Q_H/V_H = C_H V_L/V_H$. As the capacitance is further reduced from step 4 to step 1, the EM converter generates electric output to power a load at $V_H$ (or charge...
a battery, the switch on V_H side is turned on). The total energy harvested through this cycle is 
\[(Q_H - Q_L)(V_H - V_L) = (C_H V_L - C_L V_H)(V_H - V_L)\]. For some carbon based on supercapacitor electrode, 
\(C_H\) is around 50 F/cm\(^3\) and assuming \(C_L = 0.7C_H\), which has been observed in the preliminary test, 
and \(V_H = 3V\), the maximum energy harvested is 28.8 J/cm\(^3\) when \(V_L = 2.65\) V. This is orders of 
magnitude higher than any energy harvesting results reported. The power consumption of this 
circuit can be as lower as 10 \(\mu\)W according to the former work in our group.[165] In this chapter, 
we will characterize systematically the energy harvesting cycle with different \(V_H\) and \(V_L\) under 
different applied stress and strain levels or the temperature change range at selected frequencies.

### 7.3 Electric control circuit development for the variable capacitor energy harvesting

In the energy harvesting cycle of Figure 7.4, there two switches controlling the current 
flow. In this thesis, the two switches consists of two MOSFETs. In the study, we first evaluate 
the switch circuit performance by using the conventional pyroelectric or piezoelectric materials 
as the energy converting media in which the capacitance and the open circuit potential will 
change with temperature for the thermal energy harvesting or external stress (pressure) for the 
mechanical energy harvesting. The two MOSFET switches allow the charge transfer from \(V_L\) to 
the rechargeable battery \(V_H\) in the energy harvesting cycle.

For the pyroelectric energy harvesting, starting at room temperature, the voltage of the 
pyroelectric material is lower than \(V_L\), and hence the left switch is ON and right switch is OFF, 
leading to the charging from \(V_L\) to the pyroelectric element. When the temperature increases, the 
potential across the pyroelectric material increases and left switch is OFF. At this stage, the two 
NMOS devices are both OFF. Continuing heating the pyroelectric materials to a higher 
temperature, the potential of the pyroelectric (PE) material will become larger than \(V_H\), resulting
in the ON state of right switch, the PE charges the rechargeable battery. Potential drop across $R_L$ is related with time and the relationship is measured with an oscilloscope.

The current can be calculated from Ohm's law,

$$ I = \frac{V_{R-Load}}{R_L} $$  \hfill (7-5)

The power harvested is given by,

$$ P = V \cdot I $$  \hfill (7-6)

where $V = V_{R-Load} + V_H$

Then the maximum energy harvesting $U_E$ can be obtained, Equation (7-7).

$$ E = \int P \, dt $$  \hfill (7-7)

### 7.4 Mechanical energy harvesting

In the energy harvesting cycles for mechanical energy harvesting, the applied mechanical stress will change pore size of the electrodes, which could lead to a change in the static capacitance of the supercapacitors, and meanwhile, a change of the ion transport speed through the electrodes, which will lead to a change of the apparent capacitance (the supercapacitor capacitance changes with the scan rate). To evaluate this effect, we first performed the energy harvesting experiment with the initial device configuration as shown in Figure 7-4. Here, two electrodes were assembled in a Teflon holder in parallel and immersed the electrolyte of BMIBF4. One electrode remained stress-free and another was pressed with different stresses by an external mechanical driver. The P(VDF-CTFE)/CNTs composites were used as both electrodes. The electrodes here were fabricated through modified vacuum-assistant self-assembly method. The CNTs powder and copolymer P(VDF-CTFE) powder were mixed in DMF with the
mass ratio of 3/7. The mixture was sonicated for several hours to form a homogenous solution. Then the solution was vacuum filtered through Anodisc filter membrane (Whatman, with 0.02 μm pore size). The free-standing composite films with the thickness of about 50 μm thick can be obtained by peeling off the films from the filter membrane after baking at 80 °C for several hours.

![Diagram](image)

**Figure 7-4.** Parallel electrode configuration for testing the porous electrodes for mechanical energy harvesting.

The CV curves of the electrodes were measured without stress and with different stresses. By integrating the discharge part of the CV curves, the specific capacitances can be calculated. Figure 7-5 presents the normalized specific capacitances with stress.
Figure 7-5. Normalized capacitance change of supercapacitor cell with stress.

According to Figure 7-5, the capacitance from the C-V curves can be variable by about 40% after applying stress from 0 to 1.5 Mpa, which is very large and might be suitable for the mechanical energy harvesting based on variable capacitance. To assess this, the relationship between the open circuit potential and stress was also investigated by VersaSTAT 4 (for variable capacitor energy harvesting, a change of true capacitance should lead to a change of the voltage across the capacitor). In contrary, very little potential change with stress was obtained. The observed capacitance change with stress as measured by the C-V curves is caused mainly by the change of the ion transport speed through the porous electrode, rather than the true static capacitance. According to the specific capacitance calculation equation in Chapter 1, for this case the surface area that has been occupied by ions before stress and the Debye length for the interface of ions and electrodes do not change much with stress. Hence, the open circuit potential will remain unchanged with stress although the capacitive capability (as measured by the C-V scans) can be changed markedly. For mechanical energy harvesting, this parallel electrode
configuration will result in a smaller specific capacitance and a large ESR (the two electrodes are not facing each other and the ion transport speed will be limited).

In order to change the static capacitance and open circuit potential for the energy harvesting device, the asymmetric polymer matrix configuration is introduced in the optimized supercapacitor cell. Nafion and P(VDF-CTFE) were used for the binders of the two electrodes, respectively. The Nafion/CNTs composite electrode with the weight ratio of 1:1 was fabricated by an infiltration method. In this process, the first step was to fabricate free-standing CNTs films, also called buckypaper. Briefly, multiwall CNTs powder was mixed with ethanol to form 0.2 mg/ml homogenous dispersion by a sonicator. Then the dispersion was filtrated through the hydrophobic PTFE filter (0.2 μm pore size). The free standing CNT thin film can be peeled off from the filter after baking at 80 °C for 1 hour. The DMF/Nafion solution was then infiltrated into CNTs film under vacuum for several hours to remove trapped air between nanotubes. It usually takes 3 days for the slow evaporation of DMF so that the Nafion can slowly fill the open spaces between CNTs.[111] After removing the solvent, the composite was annealed at 130 °C under vacuum for 1 h to increase crystallinity of the Nafion. The P(VDF-CTFE)/CNTs composite electrode was fabricated by the method similar to that described above except now P(VDF-CTFE) solution was used. BMIBF₄ was used as the electrolyte for the supercapacitor cell. It should be noted that the molecular solvent such as PC and AN cannot be used with BMIBF₄ as the electrolytes to increase the conductivity of electrolyte because they will dissolve the Nafion matrix. The two electrodes were assembled in a face-to-face configuration as illustrated in Figure 7-6. Compared with the device configuration as shown in Figure 7-4, this face-to-face configuration, analogous to that in the supercapacitors, will reduce the ion transport resistance
(reduces ESR) and enable more conductive electrode area to take part in the absorbing/releasing of ions which increases the capacitance.

Figure 7-6. Face-to-face electrode configuration for mechanical energy harvesting.

As shown in Figure 7-7, a 50 mV open circuit potential change has been obtained when 2 Mpa stress is applied and released. Hence, the energy harvested per stress cycle can be calculated as 0.25 J/cc by the equation $U_e = Q \times \Delta V$, where $Q$ is the initial charge density stored in the supercapacitor cell while $\Delta V$ is the open circuit potential change. The energy harvested of the device per cycle is much larger compared with that of other energy harvesting materials and devices such as piezoelectric devices. The harvested energy densities are only about 2.1 mJ/cc for typical PZT and 0.044 mJ/cc for PVDF materials.\cite{166} The output power density can be calculated as 18 mW/cc, which is till larger than that of some piezoelectric materials (from
several $\mu$W/cc to 1 mW/cc).[167] The power density is based on the open circuit without the load.

**Figure 7-7.** Open circuit potential change after applying a stress of 2 MPa from $t=1041$ seconds to $t=1055$ seconds.

7.5 **Thermal energy harvesting**

Pyroelectric materials are usually used for the thermal energy harvesting devices. The electrical current can be generated from pyroelectric materials with the time dependent temperature changes. However, the relatively energy harvested per cycle have hindered the applications even with the most advanced thermodynamic cycles, such as Ericsson and Stirling cycles, have been employed. Due to the high specific capacitance, high electric energy density, strong dependence of specific capacitance with temperature for supercapacitors with suitably
selected electrolytes, supercapacitor cells are promising for thermal energy harvesting applications.

The temperature-dependence of supercapacitor capacitance has been investigated in this work. During the transition from a high temperature to a low temperature, the very lower conductivity of electrolyte will hinder ion transport which influences the ions absorption/desorption for EDLC supercapacitors and inhibits the faradic reactions for pseudocapacitors. Hence, the specific capacitance will decrease with the decrease of temperature. Here, BMIBF$_4$ was used as electrolytes in the two supercapacitor cells. The melting temperatures $T_m$ of individual ILs and eutectic mixture of the ILs were studied by differential scanning calorimetry (DSC) over a wide temperature range. The DSC data in Figure 7-8 shows that the melting temperature $T_m$ of BMIBF$_4$ is observed at -39 °C.

**Figure 7-8.** DSC curves of BMIBF$_4$ electrolyte.
Figure 7-9. CV curves for the cells with BMIBF$_4$ as the electrolytes with the scan rates of (a) 100 mV s$^{-1}$ and (b) 5 mV s$^{-1}$. 

Specific capacitance (F cm$^{-3}$) vs. Potential (V)
CV measurements were performed to investigate the electrochemical behavior of the cell with BMIBF₄ as the electrolyte at the temperature range from -60 °C to 80 °C. At each interval, the system was allowed to equilibrate for at least two hours inside the chamber to eliminate the hysteresis from previous experiments. Figure 7-9(a) and Figure 7-9(b) show the CV curves with BMIBF₄ at the scan rate of 100 mV/s and 5 mV/s, respectively.

The capacitor cells with pure ILs exhibit near ideal capacitive behavior, i.e., nearly rectangular CV curves, at temperatures above 20 °C, as shown in Figures 7-9. However, the capacitance value diminishes markedly at temperatures below 0 °C. This could be attributed to the fast diminishing conductivity of this electrolyte at lower temperatures despite its lower melting temperature. In other words, although the electrolyte is still liquid state at temperatures above \( T_m \) (~ - 39 °C), the high viscosity of the electrolyte (due to gelation before freezing) does not allow the ions to propagate in the porous electrodes during the charge/discharge cycle and consequently the capacitance reduces significantly.

As a comparison, Figure 7-10 presents the capacitance changes in the operating temperature range with BMIBF₄ as electrolyte, extracted from CV curves in Figure 7-9. The capacitances are normalized for a better exhibition. The cell shows large capacitance change as the temperature is reduced from high temperature to -60 °C with BMIBF₄ as electrolyte. The cell exhibits volumetric capacitance of 130 F cm\(^{-3}\) at the 80 °C. At – 60 °C, the volumetric capacitance decreases dramatically to 16 F cm\(^{-3}\), which is only 12 % capacitance retention.
Figure 7-10. Normalized capacitance and volumetric capacitance of cells with the BMIBF$_4$ vs. temperature from -60 °C to 80 °C at the scan rate of 5 mV/s.

Figure 7-11. Open circuit potential change with temperature change for the CNT/P(VDF-CTFE) nanocomposites with what electrolyte as the temperature was reduced from 80 °C to -20 °C.
The results and discussion above indicate that the specific capacitance of supercapacitor cell can have strong dependence with temperature at certain temperature range for specially selected electrolytes, which could be made use for the thermal energy harvesting. In the study here, CNTs/ P(VDF-CTFE) composites were used as both electrodes. A VWR heater was used to heat the cell and dry ice was used to cool the cell down. Figure 7-11 shows the open circuit potential change with temperature change from 80 °C to -20 °C. 21 mV potential change from the temperature change was obtained. From the equation of \( U_e = Q \Delta V \), it can be deduced that the energy harvested per heating/cooling cycle is 0.36 J/cc. It is noted that the open circuit potential change in Figure 7.11 is much smaller than the capacitance change in Figure 7.10. This is due to the fact that the temperature change affects both the ion mobility and mobile ion density, which can significantly affect the capacitive capability as measured by C-V scans, in addition to the intrinsic capacitance change due to the change of mobile ion concentration and the Debye length, which is the one causing the observed open circuit voltage change.

It should be mentioned that the power density of energy harvesting device is 2.5 mW/cc based on response time after cooling. The long response time (145 s) is mainly due to the low thermal conductivity of random CNTs electrodes. The power density can be improved by employing carbon materials with higher thermal conductivity such as the aligned carbon nanotube. Based on some earlier works, the thermal conductivity of aligned carbon nanotubes is 10 times larger than that of random ones.[168] We will mention it in the next chapter and work on it in the future.

Besides the CNTs/P(VDF-CTFE) supercapacitor electrodes, we also investigated a commercial supercapacitor (Gold Cap 2.5 V 10 F) under the same temperature change. Gold Cap 2.5 V 10 F supercapacitor cell was used in the energy harvesting device. As shown in Figure 7-
12, 26 mV potential change was obtained as the temperature was lowered from 80 °C to -20 °C. Hence 0.52 J energy was harvested for a heating/cooling cycle.

![Graph](image)

**Figure 7-12.** Open circuit potential change of Gold Cap 2.5 V 10 F supercapacitor cell with temperature change from 80 °C to -20 °C.

### 7.6 Conclusions
In this chapter, the working principles of energy harvesting devices based on variable capacitance was introduced. By applying stress or changing temperature of specially designed supercapacitor cells, we show that the open circuit potential will change. Such kind of voltage change can be made use of for the energy harvesting by employing the switch circuit presented in this chapter, in which the energy will be harvested through pumping the charges from a low voltage to a high voltage. For the mechanical energy harvesting devices based on supercapacitor cell, the parallel and face-to-face configurations were compared. The latter one brought to larger specific capacitance and lower ESR. 40 mV open circuit potential change was obtained, resulting
the high energy harvested of 0.2 J/cc. For the thermal energy harvesting devices, the dependence of specific capacitance with the temperature has been investigated. Through comparing the performance of cells using two different electrolytes, the dependence is strongly related to the melting temperature of electrolyte. 0.26 J/cc energy harvested per increasing/decreasing temperature cycle was achieved. The energy densities of the mechanical and thermal energy harvesting devices based on supercapacitor electrodes are much higher compared with those based on piezoelectric and pyroelectric materials (from 0.04 mJ/cc to several mJ/cc).[166, 169] Hence the supercapacitor cells with specially designed nanoporous electrodes and electrolytes are promising candidates for the energy harvesting devices.
8.1 Conclusions

This dissertation developed and studied several EDLC and pseudocapacitor cells based on aligned carbon nanotubes, graphene, conducting polymers. The very large specific capacitance and electric energy density, as demonstrated in this thesis, make them attractive for high performance energy harvesting devices. The controllable nanomorphology of the electrodes based on highly aligned carbon nanotubes provided the aligned ion transport channel to enhance the ions transport speed, leading to a high energy and power density of the supercapacitor cells. The asymmetric configuration of supercapacitor cells was developed to make full use of both positive and negative electrodes to expand the operation potential of the cells. Hence the energy density and power density has been improved further. Moreover, the specific capacitance and high energy, and large capacitance change with stress or temperature in specially designed supercapacitor cells were investigated for energy harvesting devices.

Aligned carbon nanotubes were used for the supercapacitor cells. The superior electrical conductivity and parallel ion pathways formed by A-CNTs lead to high electrochemical performance of as-assembled supercapacitor cells. The as-grown A-CNT forest only has 1% Vf. To achieve high volumetric energy and power densities, the low volume density of the as-synthesized A-CNT should be densified. A mechanical densification method was developed to allow the density of A-CNTs to be tuned precisely over a broad range while preserving the straight ion pathway between A-CNTs. The investigations of supercapacitors fabricated from A-CNTs in the volume fraction from 1% to 40% were performed. The results show that the supercapacitors fabricated from the A-CNTs with 40% Vf A-CNTs exhibit volumetric and
gravimetric power densities of 25 kW L\(^{-1}\) and 50 kW kg\(^{-1}\), respectively, for the capacitor cell with 0.8 mm thick A-CNT electrodes, compared with 1.1 kW L\(^{-1}\) and 2.5 kW kg\(^{-1}\) for the capacitor cell with 0.8 mm thick activated carbon electrodes and 13.4 kW L\(^{-1}\) and 24 kW kg\(^{-1}\) for the supercapacitors using smaller 0.5 mm thick A-CNTs densified by the liquid collapsing method.

In order to improve the specific capacitance of supercapacitor electrode further, pseudocapacitive materials PEDOT were introduced in the hybrid electrodes. The pseudocapacitors based on conducting polymer can store larger amount of charges per gram/volume compared with EDLC supercapacitor cells do as the whole bulk (not only the surface) of conducting polymer has involved the electrochemical reactions. Composites of polymerizing conductive polymer PEDOT, which conformal coated on surface of aligned CNTs, exhibit higher electronic and ionic conductivity and larger electrode specific capacitance. Moreover, larger volumetric specific capacitance in charge/discharge cycling was obtained compared with the pure A-CNTs electrodes. The porous morphology of the composite provides a larger surface area and enables the rapid diffusion of ions into the bulk of the material. The vertical directional growth of carbon nanotubes provides the straight pathways for ions to transport fast and mechanical structure to enhance the cell electrochemical stability. Symmetric supercapacitors using the 5 Vf % A-CNTs coated with 10 nm thick PEDOT as electrodes and BMI-BF\(_4\)/PC as electrolyte can achieve the highest volumetric specific capacitance (92.79 F cm\(^{-3}\)) and enhance the volumetric energy storage density (11.22 Wh L\(^{-1}\) and 35.24 kW L\(^{-1}\)) further of the cell.

The supercapacitor discharge efficiency, i.e., Columbic efficiency, was traditionally obtained by calculating the charge ratio between charging and discharging processes, which
could not exhibit the energy relationship. To correctly characterize the Columbic efficiency, we introduced the QV curve method based on the CV curve or galvanostatic curve. This new method can be used to evaluate the cell energy loss and Coulombic efficiency accurately compared with the traditional method.

The energy density and maximum power density are strongly dependent with the operation voltage window. Although the pseudocapacitors can bring relatively larger specific capacitance, the electrochemical window with electrolyte is very narrow (2 V even for organic electrolyte). In order to expand the operation potential, the asymmetric configuration was introduced in the supercapacitor cell. An asymmetric supercapacitor with high electrochemical performance has been developed with conformal coating of PEDOT on A-CNTs as one electrode and the ultra-high density A-CNTs as the other one in 2 M BMIBF_4/ PC electrolyte. The conformal CP coating on the A-CNTs enhances charge storage while the aligned nanotube morphology provides straight and fast ion transport pathways. The A-CNTs electrode, densified from a unique mechanical method, possessing high volumetric capacitance while preserving the aligned morphology to maintain the high power, provides an ideal electrode for the asymmetric supercapacitor. The positive and negative electrodes materials are individually tailored and work synergistically together in the asymmetric cell configuration so that the cell can be operated under the high operation voltage of 4 V to achieve energy and power densities with a long cycle life. Moreover, the EIS of each electrode is modeled by equivalent circuit elements to describe quantitatively the functions of pseudocapacitor and EDLC directly. The EIS of the asymmetric cell is also simulated based on the parameters from two electrodes which demonstrate the optimized asymmetric design.
Although A-CNTs as the EDLC electrodes provide the aligned channel to enhance ions transfer, the specific surface area is not high compared with more recently developed graphene, which can further improve the supercapacitor performance. In this thesis, activated graphene flakes with the higher specific area (more than 3000 m$^2$/g) were used in the asymmetric cell to improve the performance of asymmetric cell further. An asymmetric supercapacitor, exploiting the ultra-high density (> 1 g/cm$^3$) nano-porous microwave exfoliated graphite oxide (MEGO) as one electrode, and nm-scale conformal coating of a conducting polymer, PEDOT on A-CNTs as the other electrode, has been developed. The aligned MEGO electrode, fabricated via a self-assembly process, shows high specific gravimetric and volumetric capacitance for the high power and energy density electrodes. As a result of complementary tailoring of the asymmetric electrodes, the supercapacitor cell exhibits a wide 4 V electrochemical window, and the highest power and energy densities reported thus far for carbon-based supercapacitors, 149 kW L$^{-1}$ and 113 Wh L$^{-1}$ in volumetric performance and 233 kW kg$^{-1}$ and 177 Wh kg$^{-1}$ in gravimetric performance, respectively.

Finally, the supercapacitor cells, replacing the piezoelectric and pyroelectric materials, were investigated for the mechanical and thermal energy harvesting devices, due to the high specific capacitance, ultra-high electric energy density, and strong dependence of the capacitance with stress or temperature in specially designed supercapacitor cells. The preliminary study results of this thesis show that these supercapacitor cells can exhibit much higher energy density in the energy harvesting devices compared with piezoelectric and pyroelectric materials. For the mechanical energy harvesting devices based on supercapacitor cell, the parallel and face-to-face configurations were compared. The latter one brought to larger specific capacitance and lower ESR. 40 mV open circuit potential change was obtained, resulting the high energy harvested of
0.25 J/cc. For the thermal energy harvesting devices, the dependence of specific capacitance with the temperature has been investigated. Through comparing the performance of cells using two different electrolytes, the dependence is strongly related to the melting temperature of electrolyte. 0.36 J/cc energy harvested per increasing/decreasing temperature cycle was achieved. The performance of mechanical and thermal energy harvesting devices based on supercapacitor cells has been improved compared with those based on piezoelectric and pyroelectric materials.

8.2 Future work

Based on the works presented in this thesis, some future research directions are suggested and listed in this section.

8.2.1 Advanced hybrid electrode materials

As exhibited in Chapter 5, hybrid nanostructure supercapacitor electrode combines the carbon based materials (activated carbon, carbon nanotubes, graphene…) with battery type pseudocapacitive metal oxides or conducting polymers, leading to high performance of supercapacitor cells. The hybrid materials of carbon and pseudocapacitive materials will show synergistic effects combing the advantages of both materials. The pseudocapacitive materials will offer a high capacitance while the carbon materials provide a mechanical structure to sustain from the strains from charge/discharge process and improve the electrode conductivity. For the current works, A-CNTs were used as the carbon materials due to the high modulus and aligned channel configuration. However, the carbon nanotubes still suffer from relatively lower surface area which influences the specific capacitance of supercapacitor cell. Compared with carbon nanotube, graphene has larger specific surface area, very high intrinsic electrical conductivity in plane as well as high mechanical strength and chemical stability which are suitable for the carbon materials combined with pseudocapacitive materials. Considering the cost of the application in the future, the low cost of being manufactured in ton quantities for graphene-based
material derived from graphite oxide (GO) is also competitive compared with carbon nanotube, especially compared with A-CNTs. Hence, hybrid graphene and pseudocapacitive materials will receive considerable attention for the new supercapacitor cell electrode.

For the pseudocapacitive materials in the hybrid electrode, some other conducting polymers as well as PEDOT should be tried. PPy and PANi have relatively higher theoretical specific capacitance compared with PEDOT. The vacuum filtration self-assembly method should be also deployed to control the nanomorphology of hybrid electrode. Besides conducting polymer, metal oxides are also the promising candidates for the pseudocapacitive materials due to the higher theoretical specific capacitance and low cost. For example, manganese oxides (MnO$_2$) present relatively low cost, low toxicity, and environmental safety, as well as high theoretical capacities ranging from 1100 to 1300 F g$^{-1}$. MnO$_2$ and graphene hybrid materials can be prepared by redox reaction between graphene and potassium permanganate under microwave irradiation. The composition of the composites is adjusted by changing the relative ratio of KMnO$_4$ to graphene in the starting mixture. Different weight ratio of pseudocapacitive materials and graphene should be developed to exhibit the conformal coating on the graphene flakes. The lower weight ratio of pseudocapacitive materials will result in lower specific capacitance while the higher weight ratio will lead to the poor cycle life. Hence, the appropriate weight ratio should be determined to obtain the high performance of the hybrid electrodes.

8.2.2 Energy harvesting devices based on specifically designed supercapacitors

Chapter 7 demonstrated a relatively large amount of energy can be harvested in the mechanical and thermal energy harvesting devices based on supercapacitor cells. There are four research directions which have the promise to improve the performance further.
Firstly, leakage current and self-discharge of supercapacitor cells should be suppressed. Several methods were tried to reduce the leakage current. One effective way is to assemble the supercapacitor cell in the inert atmosphere. Figure 8-1 shows the leakage currents of supercapacitor cells assembled in air and N₂, respectively. 2 M BMIBF₄/PC was used as electrolyte. The leakage current can be defined as the current to maintain the potential which the cell is charged to. As a comparison, the leakage current of sample assembled in air decreased from around 120 μA to 40 μA in 7200 s, while the leakage current of sample assembled in N₂ decreased from 60 μA to 2 μA in 275 s. It could be found that the leakage current of cell assembled in N₂ was reduced dramatically and also much smaller compared with some commercial products. Other methods should be also tried such as other ionic liquids with larger ion size. Meanwhile, the pseudocapacitive materials should be introduced into the devices to reduce the self-discharge. Different with adsorption of ions on the surface of EDLC electrode, the chemical reactions between the pseudocapacitive electrodes and ions will stabilize the ions, leading to the suppression of self-discharge.

Secondly, the static capacitance and open circuit potential changes should be increased further with stress or temperature change. It is highly desired to obtain more than 50 mV open
circuit potential change of supercapacitor cells in the energy harvesting cells, resulting in much larger energy harvested. It is proposed to employ the asymmetric configuration to optimize the devices. The asymmetric configuration can be from different polymer matrices or different types of electrodes. The different responses of the two electrodes with stress or temperature will lead to concentration density of ions and the Debye length change correspondingly. Hence, the large open circuit potential and energy harvested will be obtained based on this configuration.

Thirdly, as we mentioned in Section 7.5, the long response time after cooling and relatively low power density are attributed to the low thermal conductivity of electrode with random orientation of carbon nanotubes. According to some earlier works, the thermal conductivity of aligned carbon nanotubes is much larger than that of random ones. As shown in Figure 8-2, the thermal conductivity can be increased by around 10 times by using aligned configuration. [168] Hence, for our energy harvesting device, the thermal conductivity and the power density can be improved largely by employing aligned carbon nanotube composites as electrodes.
Finally, although we discussed how to suppress the leakage current and self-discharge in supercapacitor cell, it is impossible to neglect them which will lead to the energy loss in the energy harvesting devices. To avoid this energy loss, it is high desired to create current flow spontaneously under 0 DC bias voltage after applying stress or temperature gradient. Based on this assumption, single ion conductors to assemble the ionic PN junction will be used as the mediator for energy harvesting device. From an earlier work, two ionomers with mobile anions and cations were employed for the PN junction. The structure of junction is shown in Figure 8-3. [Ru(bpy)$_3$]$^{2+}$($\text{PF}_6$)$_2$ was used as the n type side providing mobile anions. The molecule 9,10-diphenylanthracene-2-sulfonate with sodium counter ions (DPAS Na$^+$) was used as the p type side providing mobile cations. Gradients in the concentration of mobile ions at the
junction result in diffusion of cations into the N-type material and anions into the P-type. As ions diffuse, a built-in potential that opposes diffusion is established. Equilibrium is reached when the flux due to ion diffusion is balanced. Based on these PN junctions, we can apply them either for the mechanical energy harvesting device or thermal energy harvesting device. For the mechanical energy harvesting, by applying stress on the film, the concentration of donors and acceptors will change, which results in the change of built-in potential based on the equation
\[ V_{bi} = kT/e \times \ln \left( \frac{N_a N_d}{n_i^2} \right) \]. Hence, the equilibrium will be broken, leading to the current on the load. For the thermal energy harvesting device, the built-in potential will also change with the temperature based on the equation above. The output voltage will be obtained based on the temperature change. It should be noted that [Ru(bpy)$_3$]$_{2+}$PF$_6$ film based on spin casting method is very brittle. Hence, in the next step, we will incorporate nanoporous graphene or other carbon materials into the molecular matrix to improve the elastic performance and the ions affinity in the electrodes, leading to the high ion concentration of ions. The performance of energy harvesting devices will be improved further based on this configuration.
Figure 8-3. (a) Structure of PN junction and (b) detail of the junction area.[170]
References:


[125] Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li, F. Wei, Asymmetric supercapacitors based on graphene/MnO2 and activated carbon nanofiber electrodes with high power and energy density, Advanced Functional Materials, 21 (2011) 2366-2375.
Vita

Yue Zhou

Yue Zhou was born on June, 1986 in Jiangsu Province, China. In 2008, he received the Bachelor of Science degree honored in department for intensive instruction at Nanjing University in China. After that he spent three years also in Nanjing University pursuing on Master Degree in Physics. In 2011 he started his Ph.D. study in Department of Electrical Engineering at the Pennsylvania State University under supervision of Prof. Qiming Zhang. His research mainly focused on high performance energy storage and harvesting devices. He has published more than 15 papers and filed one U.S. patent during the Ph.D study. In 2015, he received Melvin P. Bloom Memorial Outstanding Doctoral Research Award in Electrical Engineering. Yue Zhou is a member of Electrochemical Society (ECS) and Society of Photographic Instrumentation Engineers (SPIE).