Carbon based self-supported electrodes for supercapacitors and batteries

Wang, Huanhuan

2018

Wang, H. (2018). Carbon based self-supported electrodes for supercapacitors and batteries.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/104893>

<https://doi.org/10.32657/10220/47832>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**CARBON BASED SELF-SUPPORTED ELECTRODES FOR
SUPERCAPACITORS AND BATTERIES**

WANG HUANHUAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

CARBON BASED SELF-SUPPORTED ELECTRODES FOR SUPERCAPACITORS AND BATTERIES

WANG HUANHUAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

Input Date Here

...15-AUG-2018...
Date

Input Signature Here

Wang Huanhuan

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

Input Date Here

...15-AUG-2018...
Date

Input Supervisor Signature Here

Input Supervisor Name Here
Shen Ze Xiang

Authorship Attribution Statement

This thesis contains material from papers published in the following peer-reviewed journals where I was the first author.

Chapter 2 contains part of a published review paper: H.H. Wang, J. Y. Lin and Z. X. Shen. Polyaniline (PANi) based electrode materials for energy storage and conversion. *Journal of Science: Advanced Materials and Devices* **1**, 225-255 (2016). DOI: 10.1016/j.jsamd.2016.08.001.

- Prof Shen Ze Xiang and Prof. Lin Jianyi provided the initial project direction and help modified the manuscript.
- I prepared the manuscript drafts.

Chapter 4 is published as H.H. Wang, J. L. Liu, Z. Chen, S. Chen, T. C. Sum, J. Y. Lin, and Z. X. Shen. Synergistic capacitive behavior between polyaniline and carbon black. *Electrochimica Acta* **230**, 236-244 (2017). DOI: 10.1016/j.electacta.2017.01.164.

The contributions of the co-authors are as follows:

- Prof Shen Ze Xiang and Prof. Lin Jianyi provided the initial project direction and help modified the manuscript.
- I prepared the manuscript drafts. The manuscript was revised by Dr Liu Jilei.
- All sample preparation, most characterizations and all electrochemical tests were conducted by me.
- The characterizations including Scanning electron microscopy, Fourier Transform Infrared Spectroscopy (FTIR), the Raman Spectroscopy and UV-vis Spectroscopy were conducted by me.
- Ms Chen Zhen assisted in the collection of the Transmission Electron Microscopy (TEM) images.
- Dr Chen Shi helped with the X-ray Photoelectron Spectroscopy (XPS) test.

Chapter 5 is published as H. H. Wang, D. L. Chao, J. L. Liu, J. Y. Lin, and Z. X. Shen, Nanoengineering of 2D Tin Sulfide Nanoflake Arrays Incorporated on Polyaniline

Nanofibers with Boosted Capacitive Behavior, *2D Materials* (2018). DOI: 10.1088/2053-1583/aabd12.

The contributions of the co-authors are as follows:

- Prof Shen Ze Xiang provided the initial project direction and help modified the manuscript.
- I wrote the drafts of the manuscript. The manuscript was revised together by Prof. Lin Jianyi, Dr. Chao Dongliang and Dr Liu Jilei.
- I performed all the materials synthesis, collected SEM/TEM images, the Raman Spectra, the X-ray diffraction (XRD) patterns and Nitrogen adsorption-desorption isotherms and pore size distributions, and conducted all the electrochemical tests.
- Dr. Chao Dongliang helped with the TEM Energy Dispersive Spectrum (EDS) mapping.

Input Date Here

...15-AUG-2018...
Date

Input Signature Here

Wang Huanhuan

Abstract

Electrochemical energy storage devices based on conducting polymers deliver higher specific capacity compared with carbon-based supercapacitors and superior kinetics compared to metal-based batteries, thus bridging the gap between capacitors and batteries. Polyaniline as a typical conducting polymer exhibits high pseudocapacitance in supercapacitors. In chapter 4, the binder-free supercapacitor electrodes of PANi and carbon black with high specific capacity and fully reversible feature are successfully synthesized via a one-step potentialdynamic co-deposition method. Significant effect of carbon black has been demonstrated, i.e., it plays an important role in producing high conductivity, porous and extended conformation structure with high oxidation state and depressed hydrolysis effect, leading to superior capacitive performance. This promotes better understanding about synergistic effect between different components in hybrid electrode materials and opens up new research in the following.

In chapter 5, much efforts have been made on nanoscale engineering in designing novel self-supported electrode based on tin sulfide and PANi network. The combination of tin sulfide and polyaniline evokes synergistic effect to enhance the performance. On one hand, the polyaniline nanofibers facilitate the growth of tin sulfide flakes in nanosize, which is helpful for improving the capacity and stability of the electrode. On the other hand, unlike carbon additives, tin sulfide nanoflakes exhibit high capacity due to greatly decreased particle size and introduced mesopores, nanoclusters, and exposed edges. Benefiting from effective nanostructure engineering, good electrochemical performance has been demonstrated and a Na^+ intercalation mechanism is unraveled. This is the first time that tin sulfide-based material is fabricated as a self-supported electrode for supercapacitors.

Supercapacitors and batteries have been playing great roles in different energy supply demands due to different electrochemical features. Besides the morphological and structural design via nanoscale engineering, the fundamental studies are equally important to improve electrochemical performance of these energy storage devices. In

chapter 6, the morphology/components and growth mechanism of solid electrolyte interface on carbon-based anode is investigated in KPF_6 and $\text{KN}(\text{SO}_2\text{F})_2$ (KFSI)-based organic electrolytes, aiming to unravel the SEI effect on K^+ ion storage mechanism. Electrochemical characterizations disclose that the KFSI-based cells deliver improved electrochemical performance in terms of coulombic efficiency and cycling stability, compared to KPF_6 -based cells. Experimental results including depth-profiling XPS study, ex-situ TEM, SEM, and FTIR analysis, reveal that KFSI salt contributing to a thin, uniform and smooth SEI layer compared to KPF_6 induced SEI layer, ensuring good cycling stability and high reversibility.

Based on the optimized electrolyte in chapter 6, the nitrogen doping effect on K^+ storage in graphite is explored. It is found that i) the induced holey active sites provide more sites for K^+ storage, ii) the enlarged interlayer spacing facilitates K^+ intercalation, and iii) the improved electronic conductivity ensures fast kinetics. All these features together, lead to superior electrochemical performance. Furthermore, the K^+ storage behavior is strongly dependent on the both nitrogen concentrations and types. Specifically, the pyridinic/pyrrolic nitrogen doping is helpful in creating holey structures via high doping intensities to accommodate more K^+ . These results promote better understanding of K^+ ion storage mechanism and provide guidance for optimized carbon-based electrode design.

Lay Summary

Nowadays, supercapacitors and batteries are superstars as energy supplies for portable devices and electric vehicles. Normally, supercapacitors have high power density, which indicates a fast rate to store and release energy. Batteries usually possess high energy density, which allows large amounts of energy stored in such devices, contributing to long working time. Although supercapacitors and batteries have great difference in performance, these two energy storage devices share similar constructions and components, including electrodes, electrolyte, membrane and current collectors.

The dissertation focuses on the electrode material synthesis, electrolyte investigation and the fundamental understanding of related underlying principles of carbon-based supercapacitors and batteries. The morphological and structural design of electrode materials are very important for these electrochemical energy storage devices. In a typical energy storage device, the electrode materials are soaked in the electrolyte. At the interphase of solid electrode material and liquid (or gel solid) electrolyte, energy starts to be stored when an external voltage is applied. In view of this, a porous material could allow large amounts of electrolyte to infiltrate into electrode material and enlarge the interphase area to promote better performance. Besides, a well-designed electrode material can guarantee high stability upon cycling, benefiting from robust structure, high mechanical stability and favorable structure to alleviate changes. Moreover, high conductivity is also critical for energy storage devices, which requires electrode material with integrated structure and good electronic properties for facilitated charge transport.

Based on these principles, electrode materials with high porosity, good conductivity and stability are highly desirable for energy storage devices with high capacity, long cycling life and fast charge-discharge. In parts of this dissertation work, the material design of polyaniline-based supercapacitor electrodes has been conducted. Polyaniline as a conducting polymer has good conductivity and high capacity. However, the mechanical and electrochemical stability of polyaniline are poor. In order to tackle these issues, polyaniline/carbon black composite and polyaniline/tin sulfide hybrid have been designed.

Here, carbon black incorporated in polyaniline nanofibers could prevent polyaniline from water attack. On the other hand, tin sulfide anchored around polyaniline could be a protective and connective layer for improved performances. When it comes to conductivity, the nitrogen doped carbon materials have been employed as electrodes in this work. Heteroatom doping, including nitrogen, plays great role in conductivity enhancement and structural tuning for carbon-based materials. Particularly, nitrogen doped carbon material possess enlarged interlayer space and surface area, which are favorable for high capacity and stability.

As mentioned above, a solid electrolyte interphase between the electrode and electrolyte is formed in an energy storage device, especially for batteries. Electrolyte plays a crucial role in the formation of this interphase, in terms of the structures and components, which could greatly affect the stability and reversibility of the electrode during charge and discharge process. Therefore, different electrolytes are involved in this work to study the effect of solid electrolyte interphase formation on electrochemical performance, which provides suggestions on electrolyte selection for energy storage devices.

No matter the electrode material design or the electrolyte modifications, the purpose is to provide scientific support to develop better energy storage devices. Meanwhile, the fundamental studies provide guidance for such progresses, which are expected to develop more effective and safer energy supplies for everyday life.

Acknowledgements

I would like to express my sincere gratitude to Ministry of Education (MOE), Singapore and CNRS International NTU THALES Research Alliance (CINTRA) for providing me scholarship during my Ph. D study. In addition, the research equipment accesses authorized by School of Material Sciences and Engineering (MSE) are equally important, without which I cannot even do anything with my research. Great thanks to MSE for the conference support. The local conferences, ICMAT 2015, ICMAT 2017 and international conference MRS Spring 2018 were all supported by MSE, where I shared ideas with other talented researchers and learned a lot from knowledgeable seniors.

Since I came to Singapore from 2014, my supervisor, professor Shen Ze Xiang and my co-supervisor, Professor Lin Jianyi give me meticulous care and tireless academic guidance. I still remember when I first came here, I knew nothing about Singapore, from academic research to everyday life. As a fresh undergraduate, I didn't know anything about how to start research effectively, without impetuous and confuse. Our group is just like a big family, where I integrated quickly and started my scientific research career step by step with help of my supervisors and seniors. I also express my sincere thanks to my TAC members, professors Huang Yizhong and Sun Handong, who always give me suggestions on my research during annual year TAC meeting. Besides, Professor Yan Qingyu as the chairman of my QE examination, gave me constructive advices promoting my following work.

I am grateful to professor Timothy White, who interviewed me before I came to Singapore and helped me to check QE report. Thanks to all administrative staffs, especially for Mr Wang Bochuan, Ms Serena Tan, Ms Navarro Serika Cara, Ms Noor Shazana Bte Senin, Ms Leong Chew Mui and Mr Ho Jun You. They gave me a lot of support on research, graduate studies and finance issues related with conferences. They helped me with the paperwork and informed me upcoming events timely every time. I also give my thanks to Mr Kenny Chow who used working in NTU and gave me a lot help on my study and research.

Great thanks to professors, Li Shuzhou, Xue Can, Dr Long Yi, Adjunct Professors Yao Kui, Gregory Goh K. L and professor Huo Fengwei, who taught me a lot of scientific principles during classes, which help me to do better in my research. Thanks to all technical staffs, especially for Mr Lim Yan Koon, Mr Gan Zi Li, Ms Yeow Swee Kuan and Ms Leong Chow Fong, who gave me trainings on equipment and helped me a lot on sample characterizations. Thanks to all technical staffs in FACTS, Dr Weiling Liu, Dr Derrick Ang, Dr Yee Yan Tay, Mr Alan Lim, Dr Teddy Salim, Dr Pio John S. Buenconsejo and Dr Samuel Morris, they gave me training on TEM, XRD and helped me to do tests. I learned a lot from them, especially in the operations and principles of equipment.

Thanks to faculties in School of Physical and Mathematical Sciences, NTU. Mr Li Yuanqing trained me SEM. Ms NG Xue Fen and Ms WON Lai Chun always help me with the access to labs/offices and help us to book rooms for group meeting. Thanks to faculties in Teaching, Learning & Pedagogy Division (TLPD), Teaching Excellence Academy, NTU, who taught us how to teach and how to be a good teaching.

I am grateful to my group members, Dr Liu Jilei, Dr Chao Dongliang, Dr Wang Jin, Dr Yan Jiaxu, Dr Yin Tingting, Ms Chen Zhen, Ms Xia Juan, Mr Qian Cheng, Mr Wang Haisheng, Ms Cai Xiaoyi, Ms Anastasiia Artemova, Ms Lekina Yulia, Ms Xiao Kuikui, Ms Jiang Haifeng, Mr Yan Liwen and Ms Chang Jing. My seniors Dr Liu Jilei, Dr Chao Dongliang and Dr Wang Jin trained me various instruments in the lab and taught me a lot of scientific principles. Our group members grow up together for a better future.

Last but not least, I should give my sincere thanks to my families, my parents and sisters. Thanks for supporting me to come to Singapore, encouraging me to be a person with dreams. Thanks to my boyfriend and his family, who give me support when I feel depressed, enlightening me to keep forward.

Table of Contents

Abstract	i
Lay Summary	iii
Acknowledgements	v
Table of Contents	vii
Table Captions	xiii
Figure Captions	xv
Abbreviations	xxi
Chapter 1 Introduction.....	1
1.1 Problem statement	2
1.2 Objectives and scope.....	4
1.3 Dissertation overview.....	6
1.4 Findings and outcomes/originality	7
References.....	8
Chapter 2 Literature Review	11
2.1 History and development of energy storage devices.....	12
2.2 Supercapacitors	14
2.2.1 Operation principles of supercapacitors.....	14
2.2.2 Electrode materials for supercapacitors	18
2.3 Polyaniline based supercapacitor electrodes	19

2.3.1	Polyaniline and carbon composites.....	20
2.3.2	Polyaniline and metal oxide composites.....	22
2.4	Lithium ion batteries	24
2.4.1	Operation principles of lithium ion batteries	24
2.4.2	Progress of finding alternatives to replace lithium	25
2.5	Early stage of potassium ion batteries.....	26
2.5.1	Progress and principles of potassium ion batteries	26
2.5.2	Carbon based anodes for potassium ion batteries	28
2.6	PhD in context of literature	32
	References.....	33
Chapter 3 Experimental Methodology.....		39
3.1	Chemicals and Instruments	40
3.2	Rationale for selection of synthesis methods.....	41
3.2.1	Chemical vapor deposition	41
3.2.2	Electrochemical deposition.....	43
3.2.3	Co-precipitation method	45
3.3	Rationale for selection of characterizations	47
3.3.1	Scanning electron microscopy	47
3.3.2	Transmission electron microscopy	49
3.3.3	Fourier transform infrared spectroscopy.....	50
3.3.4	Raman spectroscopy	51
3.3.5	UV visible spectroscopy	53
3.3.6	X-ray diffraction	54
3.3.7	X-ray photoelectron spectroscopy	55

3.3.8	Porosity measurement	56
3.4	Electrochemical test	57
3.4.1	Cyclic voltammetry	58
3.4.2	Galvanostatic charge-discharge profiles	59
3.4.3	Electrochemical Impedance Spectroscopy	60
3.4.4	Quantitative analysis based on electrochemical tests	62
	References	62

Chapter 4 Synergistic capacitive behavior between polyaniline and carbon black

4.1	Introduction	66
4.2	Synthesis and characterizations	69
4.2.1	Chemicals and instruments	69
4.2.2	Synthesis: Fabrication of PANi/CB composite electrode	70
4.2.3	Morphological studies	70
4.2.4	Structural analysis	73
4.3	Electrochemical results	76
4.4	Conclusions	80
	References	81

Chapter 5 Nanoengineering of 2D tin sulfide nanoflake arrays incorporated on polyaniline nanofibers with boosted capacitive behavior

5.1	Introduction	86
5.2	Synthesis and characterizations	88
5.2.1	Chemicals and instruments	88
5.2.2	Fabrication of SnS ₂ @PANi@GF composite electrode	88

5.2.3 Morphological studies.....	89
5.2.4 Structural analysis.....	92
5.3 Electrochemical results	94
5.4 Quantitative capacitive analysis and <i>ex</i> TEM studies	96
5.5 Full cell assembly.....	99
5.6 Conclusions	101
References.....	102

Chapter 6 Passivation study on potassium storage mechanism in doped graphite foam.....105

6.1 Introduction	106
6.2 Synthesis and characterizations.....	108
6.2.1 Chemicals and instruments	108
6.2.2 Fabrication of nitrogen doped graphene foam	108
6.2.3 Characterizations and tests.....	109
6.3 The effect of different salts, KFSI and KPF ₆ on electrochemical performance ...	109
6.4 Morphological and structural studies of SEI layer	114
6.5 Depth-profiling spectroscopic studies	117
6.6 Conclusions	122
References.....	122

Chapter 7 Nitrogen doping induced holey active sites for potassium storage.....127

7.1 Introduction	128
7.2 Experimental	130
7.3 Morphological and structural studies	130

7.4	Electrochemical tests.....	135
7.5	Conclusions	140
	References	141
Chapter 8	Conclusions and recommendations for future works.....	145
8.1	Conclusions	146
8.2	Reconnaissance work not included in main chapters	148
	8.2.1 Heteroatom doping effect on carbon-based potassium ion batteries	149
	8.2.2 Investigations on K ⁺ based hybrid cell	150
	References	152
	Appendix.....	153

Table Captions

Table 2.1 Physical, electrochemical and economic characteristics of lithium, sodium, and potassium.

Table 2.2 The illustration of problems solved in heteroatom doped carbon materials for KIBs.

Table 6.1 Influence of electrolyte on impedance parameters at different test conditions.

Table A.1 The molar ratio of different configurations in C1s with the sputtering time changing after cycling in two electrolytes in K-ion batteries.

Table A.2 Surface species concentration of C, O, N elements in N-doped graphene foams.

Table A.3 Surface species concentration of different bonding types in C1s.

Table A.4 Surface species concentration of different bonding types in N1s.

Table A.5 Surface species concentration of different bonding types in O1s.

Table A.6 Influence of nitrogen doping on impedance parameters.

Figure Captions

Figure 1.1 Regone plot for supercapacitors, batteries and fuel cells.

Figure 2.1 The schematic illustration of strategies used to improve the energy density of supercapacitors.

Figure 2.2 Schematic diagram of (a) the electrochemical double-layer capacitors and (b) the pseudocapacitors.

Figure 2.3 Illustration of pseudocapacitive behavior of the conducting polymer during the charging process.

Figure 2.4 Regone plots for carbon, metal and conducting polymer-based supercapacitors.

Figure 2.5 Schematic illustration of electrolyte diffusion paths in PANi nanowire arrays.

Figure 2.6 (a) The schematic of (i) growth mechanism of PANi on the surface of graphene oxide and (ii) nucleation of PANi in solution. (b) Schematic illustration of 3D graphene pyrrole/carbon nanotube/polyaniline architectures fabrication. (c) Schematic representation of the reduced diffusion length with whisker-like channels.

Figure 2.7 The schematic of core-shell α -Fe₂O₃/PANi nanowire arrays fabrication.

Figure 2.8 Schematic illustration of a typical potassium ion battery.

Figure 2.9 Characterizations of N-FLG and FLG during K⁺ storage. (a, b) CV curves at 0.05 mV s⁻¹. (c, d) Raman spectra at different potential during charge. (e, f) Schematic illustration of the K⁺ storage mechanism during staging process and at the nitrogen doped active sites.

Figure 3.1 The schematic illustration of the synthesis of graphite foam by chemical vapor deposition.

Figure 3.2 The synthesis of the nitrogen graphite foam by chemical vapor deposition.

Figure 3.3 The schematic illustration of the co-deposition of polyaniline and carbon black composites.

Figure 3.4 The scheme of PANi growth on the graphite paper.

Figure 3.5 The scheme of water bath deposition of tin sulfide on graphite foam supported polyaniline nanofibers.

Figure 3.6 The simplified illustration of the interactions between the incident electron beam and the sample, with the emission of secondary electrons, backscattered electrons, auger electrons, transmitted electrons and characterized X-rays.

Figure 3.7 Schematic illustration of interactions between photons and molecules. (a) Various interactions of the laser with a molecule, including Raman scattering (Stokes and anti-Stokes), Rayleigh scattering and Transmitted light. (b) Molecular energy diagram comparing these scattering interactions.

Figure 3.8 Possible electronic transitions of σ , π and n : $\sigma\text{-}\sigma^*$, $\pi\text{-}\pi^*$, $n\text{-}\sigma^*$ and $n\text{-}\pi^*$.

Figure 3.9 The schematic illustration of bragg equation.

Figure 3.10 The schematic presentation of depth profiling XPS study on solid electrolyte interface (SEI).

Figure 3.11 Coin cell assembly of the potassium ion half-cell.

Figure 3.12 A typical CV curve with a couple of cathodic and anodic peaks.

Figure 3.13 A typical galvanostatic charge discharge curve of electrode materials with faradic reactions.

Figure 3.14 A typical example of equivalent circuit diagram used for supercapacitors.

Figure 4.1 (a) The polaron formation and conversion in PANi-ES. (b) the schematic energy band structure of PANi-ES with asymmetric upper (p^*) and lower polaron bands (p). CB (π^*) and VB (π) represent of conduction band and valence band, respectively.

Figure 4.2 (a) Schematic illustration of the synthesis of PANi based samples deposited on the GP substrate (left). After electrochemical co-deposition (middle), PANi/CB nanofibers are coated on the GP substrate (right). (b), (c) FE-SEM images of PANi-20 and PANi+CB-20, respectively.

Figure 4.3 FTIR spectra of CB, PANi-20 and PANi+CB-20. (b) The schematic representation of the formation mechanism of PANi/CB composite. (c) Raman spectra of CB, PANi and PANi/CB electrodeposited on GP. (d) UV-visible spectra of PANi-20 and PANi+CB-20 deposited on Graphite paper.

Figure 4.4 (a) Wide scan XPS spectra of PANi-20 and PANi+CB-20. C 1s regions of (b) PANi-20 and (d) PANi+CB-20. N 1s regions of (c) PANi-20 and (e) PANi+CB-20, respectively.

Figure 4.5 (a) CV curves at a scan rate of 2 mV s^{-1} and (b) galvanostatic charge and

discharge curves obtained at 0.1 A g^{-1} . (c) Cycling stability at a scan rate of 20 mV s^{-1} for PANi-20 and PANi+CB-20. (d) Nyquist plots for PANi-20 and PANi+CB-20. The inset is the equivalent circuit used for impedance spectra fitting. R_{el} is the equivalent series resistance (ESR), Q_{dl} is the element related with double layer capacitance, R_{ct} is the charge transfer resistance and W is Warburg impedance.

Figure 5.1 Synthesis and morphology of the electrode materials. (a-c) Schematic illustration of the synthesis of $\text{SnS}_2@\text{PANi}@\text{GF}$. Schematic and typical SEM image of (a, d) GF, (b, e) PANi@GF and (c, f) $\text{SnS}_2@\text{PANi}@\text{GF}$. (g) FESEM image of micro-sized $\text{SnS}_2@\text{GF}$. (h) Representative photographs of (h1) the GF in black, (h2) PANi@GF in atrovirens, and (h3) $\text{SnS}_2@\text{PANi}@\text{GF}$ in claybank. (i) Low magnification SEM of as obtained $\text{SnS}_2@\text{PANi}@\text{GF}$. Inset of (i): photograph showing flexibility of $\text{SnS}_2@\text{PANi}@\text{GF}$ electrode.

Figure 5.2 TEM and HRTEM images of $\text{SnS}_2@\text{GF}$ and $\text{SnS}_2@\text{PANi}@\text{GF}$. (a, d) TEM images of $\text{SnS}_2@\text{PANi}@\text{GF}$ and $\text{SnS}_2@\text{GF}$. Inset of (b): SAED pattern of SnS_2 . (b, e) HRTEM images displaying the lateral view and (c, f) the aerial view of tin sulfide nanoflakes and microflakes for $\text{SnS}_2@\text{PANi}@\text{GF}$ and $\text{SnS}_2@\text{GF}$, respectively. (g) EDX elemental mapping of Sn, S, N, and C of $\text{SnS}_2@\text{PANi}@\text{GF}$.

Figure 5.3 Morphological and Structural characterization of $\text{SnS}_2@\text{GF}$ and $\text{SnS}_2@\text{PANi}@\text{GF}$. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of $\text{SnS}_2@\text{GF}$ and $\text{SnS}_2@\text{PANi}@\text{GF}$. (c) The Raman spectra and (d) XRD patterns of $\text{SnS}_2@\text{GF}$ and $\text{SnS}_2@\text{PANi}@\text{GF}$.

Figure 5.4 (a-d) Electrochemical performance of $\text{SnS}_2@\text{GF}$ and $\text{SnS}_2@\text{PANi}@\text{GF}$. (a) Galvanostatic charge and discharge curves obtained at 0.1 A g^{-1} . (b) Cyclic Voltammetry curves at a scan rate of 10 mV s^{-1} . (c) Specific capacitances at different current density and (d) cycling stability tested at 1 A g^{-1} . (e) Galvanostatic charge-discharge curves of $\text{SnS}_2@\text{PANi}@\text{GF}$ at various current density. (f) The comparison of rate capability for the preliminary studied tin sulfide-based electrodes for supercapacitors.

Figure 5.5 Quantitative capacitive analysis of charge storage behavior. (a, b, c) Capacitive contribution (Shaded area) calculations of $\text{SnS}_2@\text{GF}$, PANi@GF and $\text{SnS}_2@\text{PANi}@\text{GF}$ at 10 mV s^{-1} . (d) Capacitive and diffusive contributions of $\text{SnS}_2@\text{GF}$, PANi@GF, and $\text{SnS}_2@\text{PANi}@\text{GF}$, respectively.

Figure 5.6 SAED patterns of SnS₂ nanoflakes at different states. (a) At initial stage, (b) after charge and (c) after discharge.

Figure 5.7 (a) The Cyclic Voltammetry curves of SnS₂@PANi@GF and BP2000@GP at 10 mV s⁻¹. (b) The Cyclic Voltammetry curves of SnS₂@PANi@GF// BP2000@GP asymmetric supercapacitor at varied scan rates. (c) The galvanostatic charge discharge profiles of SnS₂@PANi@GF// BP2000@GP asymmetric supercapacitor at varied current density and (d) The long-term cycle stability test of SnS₂@PANi@GF// BP2000@GP ASC at 1 A g⁻¹. Inset of (d): the photograph of the full cell configuration.

Figure 6.1 Characterizations of as-obtained NGF. (a) HRTEM image and corresponding fast Fourier transform (FFT) pattern. (b, c, d) XRD pattern, Raman spectra and XPS spectra of NGF-5.12.

Figure 6.1 Electrochemical evaluations of KPF₆ and KFSI-based cells. (a), (b) CV curves obtained at 1st, 2nd, 3rd, 5th and 10th cycle at 0.1 mV s⁻¹. (c), (d) Nyquist plots acquired after 1st, 2nd, 3rd, 5th and 10th cycle's test. Insets are atomic structures of two salts, KPF₆ and KFSI. (e), (f) Galvanostatic cycling test and Coulombic efficiency during the first 30 cycles' test. Insets are the 1st charge-discharge profiles at 40 mAh g⁻¹, respectively. (g) Galvanostatic cycling test.

Figure 6.3 *Ex-situ* SEM and TEM images of NGF-5.12 anodes in (a, c) KPF₆-based and (b, d) KFSI-based electrolytes after 20th discharge to 0.01 V. Insets of (a), (b) are the corresponding low magnification images. (e) FTIR spectra of NGF-5.12 anodes after discharge in above two electrolytes.

Figure 6.4 Depth-profiling XPS spectra of NGF-5.12 in in KPF₆ and KFSI-based electrolytes. (a) C1s, (b) O1s for KPF₆-based and (c)C1s, (d)O1s for KFSI-based) at different time of Ar⁺ bombardment of discharged electrode. The outmost surface of SEI is t = 0 min.

Figure 6.5 Depth-profiling XPS spectra of (a) F1s, (b) P2p for KPF₆-based and (c) F1s, (d) S2p for KFSI-based electrolytes at different time of Ar⁺ bombardment of discharged electrode.

Figure 7.1 SEM images of (a, d) NGF-1.03, (b, e) NGF-2.22 and (c, f) NGF-8.47. (g) The EDX mapping of NGF-8.47.

Figure 7.2 Morphological and structural characterizations of NGFs. HRTEM images

of (a) NGF-1.03, (b) NGF-2.22 and (c) NGF-8.47. Inset of (a, b, c): The corresponding FFT patterns. (d) XRD patterns and (e) Raman spectra of NGF-1.03, NGF-2.22 and NGF-8.47. Inset of (d): XRD spectra centered at the characteristic peak of (002) crystal plane. (f) Nitrogen adsorption and desorption isotherms and (g) pore size distribution of NGF-1.03, NGF-2.22 and NGF-8.47.

Figure 7.3 High-resolution XPS test of NGFs. N1s spectra (a) NGF-1.03, (b) NGF-2.22 and (c) NGF-8.47, respectively. (d) The schematic illustration of PD, PL and graphitic nitrogen contents in different NGFs.

Figure 7.4 High resolution XPS spectra, C1s and O1s for (a, d) NGF-1.03, (b, e) NGF-2.22 and (c, f) NGF-8.47, respectively.

Figure 7.5 Electrochemical test of NGF-1.03, NGF-2.22 and NGF-8.47. (a) cyclic voltammetry at 0.1 mV s^{-1} . (CV) curves, (b) selected range CV curves, (c) 1st discharge, (d) 1st charge and 2nd discharge of the galvanostatic profiles. (e) Rate performance evaluations, (f) cycling stability test at 40 mA g^{-1} and (g) Nyquist plots after 10 cycles' test of NGFs. (h) The corresponding equivalent circuit diagram and pictorial model of the affiliated impedance elements, the fitted results are exhibited in Table A.6.

Figure 7.6 *In-situ* kinetic diagnosis during charge and discharge. (a) The galvanostatic profiles of NGF-1.03, NGF-2.22 and NGF-8.47 at 40 mA g^{-1} at 40 mA g^{-1} . (b-d) Nyquist plots of NGF-1.03 at different states of charge. (e-g) Nyquist plots of NGF-2.22 at different states of charge. (h-j) Nyquist plots of NGF-8.47 at different states of charge.

Figure A.1 SEM imagines of (a) PANi+CB-10, (b) PANi+CB-50 and (c) PANi+CB-20-SS. The scale bar in FE-SEM figures is 100 nm.

Figure A.2 (a) and (b) N_2 adsorption/desorption isotherms pore size distribution curves of CB. (c) and (d) N_2 adsorption/desorption isotherms and pore size distribution curves of PANi+CB-20-SS.

Figure A.3 (a) CV curves at 2 mV/s of PANi based samples deposited at different scan rates (10, 20, 50 mV/s) on different substrates (GP and SS).

Figure A.4 (a-c) CV curves of SnS_2 @GF, PANi@GF, SnS_2 @PANi@GF at various scan rates, respectively.

Figure A.5 SEM images of (a, d) as-obtained NGF-5.12. And the morphologies after different cycle cycling test in (b, e) KPF_6 -based electrolyte and (c, f) KFSI-based

electrolyte.

Figure A.6 Elemental mapping and the EDS spectra of the discharged NGF anodes cycled in (a) KPF_6 and (b) KFSI-based electrolytes.

Abbreviations

SC	Supercapacitor
EDLC	Electric double-layer supercapacitor
ASC	Asymmetric supercapacitor
LIBs	Lithium ion batteries
KIBs	Potassium ion batteries
PANi	Polyaniline
LE	Leucoemeraldine
EB	Emeraldine base
BQ	p-bernigraniline
HQ	Hydroquinone
CNTs	Carbon nanotubes
GO	Graphene oxide
CB	Carbon black
GP	Graphite paper
SS	Stainless steel
GF	Graphite foam
NGF	Nitrogen doped graphite foam
PD	Pyridinic
PL	Pyrrolic
SEI	Solid electrolyte interface
SCE	Saturated calomel electrode
WE	Working electrode
CE	Counter electrode
RE	Reference electrode
SSA	Specific surface area
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
SAED	Selected area electron diffraction
EDS	Energy dispersive X-ray spectroscopy

FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
CV	Cyclic voltammetry curve
EIS	Electrochemical impedance spectroscopy

Chapter 1

Introduction

This chapter gives an overview of the latest development and progress in energy storage devices, especially for supercapacitors and metal ion batteries. Thereinto, several possible routes are involved to solve the existing problems and obstacles in this area. The objectives, findings and originalities of research studies during last four years are discussed in detail.

1.1 Problem statement

With the rapid development of economy, supplying of energy cannot meet the increasing demands. Therefore, clean and efficient energy storage devices are desirable due to the energy and environment crisis.[1] Over the past decades, clean and sustainable energy technologies have been rapidly developed. As illustrated in Figure 1.1, fuel cells have high energy density, which is promising for energy supply. However, the technique related with the electro-catalysts for fuel cell is not mature enough for practical applications.[2] Among varied kinds of batteries, Lithium ion batteries (LIBs) with high energy density and long cycling life are playing an important role in commercial power supply. Meanwhile, supercapacitors with high power density, extremely good stability and high safety are suitable for high-rate discharge transients. These two sustainable energy storage devices have been in the ascendance, becoming “super stars” in the investigation fields.[3]

Figure 1.1 Ragone plot for supercapacitors, batteries and fuel cells.

Supercapacitors and LIBs are commercialized products nowadays, which are capable as different energy supplies. Specifically, supercapacitors are employed in intermittent renewable power sources, which attracted high attention in various of applications, like portable devices, electric vehicles and smart grids owing to high power density. For

example, supercapacitor could provide short-term acceleration energy during braking of vehicles, which could protect the main power supply, like batteries, from being damaged via high frequency charge/discharge.[4] LIBs have been widely used to power up the portable devices, like mobile phones, laptops, digital cameras, almost all handy electric facilities being used every day. Furthermore, they infiltrate into the transportation to supply the electric vehicles like electric bicycles, motors, automobiles and trains, acting as the pure or hybrid power sources.[2, 5]

Even both supercapacitors and LIBs have made great success and been used for commercial applications, there are still unsolved problems. The uppermost one is the optimization of electrode material to achieve both high energy and power density. Carbon species, metal compounds and conducting polymers are the three main types of electrode materials. In detail, carbon-based electrodes (activated carbon, graphene, carbon nanotubes, etc.) with high conductivity and stability usually have excellent cycling stability and high-power density but low energy density. Metal compounds exhibit excellent electrochemical performance, due to their high activity and good intrinsic electrochemical properties, but they still have problems like low conductivity, high cost and limited natural abundance. Conducting polymers, especially polyaniline (PANI), have attracted great interests in energy storage, sensors and electrochromic devices since the discovery in 1960,[6] exhibiting high flexibility, good conductivity and high capacities compared to electrochemical double-layer supercapacitors.

However, the monotonous material usually suffers from a verity of problems when used as electrode materials. In view of this, researchers have paid a lot of attention on hybrids and composites, to make full use of advantages of each component.[7] Moreover, the electrode design is equally important besides the material hybridization. Particularly, wearable and portable electronic devices have drawn much attention recently and proposed increasing demands for flexible and self-supported electrodes.[8] Compared to powder electrode materials, self-supported electrode without extra weight of additives, polymer binders and current collectors could further increase the energy and power density of the whole device.

Besides material hybridization and electrode design for improved performances, LIBs confront with other challenge such as the limited abundance (0.0017 wt. %) and uneven distribution of Li resource.[9] These features impede LIBs sustainable applications. [10] Accordingly, the exploration of the alternatives is highly desirable.

1.2 Objectives and scope

Much effort should be made in rational electrode design, material hybridization and exploration of new alternatives of LIBs, to settle the problems mentioned above. This dissertation just focuses on these important areas and proposes some solutions to address these challenges.

Supercapacitors generally delivers fast kinetics with relatively low energy density. To improve the energy density without scarifying the power density becomes extremely important. Polyaniline (PANi) as a conducting polymer, exhibits high flexibility, multi-redox reactions, good electronic properties,[11] and low cost. PANi based devices show high specific capacity compared with conventional carbon based supercapacitors, and faster kinetics than most inorganic batteries, which can narrow the gap between inorganic batteries and carbon based capacitors, demonstrating high potential for practical applications.[12] Moreover, PANi could be easily synthesized by chemical or electrochemical methods, and formatted into self-supported electrodes, expanding its application into flexible devices.[6]

PANi has been wildly studied as supercapacitor electrodes. However, most investigations are based on hybridizations of different components without sufficient explanation. The underlying mechanism is still unrecognized even the performance is quite good. In the first part (chapter 4) of this thesis, a facile electrochemical co-deposition method was adopted to fabricate the self-supported electrode material on porous graphite substrates, using low cost precursors, aniline and carbon black. The commercial carbon black was chosen because: i) it promotes extended PANi chains to be thinner and longer than pure PANi; and ii) it increases the doping level and decreases the defect density of PANi.

FTIR, Raman and UV-vis spectroscopy were used to verify the bonding interactions between PANi and CB, which are beneficial to high quality PANi and good electrochemical performance. In the following work (chapter 5), tin sulfide nanoflake anchored PANi network as flexible supercapacitor electrode was fabricated for the first time. The synergistic effect between PANi and tin sulfide was identified: PANi can facilitate the growth of tin sulfide in nanoscale. The nanosized tin sulfide exhibits superior pseudocapacity and diffusion-controlled capacity compared to micro-sized one. Simultaneously, tin sulfide can protect PANi from structural changes and electrochemical distortion, improving the cycling stability. The unclear storage mechanism in tin sulfide-based supercapacitor electrode is also studied and the Na^+ intercalation mechanism was proposed in this work.

Considering an electrochemical power source supplied vehicles, the feature of supercapacitors is “fast” (fast charge & discharge), while “long” (large energy density allows for long working time) for LIBs. As mentioned above, both power sources are promising in energy storage. In terms of low abundance of Li metal, researchers have made intense efforts to explore the alternatives. Sodium is attractive due to its large crust reserves (2.3 wt. %).[9] However, the storage of sodium in graphite is rather poor because the Na^+ cannot well intercalate in graphite.[13, 14] This signifies that the commercialized and mature graphite based technology for LIBs could not be transferred to the sodium ion batteries.[15, 16] Interestingly, a specific capacity of 279 mAh g^{-1} can be achieved for reversible K^+ storage in graphite, via the formation of stage 1 K-intercalated graphite intercalation compounds (K-GICs).[17-21] This demonstrates the practical feasibility of graphite anode for potassium ion batteries (KIBs).

The KIBs are still at early stage with varied problems unsettled, like the optimized electrode materials, the suitable electrolytes, membranes and the fundamental principles/mechanisms that limited the K^+ storage. In order to improve the specific capacity and cycling stability, the heteroatom doped (especially N-doped) carbon materials, especially for nitrogen, are promising as KIB anodes. Several advantages could be demonstrated via nitrogen doping, i) enhanced conductivity; ii) increased active sites

for K^+ storage; iii) favorable structural change, eg. enlarged interlayer space, which is beneficial for K^+ storage as K^+ has larger radius. In this work, the effect of nitrogen doping level and doping configurations on K^+ storage will be discussed in detail.

Other than electrode material modification, the study of electrolytes is also involved to investigate the inferior stability and reversibility of KIBs. Analogy to LIBs and NIBs, the intact and stable solid electrolyte interface (SEI) is essential to the long-term performance and coulombic efficiency. The formation and growth of SEI in terms of chemical composition, morphology, thickness and stability are greatly dependent on the electrode structure/morphology, electrolyte constituents and electrochemical conditions,[22-25] while intense investigations have been conducted on electrode materials, the synergy of electrode and electrolyte was overlooked. In this work, a comprehensive investigation of the SEI formation or growth on binder free anodes has been conducted via a combination of spectroscopic and microscopic techniques in KIB system.

1.3 Dissertation overview

In this dissertation, the synthesis and fabrication of self-supported electrodes for supercapacitors and KIBs are expound profoundly. The electrochemical performance of self-supported electrodes is evaluated. The structure-property and electrolyte correlations are studied in detail. Especially the vital role of solid electrolyte interface is discussed.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning about the history, progress and working principles of various energy storage devices, especially for supercapacitors and potassium ion batteries.

Chapter 3 discusses the principles underlying the synthesis, characterization and electrochemical tests. The explanations on why particular method is employed and how the particular method works are involved.

Chapter 4 elaborates the first major set of results: Synergistic capacitive behavior between polyaniline and carbon black. The positive impact of carbon back during polyaniline deposition is proposed and verified by numbers of characterizations, in terms of FTIR, Raman spectroscopy, UV-vis spectroscopy and XPS.

Chapter 5 elaborates the second major set of results: Nanoengineering of 2D tin sulfide nanoflake arrays incorporated on polyaniline nanofibers with boosted capacitive behavior. The synergistic effect between polyaniline and tin sulfide nanoflakes is demonstrated. The energy storage mechanisms, surface induced double layer/pseudocapacitive behaviors and diffusion-controlled Na⁺ insertion in tin sulfide nanoflakes, are studied.

Chapter 6 elaborates the third major set of results: Passivation study on potassium storage mechanism in Doped Graphite Foam. The formation and growth of SEI in terms of chemical composition, morphology, thickness and stability are examined, and the effect on electrochemical performances is investigated.

Chapter 7 elaborates the fourth major set of results: Nitrogen doping effect on potassium storage mechanism in graphite foam. The nitrogen concentration and configuration effects on alkali metal ion battery are first systematically studied in this work.

Chapter 8 draws together the threads of this thesis and the strategies for future work are also included.

1.4 Findings and outcomes/originality

This dissertation led to several novel outcomes by:

1. Unraveled the synergistic effects between polyaniline and carbon black in boosting supercapacitor performance.

2. Proposed CVD route as an ideal for the synthesis of flexible/self-supported carbon-based electrodes (heteroatom doped or undoped ones).
3. Uncovered energy storage mechanism in tin sulfide-based supercapacitor electrode.
4. Identified the structure, components and formation mechanism of SEI layer on carbon-based anode.
5. Uncovered nitrogen doping effect on potassium storage.

References

- [1] L.L. Zhang, X. Zhao, *Chem. Soc. Rev.*, **2009** 38 2520-2531.
- [2] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.*, **2011** 4 3243-3262.
- [3] S.L. Candelaria, Y. Shao, W. Zhou, X. Li, J. Xiao, J.-G. Zhang, Y. Wang, J. Liu, J. Li, G. Cao, *Nano Energy*, **2012** 1 195-220.
- [4] C. Zhong, Y.D. Deng, W.B. Hu, J.L. Qiao, L. Zhang, J.J. Zhang, *Chem. Soc. Rev.*, **2015** 44 7484-7539.
- [5] S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, K. Fujiwara, *Adv. Funct. Mater.*, **2011** 21 3859-3867.
- [6] S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, *Prog. Polym. Sci.*, **2009** 34 783-810.
- [7] J. Liu, L. Zhang, H.B. Wu, J. Lin, Z. Shen, X.W.D. Lou, *Energy Environ. Sci.*, **2014** 7 3709-3719.
- [8] Z. Weng, Y. Su, D.W. Wang, F. Li, J.H. Du, H.M. Cheng, *Adv. Energy Mater.*, **2011** 1 917-922.
- [9] J.C. Pramudita, D. Sehwat, D. Goonetilleke, N. Sharma, **2017**.
- [10] T.C. Wanger, *Conserv. Lett.*, **2011** 4 202-206.
- [11] C.H. Silva, N.A. Galiote, F. Huguenin, É. Teixeira-Neto, V.R. Constantino, M.L. Temperini, *J. Mater. Chem.*, **2012** 22 14052-14060.
- [12] G.A. Snook, P. Kao, A.S. Best, *J. Power Sources*, **2011** 196 1-12.
- [13] R. Asher, S. Wilson, **1958** 181 409-410.

- [14] Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cumings, C. Wang, **2014** 5 4033.
- [15] S.W. Kim, D.H. Seo, X. Ma, G. Ceder, K. Kang, **2012** 2 710-721.
- [16] P. Ge, M. Fouletier, **1988** 28 1172-1175.
- [17] Y. Mizutani, T. Abe, K. Ikeda, E. Ihara, M. Asano, T. Harada, M. Inaba, Z. Ogumi, *Carbon*, **1997** 35 61-65.
- [18] S. Komaba, T. Hasegawa, M. Dahbi, K. Kubota, *Electrochem. Commun.*, **2015** 60 172-175.
- [19] Z.L. Jian, W. Luo, X.L. Ji, *J. Am. Chem. Soc.*, **2015** 137 11566-11569.
- [20] W. Luo, J.Y. Wan, B. Ozdemir, W.Z. Bao, Y.N. Chen, J.Q. Dai, H. Lin, Y. Xu, F. Gu, V. Barone, L.B. Hu, *Nano Lett.*, **2015** 15 7671-7677.
- [21] K. Share, A.P. Cohn, R.E. Carter, C.L. Pint, *Nanoscale*, **2016** 8 16435-16439.
- [22] S.H. Lee, H.G. You, K.S. Han, J. Kim, I.H. Jung, J.H. Song, *J. Power Sources*, **2014** 247 307-313.
- [23] M.Y. Nie, B.L. Lucht, *J. Electrochem. Soc.*, **2015** 162 X1-X1.
- [24] J.M. Zheng, J.A. Lochala, A. Kwok, Z.Q.D. Deng, J. Xiao, *Adv. Sci.*, **2017** 4 19.
- [25] S.J. An, J.L. Li, C. Daniel, D. Mohanty, S. Nagpure, D.L. Wood, *Carbon*, **2016** 105 52-76.

Chapter 2

Literature Review

This chapter presents the historical progress and development of energy storage devices, especially for the working principles, electrode materials and electrolytes of supercapacitors and metal ion batteries. Emphasis is placed on the synthesis and strategies of hybridizations of electrode materials. New ideas and perspectives included in this work are also summarized in view of the gaps in literatures.

2.1 History and development of energy storage devices

Unquestionably, energy storage is one of the greatest challenges nowadays, to meet the increasing energy need and environmental crisis concerns. These reversible devices, like supercapacitors and rechargeable batteries, depend intimately on the electrode properties, hence the comprehensive investigations of material hybridization and electrode design are involved in this field.

In 1957, the first patent of electrochemical capacitors was filed. But it did not cause a stir until 1990s when the concept of electrochemical supercapacitor with high power density started to draw attention.[1] Since then, supercapacitors have been used to recuperate brake energy in hybrid vehicles. They were used as back-up power supplies, which could protect the main power from disruptions against high frequency voltage change. Many governments and academies, including the US Department of Energy turned attention to supercapacitors with a lot of money was invested.[2] In recent years, great progress has been made, but the distinct disadvantage, low energy density compared with batteries still exists. As illustrated in Figure 2.1, varied strategies have been employed to improve the energy density of supercapacitors.

Since being introduced into the market, the charge storage in supercapacitors are normally based on carbon materials, with limited double layer capacity. Various carbon allotropes like zero-dimension (0D) carbon particles/onions, 1D carbon nanotubes/nanofibers, 2D graphene and 3D carbon aerogel and templated carbons have been used in supercapacitors.[3] However, the charge storage on these carbon electrodes is still confined by the surface properties, like surface area and pore structures, which are vital for surface induced energy storage. Continuous improvements in energy density are needed. These motivate the development of faradaic materials, like conducting polymers and metal-based compounds. Via faradic reactions, the amount of charge stored at or near the surface of electrode materials can be greatly enhanced, sometimes even 100 foldshigher than typical carbon-based supercapacitors. Both the carbon-based electrochemical double layer and faradic capacitive behaviors greatly depend on the

electrode surface properties. In view of this, fabrication of nanomaterials has great significance. The strategies, like size control, chemical/physical activation have been adopted for electrode material synthesis. Besides, the hybridization of carbon and faradic materials have drawn more and more attentions. As the energy density is greatly dependent on voltage according to $E = \frac{1}{2} CV^2$, much effort has been devoted to increase the working voltage of supercapacitor, like employing ionic-liquid electrolytes and assembling asymmetric cells. Besides, high power density could be attained by reducing the internal resistance in the whole system, including electrode materials, electrolytes, membrane, current collector and electric wires. Nanomaterials with new structures, new hybridization of electrode materials, new design of electrode structure, the development of new electrolytes and the hybrid devices, could predominate the future developments of supercapacitors.

Figure 2.1 The schematic illustration of strategies used to improve the energy density of supercapacitors.[3]

The concept of lithium ion battery (LIB) was introduced by Murphy and Scrosati in the end of 1980s. However, the LIBs developed slowly at that time due to the lack of favorable negative electrode material/suitable electrolyte and high cost. The discovery of

reversible carbonaceous anode materials promote the commercialized carbon and lithium cobalt oxides (C/LiCoO₂) rocking chair cell in 1991. Graphite carbon and lithium cobalt oxides (C/LiCoO₂) are as anode and cathode respectively, and this electrode couple is still popular.[4] Capitalizing on the earlier studies about LiCoO₂, other analogical cathode materials, like LiMn₂O₄, LiNiO₂, LiFePO₄, and the hybridizations, LiCo_xNi_{1-x}O₂, LiAl_xNi_{1-x}O₂ and LiAl_xCo_yNi_{1-x-y}O₂ were investigated. LiCo_xNi_{1-x}O₂ was proposed as one of the most promising alternatives to LiCoO₂ in 2001.[5] Owing to the prosperous development, current LIBs have been widely used in electric vehicles, without being restricted in portable devices, like phones, cameras and laptops.[6]

Advances in LIB anode and cathode materials have been anticipated. However, the availability of lithium source limits the future development facing the increasing demand of energy storage. As promising alternatives, sodium ion batteries and potassium ion batteries have drawn much attention. In terms of intercalation failure of sodium ion in graphite, potassium ion batteries have overwhelming superiority in the transition from commercialized LIB technology to KIB system, which is discussed in detail in the following sections.

2.2 Supercapacitors

Supercapacitors have high power density and long cycling life, which are able to store much more energy than traditional capacitors because of the enlarged electrode material surface area and the decreased distance between two charged layers (positive electrode//negative electrode). Supercapacitors can be divided into two categories: electric double-layer supercapacitor (EDLC) and pseudocapacitor.

2.2.1 Operation principles of supercapacitors

EDLC stores electrical energy by the electrostatic adsorption and desorption of ions in the conductive electrolyte, thus creating the double layers at the electrode and electrolyte interface on both positive and negative electrodes (Figure 2.2a). Porous carbon materials

with low cost are usually used as double-layer supercapacitor electrode materials due to the high specific surface area and excellent mechanical/electrochemical stability. The electrochemical processes for charging and discharging can be expressed as: $E_{s1} + E_{s2} + A^- + C^+ \leftrightarrow E_{s1}^+/A^- + E_{s2}^-/C^+$, where E_{s1} and E_{s2} are the two electrode surfaces, ' A^- ' and ' C^+ ' are anion and cation coming from the electrolyte, and '/' is the electrode and electrolyte interface. During charge, the electrons travel through an external load between two electrodes. Cations and anions in the electrolyte move towards the corresponding electrodes, forming electrostatic double layers.[1] During discharge, the process is reversed, when ions go back to the electrolyte. There is no electron transfer across the electrode and electrolyte interface, and nor ion exchange between the two electrodes in EDLC. The double layer capacitance can be expressed as $C = A\epsilon/(4\pi d)$, just like conventional capacitors, where ' A ' is the area of the electrode surface, ' ϵ ' is the medium (electrolyte) dielectric constant, and ' d ' is the effective thickness of the electrical double layer. The double layer thickness ' d ' is typically a few tenths of nanometer and hence the specific capacitance is much higher than conventional capacitors. However, the area ' A ' and distance ' d ' can't be measured in real capacitors. Therefore, the capacity of EDLC is usually estimated by cyclic voltammetry (CV) curves or charge discharge profiles, which will be discussed in chapter 3.

Pseudocapacitor stores energy through the redox reactions between electrode and electrolyte(Figure 2.2b).[7] Pseudocapacitance occurs together with static double-layer capacitance while the electron charge transfer is accomplished by electrosorption, intercalation and very fast reversible faradaic redox processes on the electrode surface. The adsorbed ions have no chemical bonds and chemical reaction with the atoms of the electrode since only a charge-transfer take place. The pseudocapacitors may show much (10-100x) higher capacitance than EDLCs of the same surface area, since the electrochemical processes occur both on the surface and in the bulk near the surface of the solid electrode. But pseudocapacitor normally possess relatively low conductivity and cycling stability in comparison with EDLC, which seems to impede the wide application. To address these drawbacks, carbonaceous scaffolds are usually added into the electrode for improved performance. Pseudocapacitance strongly depends on the chemical affinity

of electrode materials to the ions adsorbed on the effective surface of electrode. There are two types of materials exhibiting redox behavior for use as pseudocapacitor electrodes: one is transition metal oxides/chalcogenides and the other is conducting polymers[8].

Figure 2.2 Schematic diagram of (a) the electrochemical double-layer capacitors and (b) the pseudocapacitors.[7]

Many transition metal oxides/sulfides, like RuO_2 , IrO_2 , V_2O_5 , Fe_3O_4 , Co_3O_4 , MnO_2 , NiO , MoS_2 and TiS_2 , generate faradaic electron-transferring reactions with low conducting resistance. These metal compounds undergo multiple oxidation states at specific potentials, leading to high capacitance. Ruthenium oxide (RuO_2) with aqueous H_2SO_4 electrolyte provides the best example, with a working potential of 1.2V. High capacitance of 1340 F g^{-1} with several hundred-thousand cycles has been achieved on hydrous RuO_2 [9]. The redox reaction takes place according to: $\text{RuO}_2 + x\text{H}^+ + xe^- \leftrightarrow \text{RuO}_{2-x}(\text{OH})_x$ ($0 \leq x \leq 2$). During charge/discharge, H^+ ions are inserted-into or removed-from the RuO_2 lattice, without chemical bonding or phase transformation. The OH^- groups cling as a molecular layer on the electrode surface and remain in the region of the Helmholtz layer, while the Ru ions anchoring protons are reduced their oxidation state from +4 to +3.

For conducting polymer based pseudocapacitors, the electron charge storage is implemented by switching the polymer between two doping states (p-doping/n-doping) where electrolyte ions are inserted/extracted from the polymer backbones. The conducting polymers, like polyaniline, become polycations during the charging process (oxidative p-doping). The positively charged polycations will attract the anions (like Cl^- in Figure 2.3) in the electrolyte to intercalate into the polymer backbone for

electroneutrality. And then, the conducting polymers are oxidized and they p-doped with anions ($(P)_m + xA^- - xe^- \leftrightarrow (P)_{x+m}(A^-)_x$), where $(P)_m$ is the conducting polymer with conjugated double bonds, m is the degree of polymerization. To the contrary, the conducting polymers are reduced and n-doped with cation (M^+) during discharge ($(P)_m + yM^+ + ye^- \leftrightarrow P_{y-m}(M^+)_y$). [10] A^- and M^+ are the anions and cations of the electrolyte, respectively. Unlike metal oxides, the entire polymer chains are exposed to the doping/depoing of ions during charge/discharge. This grants high capacitance but also leads to distortion of the polymer structure, shortening the overall cycling life. To improve the life cycle, conducting polymers and other species, such carbon support and metal compound are coupled, forming hybrid electrodes.

Figure 2.3 Illustration of pseudocapacitive behavior of the conducting polymer during the charging process.[8]

Usually, supercapacitors, including both EDLCs and pseudocapacitors, have lower energy density compared with batteries. Scientists have been investigating many routes to increase the energy density and trying to realize the ideal case: long cycling life, high power density and high energy density. The design of hybrid capacitors paves the way to supercapacitors with high capacitance and energy density. The combined devices based on the hybrid of carbon based EDLCs, pseudocapacitive electrodes, and even battery-type electrodes have shown rather good electrochemical performance. In the following section, the recent progress and innovations on electrode materials, especially for polyaniline-based supercapacitor electrodes will be discussed in detail.

2.2.2 Electrode materials for supercapacitors

According to the different mechanisms, capacitor electrode materials may possess very different energy/power densities, which have been chosen for certain purposes. In principle, carbon-based materials induce double layer capacitance with lower capacitance and lower energy/power density, while metal compounds induce faradic capacity with much higher energy/power densities. The conducting polymers, like polyaniline can bridge the gap between the carbon based and metal-based energy storage devices. On one hand, conducting polymer stores energy via changing different oxidation states, the kinetic is slower than charge adsorption on carbon surface but faster than redox reactions at metal-based species. On the other hand, conducting polymer stores more energy compared to electrochemical double layer behaviors and it could be comparable to some metal-based materials. These features are well illustrated in Ragone plot in Figure 2.4, exhibiting the significance of conducting polymer-based devices. Among the conducting polymers, polyaniline (PANi) generates most attention because it has the highest specific capacitance due to multi-redox reactions, good electronic properties due to protonation,[11] and low cost for its infinite abundance. Moreover, it has good thermal stability and can be easily synthesized by chemical or electrochemical methods, resulting in powder or thin film.[12] In the subsequent section, PANi based electrode materials for supercapacitors will be discussed in detail.

Figure 2.4 Ragone plots for carbon, metal and conducting polymer-based supercapacitors.

2.3 Polyaniline based supercapacitor electrodes

PANi based electrodes for supercapacitors have multi-redox reactions, high conductivity and excellent flexibility. Pure PANi could act as a supercapacitor electrode in aqueous electrolyte due to its good pseudocapacitive properties.[13] However, the inferior stability due to structural change and chemical degradation could result in cycling instability and poor rate performance. Moreover, the agglomerate morphologies of roughly synthesized PANi usually lead to the inefficient utilization of PANi. Researchers found that the electrochemical performance is highly dependent on PANi structures. PANi with unique nanowire/nanofiber structure as active material for supercapacitor could induce high capacity. As shown in Figure 2.5, the PANi nanowire arrays could facilitate the electrolyte ions diffusion, resulting in high utilization of PANi and fast doping and dedoping process.[14] Moreover, the high flexibility of PANi makes it possible for PANi to combine with other materials harmoniously, forming PANi composites with improved capacitive properties.[15] Carbon materials are suitable for the fabrication of PANi based composites due to their high stability, good conductivity and large surface area, which can reinforce the structures of PANi during the doping and de-

doping of counter ions.[16]

Figure 2.5 Schematic illustration of electrolyte diffusion paths in PANi nanowire arrays.[14]

2.3.1 Polyaniline and carbon composites

Carbon materials with large surface area, good chemical stability and high conductivity, which could make up the disadvantages of PANi, are popularly used to enhance the stability along with the conductive PANi. The large surface area of carbon materials, like graphene ($2630\text{m}^2\text{g}^{-1}$), [17] could improve the dispersion of PANi, resulting in high utilization of PANi as active material. Meanwhile, the double layer capacitance provided from such carbon materials and the pseudo-capacitive contribution from PANi could further maximize the specific capacity of the whole electrodes, and the electrochemical performance of full cell.[18] Graphene,[19, 20] carbon nanotubes[21] and porous carbon materials, like activated carbon,[15, 22, 23] ordered mesoporous carbon[24, 25] and porous carbon nanospheres[26] have gained much interest for the fabrication of PANi/carbon composites.[17]

As show in Figure 2.6 a(i) and a(ii), the growth of PANi on GO is highly dependent on the concentration of aniline monomer, which gives a guidance to optimize the products. The flocculent PANi/graphite oxide composites showed a high specific capacitance of 555 F g^{-1} and high capacitance retention of 92% after 2000 cycles due to the synergistic effect between layered graphite oxide sheets and pseudocapacitive PANi. Electrochemical co-deposition is a facile method and the obtained PANi/graphite oxide

composites also show good electrochemical performance, high specific capacitance ($C_{sp} > 640 \text{ Fg}^{-1}$) and long cycling stability (~90% after 1000 cycles) reported.[19, 20] A simple and scalable method was introduced by Hongxia Yang et al for fabricating hybrids graphene pyrrole/carbon nanotube-PANi, using graphene foam as the supporting template.[21] As illustrated shown in Figure 2.6b, the as-synthesized GPCP maintained its original three-dimensional hierarchical porous architecture, which favors the diffusion of the electrolyte ions into the inner region of the active materials.

The ordered mesoporous/macroporous carbons are favorable for PANi/carbon composites because of their high specific surface area, unique structures as well as fast ionic transport. Their specific surface area can be as high as $1000\text{-}2000 \text{ m}^2 \text{ g}^{-1}$. The thin and porous PANi layer coated on the carbon surface could result in high utilization of active materials and short ionic diffusion length. The nanostructured PANi is desired because of nanostructures with more exposed active sites. Well-ordered whisker-like polyaniline structure was synthesized on ordered mesoporous carbons with high electrochemical performance because of the facilitated ionic transport and improved PANi utilization.[24, 25] The nano-sized PANI whiskers formed numerous “V-type” nanopores inside the active material (Figure 2.6c),[26] and thus yield a high electrochemical capacity due to the fast penetration of electrolyte and decreased diffusion length, leading to high specific capacitance.

Figure 2.6 (a)The schematic of (i) growth mechanism of PANi on the surface of graphene oxide and (ii) nucleation of PANi in solution.[27] (b) Schematic illustration of 3D graphenepyrrole/carbon nanotube/polyaniline architectures fabrication[21]. (c) Schematic representation of the reduced diffusion length with whisker-like channels.[24]

Porous carbon nanofibers are promising support for PANi owing to the excellent conductivity, remarkable flexibility, good mechanical/chemical stability and attractive 3D structures. They can serve as free standing current collectors for chemical and electrochemical polymerization of PANi.[28] No matter how to fabricate the hybridizations of PANi based electrode materials, the key point is to improve the structural and electrochemical stability of PANi and make full use of the active material by increasing the exposure area of PANi to electrolyte. In fact, PANi itself could be a promising nitrogen doped carbon matrix after carbonization.

2.3.2 Polyaniline and metal oxide composites

Owing to the high flexibility and good conductivity, PANi could also be used as a

conductive, connective and protective layer on metal-based compounds to gain improved stability and rate performances. The core-shell structural transition metal oxide/PANi could be synthesized through a two-step process. Metal oxides are obtained through a chemical or electrochemical method, following with an annealing process, while chemical or electrochemical PANi coating was carried out as the second step, resulting in metal oxides/PANi core-shell nanostructures. In Figure 2.7, the synthesis of core-shell α -Fe₂O₃/PANi nanowire arrays is schematically illustrated. The galvanostatic polymerization of PANi were conducted on as-obtained α -Fe₂O₃ nanowire arrays, with a porous layer of PANi were uniformly coated on the surface of the α -Fe₂O₃ nanowire arrays. The resultant α -Fe₂O₃/PANi composite could achieve high stability, fast ion/electron transport and large reaction area.[29]

Figure 2.7 The schematic of core-shell α -Fe₂O₃/PANi nanowire arrays fabrication.[29]

There are quite a few studies on the PANi based core-shell structures, like PANi/NiO nanoparticles,[30] PANi/TiO₂ or PANi/TiN nanowire arrays,[31, 32] PANi/MnO_x,[33, 34] PANi/WO₃ and PANi/V₂O₅ composites[35-37] used as supercapacitor electrodes. Several ternary cobalt, nickel and manganese ferrites/carbon/PANi hybrids based electrodes were also reported for high performance supercapacitors.[38-40] Besides metal oxides and spinel ferrite, there are also some metal sulfides and metal compounds with unique crystal structures, desiring for a conducting polymer coating layer due to inferior conductivity[41-43]. Among them, Metal-organic frameworks (MOFs), have received increasing attention as a new class of porous materials for energy storage and conversion applications due to their high specific surface area, exceptional porosities and well-defined tailored pore structure to facilitate the ion diffusion. However, the major problem of MOFs is their poor conductivity, which could be tackled by the conducting polymers,

like PANi.

2.4 Lithium ion batteries

This section discusses the basic operation principles of lithium ion batteries (LIBs) and the progress of finding and alternative to replace lithium. This is a transitional paragraph to bring out the topic of potassium ion batteries (KIBs). KIBs are still at the early stage and they share most properties and electrochemical behaviors with LIBs. Therefore, this part will give a brief introduction to LIBs in order to understand more about KIBs.

2.4.1 Operation principles of lithium ion batteries

In a typical LIB cell with graphite anode, LiCoO_2 cathode and LiPF_6 containing organic electrolyte, Li^+ could intercalate into anode material during charge. In some other cases, Li^+ may have alloy (like Si) or conversion (for most metal sulfides) reactions with anode material if Si or metal sulfides is used as the active material for anode. This work mainly focuses on the carbon-based material (intercalation mechanism) since it is the anode material for the KIB we are studying.

When the battery is charged, lithium ions are continuously extracting from the cathode with the increasing of external voltage (Equation 2.1), passing by the organic electrolyte and continuously intercalating into the layered anode material to form Li-intercalated graphite intercalation compounds (Li-GICs) (Equation 2.2). To the contrary, lithium ions release from the anode and intercalate into the cathode during discharge. The overall electrochemical reaction could be represented by Equation 2.3.[6]

Usually, carbon based electrodes are firstly evaluated in a half cell, with lithium metal as the anode, carbon as the cathode and organic electrolyte as the intermediary.[44] During discharging, Li is oxidized (Equation 2.4) and the Li^+ ions move through electrolyte, intercalate into carbon (Equation 2.2). Meanwhile, the electrons from external circuit travel to the carbon electrode to couple with positively charged Li^+ . During charging, Li^+ extracts from carbon electrode and travels to the counter electrode, Li metal. The overall reaction is illustrated in Equation 2.5.

2.4.2 Progress of finding alternatives to replace lithium

Even great progress has been made in LIBs, the alternatives are urgent due to the limited lithium source. Studies on Na^+ as charge carrier for electrochemical energy storage devices started around 1980.[45] But the sodium insertion materials were not given significant attention in last three decades when the lithium ion batteries have continued to thrive and grow.[46] In 2000, a high reversible capacity of 300 mAh g^{-1} in hard carbon-based sodium ion batteries was reported, which is a turning point for the development of sodium insertion materials. Later, the discovery of an analogical cathode material to LiCoO_2 , NaFeO_2 further promoted the development of sodium ion batteries.[47] However, Na^+ could not well intercalate into commercial graphite, and the hard carbons usually evoke high expenses and low material density. Thus, the potassium ion batteries (KIBs) have sprung up as possible energy storage devices.[48] With the advantages of high abundance, low cost, low standard redox potential (as illustrated in Table 2.1), potassium ion batteries are promising in the future energy storage system. Above all, the most significant advantage of potassium over sodium is that potassium could intercalate into the commercial graphite, with considerable capacity of 279 mAh g^{-1} . [49, 50] Taking all the advantages into account, KIBs have attracted high interest in recent years.

Table 2.1 Physical, electrochemical and economic characteristics of lithium, sodium, and potassium.[51]

	Lithium	Sodium	Potassium
Atomic Number	3	11	19
Atomic Weight	6.94	22.98	39.09
Atomic Radius (pm)	145	180	220
Covalent Radius (pm)	128	166	203
Melting Point (°C)	180.54	97.72	63.38
Crust Abundance (mass %)	0.0017	2.3	1.5
Crust Abundance (molar %)	0.005	2.1	0.78
E_0 (A^+aq/A)/V vs. SHE	-3.040	-2.714	-2.936
E_0 (A^+pc/A)/V vs. SHE	-2.79	-2.56	-2.88
Gravimetric capacity (Ah g ⁻¹)	3.86	1.16	0.68
Volumetric capacity (Ah cm ⁻³)	2.06	1.12	0.58
P ₂ -type A _{2/3} CoO ₂ vs. LiCoO ₂ Weight ratio	1	1.08	1.19
Capacity of commercial graphite anode(mAh g ⁻¹)	372	N.A.	279
Cost of carbonate (US\$ ton ⁻¹)	23000	200	1000
Cost of industrial grade metal (US\$ ton ⁻¹)	100000	3000	13000
Cost of electrolyte (X-PF ₆ /US\$ kg ⁻¹)	7755	2823	369
Cost of electrolyte (X-ClO ₄ /US\$ kg ⁻¹)	2310	307.5	270
Cost of anode current collector (US\$1cm ²)	2.95(Cu foil)	2.10(Al foil)	2.10(Al foil)

* Footnotes to tables. Cost of anode current collector (US\$1cm²) prize from sigma in March, 2018; aq and pc are denoted as aqueous and polyacetylene carbonate, respectively.

2.5 Early Stage of potassium ion batteries

2.5.1 Progress and principles of potassium ion batteries

Potassium ion batteries (KIBs) have numbers of advantages compared to LIBs, including high abundance, low cost, uniform distribution in the world,[48] low standard redox potential and higher mobility of K⁺. [52] Above all, the most significant advantage is that graphite could accommodate the intercalation and de-intercalation of K⁺ reversibly, which is a key merit over sodium ion batteries.[53] The reports about potassium

intercalated compounds were as early as 1950s, when researchers synthesized the potassium and graphite intercalation compounds (K-GICs) through a non-electrochemical method in the furnace.[54] Nowadays, the K-GICs have an extensive and in-depth study in the electrochemical energy storage.[49, 50, 55, 56]

As schematically illustrated in Figure 2.8, KIBs share similar working principles with LIBs. In brief, the K^+ moves from cathode to anode during charge and the K-GIC forms. To the contrary, the K^+ de-intercalates from the graphite electrode and travels to the cathode during discharge. The detailed staging process in graphite has been studied in a few reports.[49, 50, 55, 56] Xiulei Ji and co-workers first report the potassium storage in graphite by an *ex-situ* XRD method. During first potassiation and depotassiation, the XRD patterns of graphite electrode at different charge/discharge potential were obtained. Upon first potassiation, graphite diffraction peaks vanished around 0.3 V and a new peak attributed to KC_{36} appeared, corresponding to the stage-three K-GIC. KC_{36} changed to KC_{24} via further potassiation and the full intercalated stage-one K-GIC formed when discharged to 0.01 V, with a formula of KC_8 . During depotassiation (charge), the staging process is vice versa.[50] Further investigations on staging process of potassium storage in graphite are conducted via theoretical studies and Raman analysis.[49, 55, 56] Although it is still a controversial issue about the constitutions of stage one/two GICs, KC_{36} , KC_{24} or KC_{16} , the stage-one GIC, KC_8 gets recognition in this investigated area. According to this formula, the theoretical specific capacity could be calculated as 279 mAh g^{-1} .

Figure 2.8 Schematic illustration of a typical potassium ion battery.[57]

2.5.2 Carbon based anodes for potassium ion batteries

The understanding of staging process during potassiation and depotassiation in graphite evokes numerous studies in this area, a variety of carbon-based anode materials have been involved in KIB study since then. Graphite modified carbon materials are also promising in potassium storage. The activated carbon is synthesized via high temperature annealing with graphite as the precursor, which has enlarged interlayer space and nanosized carbon sheets on the particles, beneficial to K^+ intercalation and diffusion. As verified by the peak current versus scan rate studies, the diffusion coefficient of K^+ in electrode material has been improved 7 times of activated carbon compared to graphite.[58] Other than activated carbon, graphite could also be used to produce expanded graphite, exhibiting good electronic properties and enlarged spacing for facilitated potassium intercalation/de-intercalation.[59]

Other carbonaceous materials, like hard carbon, soft carbon, carbon fibers and porous carbon, have been synthesized and exhibit excellent performance in KIBs. The mechanical degradation of carbon nanofibers during potassiation was examined by *in-situ* TEM.[60] And then, the hard carbon microspheres were used to fabricate anode for KIB with good electrochemical performance, exhibiting 229 mAh g^{-1} at C/2 (139.5 mA g^{-1}). This is the first time that hard carbon is used in KIBs. The kinetics of K^+ diffusion in electrode materials was studied by Galvanostatic Intermittent Titration Technique (GITT) to understand the high rate performance.[61] Since then, the electrochemical properties of hollow carbon spheres and mesoporous carbon in KIBs were also investigated.[62, 63] The Nyquist plots were used to analyze the kinetics of electrode after different cycles and the calculated diffusion coefficient was comparable to LIBs. The ex-situ XRD, XPS and Raman spectra were further conducted to verify the reversible K^+ intercalation and de-intercalation in the mesoporous structure during charge and discharge.[63] As pure hard carbon suffers from inferior rate performance, soft-hard carbon composite based anode was fabricated for KIBs, exhibiting synergistic effect, in terms of high rate capability and long cycling life.[64] Owing to advantages of self-supported, the carbon nanofiber paper fabricated by electrospun also shows good rate capability and long-term cycling

stability.[65] Carbon materials derived from biomass have been evolved in the KIB studies. Hard carbons from wood and waste rubbers exhibit great electrochemical performance for K^+ storage.[66, 67] These sustainable are promising for a greener future.

Figure 2.9 Characterizations of N-FLG and FLG during K^+ storage. (a, b) CV curves at 0.05 $mV s^{-1}$. (c, d) Raman spectra at different potential during charge. (e, f) Schematic illustration of the K^+ storage mechanism during staging process and at the nitrogen doped active sites.[68]

Heteroatom doping plays great role in carbon-based anodes for energy storage devices. Heteroatom doping could help to enlarge the interlayer space of carbon materials and induce large amounts of charged/active sites. Dopants, like nitrogen, oxygen, fluorine, phosphorus and sulfur, could promote the reactivity and alter the electronic structure of carbon materials. Figures 2.9a-2.9b exhibit the CV curves of N-FLG and FLG, with different color of circles indicating the corresponding Raman spectra obtained at different charge potential in Figures 2.9c, 2.9d.[68] The *in-situ* Raman spectra of both exhibit a typical G band around 1600 cm^{-1} , which could be divided into two subpeaks, uncharged G peak (G_{uc}) and the blue shifted charged G peak (G_c). It could be observed that the ratio of G_{uc}/G_c decreases with the progressing of staging process of both N-FLG and FLG, which indicates the similar staging process in both electrode materials. This elucidates that the doped nitrogen does not disrupt the staging process for a fully intercalated K-GIC. But the nitrogen doping greatly improve the K^+ storage indeed. In order to understand the K^+ storage mechanism in nitrogen induced active sites, Figures 2.9e, 2.9f are depicted to explain the underlying principles. The staging process is not hindered via nitrogen doping. Meanwhile, the nitrogen act as additional K^+ storage sites, which promotes the capacity of N-FLG.

Since then, the nitrogen doped carbon materials have been the trend and the dual doped carbon materials with synergy are also beginning to catch up. The staging process of K^+ intercalation in heteroatom doped carbon were also studied. Raman spectroscopy and XRD as two powerful tools play great role in the investigation of K-GICs formation at different charge and discharge state.[68-71] Besides, TEM and SEM have been used to characterize the morphological and structural changes of heteroatom doped carbon materials via cycling test.[72, 73] In order to study the kinetics during K^+ diffusion and intercalation, CV, EIS and GITT have been employed.[74, 75] The heated studies of porous carbon materials with large surface area are also in trend, which allows for high capacity owning superior surface induced capacitive behaviors. Thus the quantitative capacitive analysis has been employed to distinguish the capacitive and diffusive controlled capacity.[70, 76-78] As shown in Table 2.2, various heteroatom doped carbon materials have been studied in KIBs and several problems have been presented and

solved. However, all these studies focus on electrode materials, few reports illuminated. Moreover, the heteroatom doping concentrations and doping types have been studied in detail.

Table 2.2 The illustration of problems solved in heteroatom doped carbon materials for KIBs.

Anode materials	Problem solved	Journals & Year
N-doped graphene	The <i>in-situ</i> Raman was used to postulate that the nitrogen doping is not disruptive to the staging process to form K-GIC by comparing the spectra doped and undoped graphene. Meanwhile, the fitted G band was employed to evaluate the ratio of charged graphene via K^+ intercalation to verify the staging process in graphene.	ACS nano (2016)
N-doped porous carbon monolith	Porous carbon with high pyridinic N doping level (10.1 %) was synthesized to study the K^+ storage in KIBs. <i>Ex-situ</i> XRD patterns at different potassiation and depotassiation states were provided to study the staging process.	Advanced Materials (2017)
Chitin derived N-doped carbon	The biomass derived N-doped carbon nanofibers were studied as KIB anode.	Carbon (2017)
N-doped CNT (from MOF)	<i>Ex-situ</i> TEM was used to identify the interlayer distance changes of MOF derived N-doped carbon nanotubes via charge and discharge in KIB systems.	Chemsuschem (2017)
N-doped Carbon Network (from MOF)	This worked illustrated that the nanosized MOF(ZIF-67) could facilitate to yield continuous 3D carbon networks via pyrolysis, which is owing to the catalytic properties of nanosized Co in the organic ligands. The as-obtained material shows good electrochemical performances in KIBs.	Angewandte Chemie (2017)
N-doped hard carbon	The capacitive and diffusion controlled capacity was distinguished based on the quantitative capacitive analysis. The N-doped hard carbon exhibited a capacitive dominated behavior as KIB anode. The pyridinic N doping configuration was verified to be favorable for K^+ adsorption by the DFT calculations.	Energy Storage Materials (2017)
N-doped carbon nanofibers	The dominated surface controlled capacitive capacity was verified by the quantitative capacitive analysis and the DFT calculations.	Nature Communications (2018)
N-doped cup-stacked CNT	Although the morphology of CNT retained after cycling test as verified by SEM, there are structural changes via K^+ intercalation, resulting in enlarged interlayer space, which is responsible for the capacity loss.	ACS Applied Energy Materials (2018)
F-doped graphene	The Nyquist plots were used to study the kinetics during K/Li ion diffusion and intercalation in the anode. After cycling, the charge transfer resistance decreased owing to the successful formation of SEI layer and enhanced ion conductivity via continuous ion intercalation.	ACS Applied Materials&Interface (2016)
N-O dual doped carbon nanofiber	<i>Ex-situ</i> characterizations, including XRD, Raman and EDS mapping were conducted to analysis the structural change after long-term cycling test. The graphitic interlayer spacing was enlarged via K^+ intercalation without damaging the one-dimentional structures.	ACS Applied Materials&Interface (2017)
N-O dual doped hard carbon	The dual doped hard carbon was favourable for capacitive behaviour and the K^+ intercalation was facilitated with the enlarged interlayer spacing via dual doping.	Advanced Materials (2017)
P-O dual doped graphene	The dual doping contributed to enlarged interlayer spacing, beneficial to K^+ storage. As indicated by EIS, the K^+ diffusion in electrode material was blocked by irreversible intercalation of some K^+ during first 5 cycles, resulting in capacity fading.	Journal of Materials Chemistry A (2017)
S-O dual doped porous hard carbon microsphere	The DFT calculations illustrated that he codoping favoured K adsorption and helped to alleviate the volume changes during K^+ intercalation/de-intercalation.	Advanced Energy Materials (2018)

* Footnotes to tables. MOF is the abbreviation of metal-organic framework and DFT is the abbreviation of density functional theory.

2.6 PhD in context of literature

According to the literature review, polyaniline (PANi) based supercapacitors suffer from inferior stability due to the structural and electrochemical degradation. In the first part of this work, carbon black as a commercial material was shown to effectively enhance the cycling stability of PANi based electrode materials, in terms of i) it could promote the extended PANi chains, which are more stable compared with short chain oligomers during cycling test; ii) it could combine with the active sites of PANi chain via certain chemical bonding, which could mitigate the side reactions in electrolyte; iii) it could help to increase the doping level and decrease the defect density, which could confirm a good stability of PANi chains.

In the second part of PANi based electrode material study, tin sulfide nanoflakes were employed, which exhibits synergistic effect when combined with PANi, resulting in high specific capacity and good cycling life. On one hand, PANi as an attractive electrode material acts as not only a conductive support but also facilitates the growth of tin sulfide in nanosize, which shows superior pseudocapacitive and diffusion-controlled behavior compared to tin sulfide in microsize. On the other hand, tin sulfide nanoflakes could not only exhibit high capacity but also act as a protective coating to prevent PANi from the structural and electrochemical changes, which could greatly enhance the cycling stability of the whole electrode.

As the critical limitation of supercapacitors is the low energy density, they are usually used in high power device applications. To satisfy various energy demands, the development of both high power and high energy devices is important. Thus, the investigations on both supercapacitors and lithium ion batteries have attracted a lot of attentions. However, the lithium resource is limited and unevenly distributed. That is why the sodium ion battery and potassium ion battery are in trend. Potassium ion battery has been chosen as one study topic in the PhD context owing to numbers of advantages as stated in section 2.4.2.

However, the development of potassium ion batteries is still at an early stage and many related problems have not been addressed yet, especially the inferior stability and reversibility of KIB electrode materials. Many investigations about carbon-based anodes have paid much attention on the modification of electrode materials, which is vital for the electrochemical performance. However, another key factor, electrolyte, also plays great role in the electrochemical performance of batteries, especially for cycling stability and coulombic efficiency. There are few investigations on the electrolyte effect of carbon anode based KIBs. In this work, the electrolyte study will be studied in detail and the solid electrolyte interface will be investigated comprehensively.

In last part, both the nitrogen doping concentrations and configurations in carbon-based materials will be studied as KIB anodes. As mentioned in 2.5, the heteroatom (especially nitrogen) doped, especially for nitrogen doped carbon materials could have superior electrochemical performance compared to the undoped ones owing to i) enhanced conductivity, ii) induced active sites and iii) favorable structural changes, like enlarged interlayer spacing and surface area. Most previous reports did not study further in nitrogen doping effect in detail, or neglect one or another. That is why both the doping levels and types will be both talked about in this work to give a comprehensive understanding of nitrogen doping effect in KIBs.

References

- [1] G.P. Wang, L. Zhang, J.J. Zhang, *Chem. Soc. Rev.*, **2012** 41 797-828.
- [2] P. Simon, Y. Gogotsi, *Nat. Mater.*, **2008** 7 845-854.
- [3] M.F. El-Kady, Y.L. Shao, R.B. Kaner, *Nat. Rev. Mater.*, **2016** 1 14.
- [4] J.M. Tarascon, M. Armand, *Nature*, **2001** 414 359-367.
- [5] T. Ohzuku, R.J. Brodd, *J. Power Sources*, **2007** 174 449-456.
- [6] M.M. Thackeray, C. Wolverton, E.D. Isaacs, *Energy Environ. Sci.*, **2012** 5 7854-7863.
- [7] C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, J. Zhang, *Chem. Soc. Rev.*, **2015** 44 7484-7539.
- [8] C. Peng, S. Zhang, D. Jewell, G.Z. Chen, *Prog. Nat. Sci.*, **2008** 18 777-788.

- [9] M. Zhi, C. Xiang, J. Li, M. Li, N. Wu, *Nanoscale*, **2013** 5 72-88.
- [10] G. Lota, K. Fic, E. Frackowiak, *Energy Environ. Sci.*, **2011** 4 1592.
- [11] C.H. Silva, N.A. Galiote, F. Huguenin, É. Teixeira-Neto, V.R. Constantino, M.L. Temperini, *J. Mater. Chem.*, **2012** 22 14052-14060.
- [12] S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, *Prog. Polym. Sci.*, **2009** 34 783-810.
- [13] H.H. Zhou, H. Chen, S.L. Luo, G.W. Lu, W.Z. Wei, Y.F. Kuang, *J. Solid State Electrochem.*, **2005** 9 574-580.
- [14] K. Wang, J. Huang, Z. Wei, *J. Phys. Chem. C*, **2010** 114 8062-8067.
- [15] K.S. Ryu, Y.-G. Lee, K.M. Kim, Y.J. Park, Y.-S. Hong, X. Wu, M.G. Kang, N.-G. Park, R.Y. Song, J.M. Ko, *Synth. Met.*, **2005** 153 89-92.
- [16] C.C. Hu, W.Y. Li, J.Y. Lin, *J. Power Sources*, **2004** 137 152-157.
- [17] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, *Nano Lett.*, **2008** 8 3498-3502.
- [18] S. Mondal, K. Barai, N. Munichandraiah, *Electrochim. Acta*, **2007** 52 3258-3264.
- [19] X.M. Feng, R.M. Li, Y.W. Ma, R.F. Chen, N.E. Shi, Q.L. Fan, W. Huang, *Adv. Funct. Mater.*, **2011** 21 2989-2996.
- [20] Q. Zhang, Y. Li, Y. Feng, W. Feng, *Electrochim. Acta*, **2013** 90 95-100.
- [21] H.X. Yang, N. Wang, Q. Xu, Z.M. Chen, Y.M. Ren, J.M. Razal, J. Chen, *2D Mater.*, **2014** 1 1-14.
- [22] M.J. Bleda-Martinez, E. Morallon, D. Cazorla-Amoros, *Electrochim. Acta*, **2007** 52 4962-4968.
- [23] O. Misoon, K. Seok, *Electrochim. Acta*, **2012** 59 196-201.
- [24] Y.G. Wang, H.Q. Li, Y.Y. Xia, *Adv. Mater.*, **2006** 18 2619-2623.
- [25] Y. Yan, Q. Cheng, G. Wang, C. Li, *J. Power Sources*, **2011** 196 7835-7840.
- [26] X. Ning, W. Zhong, L. Wan, *RSC Adv.*, **2016** 6 25519-25524.
- [27] J. Xu, K. Wang, S.-Z. Zu, B.-H. Han, Z. Wei, *ACS nano*, **2010** 4 5019-5026.
- [28] Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya, L.-C. Qin, *J. Phys. Chem. C*, **2011** 115 23584-23590.
- [29] X.-F. Lu, X.-Y. Chen, W. Zhou, Y.-X. Tong, G.-R. Li, *ACS Appl. Mater. Interfaces*, **2015** 7 14843-14850.
- [30] D. Das, L.J. Borthakur, B.C. Nath, B.J. Saikia, K.J. Mohan, S.K. Dolui, *RSC Adv.*, **2016** 6 44878-44887.

- [31] K. Xie, J. Li, Y. Lai, Z.a. Zhang, Y. Liu, G. Zhang, H. Huang, *Nanoscale*, **2011** 3 2202-2207.
- [32] Y. Xie, C. Xia, H. Du, W. Wang, *J. Power Sources*, **2015** 286 561-570.
- [33] W.-y. Zou, W. Wang, B.-l. He, M.-l. Sun, Y.-s. Yin, *J. Power Sources*, **2010** 195 7489-7493.
- [34] L.-J. Sun, X.-X. Liu, K.K.-T. Lau, L. Chen, W.-M. Gu, *Electrochim. Acta*, **2008** 53 3036-3042.
- [35] X.-Y. Peng, X.-X. Liu, P.-J. Hua, D. Diamond, K.-T. Lau, *J. Solid State Electrochem.*, **2010** 14 1-7.
- [36] B.-X. Zou, Y. Liang, X.-X. Liu, D. Diamond, K.-T. Lau, *J. Power Sources*, **2011** 196 4842-4848.
- [37] M.-H. Bai, T.-Y. Liu, F. Luan, Y. Li, X.-X. Liu, *J. Mater. Chem. A*, **2014** 2 10882-10888.
- [38] D. Zha, P. Xiong, X. Wang, *Electrochim. Acta*, **2015** 185 218-228.
- [39] W. Wang, Q. Hao, W. Lei, X. Xia, X. Wang, *J. Power Sources*, **2014** 269 250-259.
- [40] P. Xiong, H. Huang, X. Wang, *J. Power Sources*, **2014** 245 937-946.
- [41] K.-J. Huang, L. Wang, Y.-J. Liu, H.-B. Wang, Y.-M. Liu, L.-L. Wang, *Electrochim. Acta*, **2013** 109 587-594.
- [42] S. Guo, Y. Zhu, Y. Yan, Y. Min, J. Fan, Q. Xu, H. Yun, *J. Power Sources*, **2016** 316 176-182.
- [43] L. Wang, X. Feng, L. Ren, Q. Piao, J. Zhong, Y. Wang, H. Li, Y. Chen, B. Wang, *JACS*, **2015** 137 4920-4923.
- [44] B. Scrosati, J. Garche, *J. Power Sources*, **2010** 195 2419-2430.
- [45] G.H. Newman, L.P. Klemann, *J. Electrochem. Soc.*, **1980** 127 2097-2099.
- [46] D.A. Stevens, J.R. Dahn, *J. Electrochem. Soc.*, **2000** 147 1271-1273.
- [47] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, *Chem. Rev.*, **2014** 114 11636-11682.
- [48] H. Kim, J.C. Kim, M. Bianchini, D.H. Seo, J. Rodriguez-Garcia, G. Ceder, *Adv. Energy Mater.*, **2018** 8 19.
- [49] W. Luo, J.Y. Wan, B. Ozdemir, W.Z. Bao, Y.N. Chen, J.Q. Dai, H. Lin, Y. Xu, F. Gu, V. Barone, L.B. Hu, *Nano Lett.*, **2015** 15 7671-7677.
- [50] Z.L. Jian, W. Luo, X.L. Ji, *J. Am. Chem. Soc.*, **2015** 137 11566-11569.

- [51] J.C. Pramudita, D. Sehwat, D. Goonetilleke, N. Sharma, **2017**.
- [52] S. Komaba, T. Hasegawa, M. Dahbi, K. Kubota, *Electrochem. Commun.*, **2015** 60 172-175.
- [53] M. Okoshi, Y. Yamada, S. Komaba, A. Yamada, H. Nakai, *J. Electrochem. Soc.*, **2017** 164 A54-A60.
- [54] R. W., S. E., **1954** 277 156-171.
- [55] K. Share, A.P. Cohn, R.E. Carter, C.L. Pint, *Nanoscale*, **2016** 8 16435-16439.
- [56] J. Zhao, X.X. Zou, Y.J. Zhu, Y.H. Xu, C.S. Wang, *Adv. Funct. Mater.*, **2016** 26 8103-8110.
- [57] X.Y. Wu, D.P. Leonard, X.L. Ji, *Chem. Mat.*, **2017** 29 5031-5042.
- [58] Z.X. Tai, Q. Zhang, Y.J. Liu, H.K. Liu, S.X. Dou, *Carbon*, **2017** 123 54-61.
- [59] Y.L. An, H.F. Fei, G.F. Zeng, L.J. Ci, B.J. Xi, S.L. Xiong, J.K. Feng, *J. Power Sources*, **2018** 378 66-72.
- [60] Y. Liu, F.F. Fan, J.W. Wang, Y. Liu, H.L. Chen, K.L. Jungjohann, Y.H. Xu, Y.J. Zhu, D. Bigio, T. Zhu, C.S. Wang, *Nano Lett.*, **2014** 14 3445-3452.
- [61] Z.L. Jian, Z.Y. Xing, C. Bommier, Z.F. Li, X.L. Ji, *Adv. Energy Mater.*, **2016** 6 5.
- [62] D.S. Bin, Z.X. Chi, Y.T. Li, K. Zhang, X.Z. Yang, Y.G. Sun, J.Y. Piao, A.M. Cao, L.J. Wan, *J. Am. Chem. Soc.*, **2017** 139 13492-13498.
- [63] W. Wang, J.H. Zhou, Z.P. Wang, L.Y. Zhao, P.H. Li, Y. Yang, C. Yang, H.X. Huang, S.J. Guo, *Adv. Energy Mater.*, **2018** 8 8.
- [64] Z.L. Jian, S. Hwang, Z.F. Li, A.S. Hernandez, X.F. Wang, Z.Y. Xing, D. Su, X.L. Ji, *Adv. Funct. Mater.*, **2017** 27 6.
- [65] X.X. Zhao, P.X. Xiong, J.F. Meng, Y.Q. Liang, J.W. Wang, Y.H. Xu, *J. Mater. Chem. A*, **2017** 5 19237-19244.
- [66] S.J.R. Prabakar, S.C. Han, C. Park, I.A. Bhairuba, M.J. Reece, K.S. Sohn, M. Pyo, *J. Electrochem. Soc.*, **2017** 164 A2012-A2016.
- [67] Y. Li, R.A. Adams, A. Arora, V.G. Pol, A.M. Levine, R.J. Lee, K. Akato, A.K. Naskar, M.P. Paranthaman, **2017** 164 A1234-A1238.
- [68] K. Share, A.P. Cohn, R. Carter, B. Rogers, C.L. Pint, *ACS Nano*, **2016** 10 9738-9744.
- [69] Y.H. Xie, Y. Chen, L. Liu, P. Tao, M.P. Fan, N. Xu, X.W. Shen, C.L. Yan, *Adv. Mater.*, **2017** 29 9.

- [70] R.A. Adams, J.M. Syu, Y.P. Zhao, C.T. Lo, A. Varma, V.G. Pol, *ACS Appl. Mater. Interfaces*, **2017** 9 17872-17881.
- [71] M. Chen, W. Wang, X. Liang, S. Gong, J. Liu, Q. Wang, S. Guo, H. Yang, **2018** 1800171.
- [72] P.X. Xiong, X.X. Zhao, Y.H. Xu, *ChemSusChem*, **2018** 11 202-208.
- [73] X. Zhao, Y. Tang, C. Ni, J. Wang, A. Star, Y. Xu, **2018** 1 1703-1707.
- [74] Z.C. Ju, S. Zhang, Z. Xing, Q.C. Zhuang, Y.H. Qiang, Y.T. Qian, *ACS Appl. Mater. Interfaces*, **2016** 8 20682-20690.
- [75] G.Y. Ma, K.S. Huang, J.S. Ma, Z.C. Ju, Z. Xing, Q.C. Zhuang, *J. Mater. Chem. A*, **2017** 5 7854-7861.
- [76] C.J. Chen, Z.G. Wang, B. Zhang, L. Miao, J. Cai, L.F. Peng, Y.Y. Huang, J.J. Jiang, Y.H. Huang, L.N. Zhang, J. Xie, *Energy Storage Mater.*, **2017** 8 161-168.
- [77] Y. Xu, C.L. Zhang, M. Zhou, Q. Fu, C.X. Zhao, M.H. Wu, Y. Lei, *Nat. Commun.*, **2018** 9 11.
- [78] J.L. Yang, Z.C. Ju, Y. Jiang, Z. Xing, B.J. Xi, J.K. Feng, S.L. Xiong, *Adv. Mater.*, **2018** 30 11.

Chapter 3

Experimental Methodology

In this chapter, the selection of material synthesis method, the characterizations and the electrochemical evaluations are explained in detail. More importantly, the rationale underlying every method or test is emphatically discussed in the subsequent sections.

3.1 Chemicals and Instruments

Chemicals and reagents: The chemicals, Tin chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) (98%), Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) (ACS reagent, $\geq 99.5\%$), Thioacetamide ($\text{C}_2\text{H}_5\text{NS}$) (ACS reagent, $\geq 99.0\%$) and Poly (vinylidene fluoride) (PVDF), melamine ($\text{C}_3\text{H}_6\text{N}_6$) (ACS reagent, $\geq 99\%$), Iron(III) chloride (FeCl_3) (reagent grade, 97%) and reagents Ethylene carbonate (EC, 98%)/ Diethyl carbonate (DEC, 99%) were purchased from SIGMA-ALDRICH and used as received. The potassium bis(fluorosulfonyl)imides (KFSI) (Cica-Reagent) and Potassium hexafluorophosphate (KPF_6 , $\geq 99\%$) were bought from Kanto chemical CO., INC, Japan and Sigma. The Hydrochloric acid (37%), 1-Methyl-2-pyrrolidinone (NMP, anhydrous, 99.5 %) and Ethanol, absolute (analytical reagent grade) involved in this work were bought from VWR CHEMICALS (PROLABO), Alfa Aesar and Fisher Chemical, respectively. The commercial carbon for negative electrode fabrication was purchased from Shanghai Lisheng Industry CO.,LTD. A platinum plate (area 4cm^2) and a saturated calomel electrode (type, 217) purchased from Xuzhou Zhenghao Electronic Technology CO.,LTD and Shanghai Leici Instrument Factory were used during the electrochemical deposition and tests. Nickel foams (NFs) (Pore size, 0.1mm-10mm) were bought from Shanghai Zhongwei New Material Co., Ltd. Through the synthesis and electrode fabrication, deionized water (DIW, $18.2\text{ M}\Omega$) was employed for electrolyte and sample clean.

Instruments:

Field Emission Scanning Electron Microscope (FE-SEM) (Model Jeol JSM 6700F) and Transmission Electron Microscope (JEM-2010F, TEM, acceleration voltage: 200 kV; JEOL-2100F, TEM, acceleration voltage: 200 kV) were employed to study the morphology of the samples. The crystallinity of NGFs obtained at different experimental conditions was detected by X-Ray Diffraction (XRD) that were performed on Bruker D8 Advance XRD and the graphitization were studied by Raman spectroscopy (Renishaw, laser wavelength: 532 nm), respectively. Structural and bonding information were obtained by Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy and UV-visible spectroscopy that were performed on PerkinElmer Spectrum GX, Renishaw

(laser wavelength: 532 nm), and SHIMADZU UV-2700, respectively. The elemental studies were conducted on the X-ray Photoelectron Spectroscopy (XPS) using a VG ESCALAB 220i-XL system with a nonmonochromatic Al K α photon source ($h\nu=1486.7\text{eV}$). The nitrogen adsorption and desorption isotherms for surface features and pore analysis were obtained by ASAP 3020 and ASAP 2020 Surface area and Porosity Analyzer.

3.2 Rationale for selection of synthesis methods

Chemical vapor deposition (CVD), electrochemical deposition and Co-precipitation methods (water-bath in this case) have been employed in this thesis for the synthesis of electrode materials, including graphene foam, PANi nanostructures, tin sulfide and their composites. These synthesis methods were chosen due to the easy accessibility, simple control of material morphology and high availability to scale up. In the subsequent parts, these three techniques will be discussed separately and systematically.

3.2.1 Chemical vapor deposition

The chemical vapor deposition (CVD) method plays a vital role throughout the entire PhD work. It is a facile method to obtain materials, such as N-doped carbon as well as graphene foam of high quality, high purity and on large area. In order to synthesize flexible graphene based carbon matrix, a few metal substrates could be used as templates and catalysts, like nickel, copper foils and substrates with nickel, cobalt, copper, ruthenium single crystals.[1] However, the graphene grown on nickel or copper foil is usually a few-layer film and it is difficult to transfer from one substrate to another one.[2] In this work, the nickel foams are employed as template and catalyst for flexible and robust graphite foam fabrication, which could be directly used as current collector in energy storage devices. In this thesis, the graphite foam builds the foundation of all self-supported electrodes for energy storage devices, like supercapacitors and batteries.

As schematically shown in Figure 3.1, methane (CH_4) is the precursor gas for graphene deposition and nickel foam is the deposition substrate. The reaction tube is first evaluated and purged with argon flow gas. After that, hydrogen gas is introduced into the system during the temperature rise for the pre-reduction of nickel foam. At the critical point of $1000\text{ }^\circ\text{C}$, methane is filled into the system and the deposition of graphite foam was initiated. The growth of graphite foam follows a carbon segregation/precipitation mechanism. At high temperature ($1000\text{ }^\circ\text{C}$), methane decomposes into carbon species by pyrolysis. And then, the carbon species dissolve into nickel foam as nickel has high carbon solubility.[3] The growth of graphite foam follows a carbon segregation/precipitation mechanism, with the precipitation of carbon species into the skeleton structure of nickel foam. of carbon. In the final stage, the system starts to cool down and the pure graphite foam on large area can be obtained with hydrochloric acid.

Figure 3.1 The schematic illustration of the synthesis of graphite foam by chemical vapor deposition.

Besides pure carbon-based material synthesis, CVD is also the mostly used methods for in-situ doping carbons materials.[4] Usually, the substrates are placed in the high temperature zone. When the heteroatom containing precursor, like NH_3/CH_4 , is introduced into the system, some of carbon atoms will be replaced by nitrogen to realize doping.[5] Some solid or liquid precursor, like pyridine, melamine and urea, contain both carbon and nitrogen in the precursor. They are usually placed in the low temperature zone to realize the in-situ nitrogen doping.[6, 7]

In this work, the nitrogen doped graphite foam is synthesized by a facile one-step CVD method, using melamine ($C_3N_6H_6$). Melamine which has a melting temperature of $354\text{ }^{\circ}\text{C}$ under barometric pressure is easy to sublime at temperature around $300\text{ }^{\circ}\text{C}$. [8] At higher temperatures around 400°C , they may decompose forming $g\text{-}C_3N_4$. As shown in Figure 3.2, melamine is placed in the low-temperature zone, while nickel foam, the template/catalyst, is placed in the high-temperature zone. When the temperature of the substrate increases to $800, 900$ or $1000\text{ }^{\circ}\text{C}$, the sublimation and pyrolysis of melamine in the low-temperature zone may happen at temperatures around $300\text{-}400\text{ }^{\circ}\text{C}$. In the high temperature zone, the pyrolysis products, like $g\text{-}C_3N_4$ and the sublimated $C_3N_6H_6$ are catalyzed by nickel and decompose at high temperature, following by the diffusion and recombination of C and N atoms on nickel foam. [9] As a result, the in-situ doped graphite foam would be obtained. Such processes are safer without the use of highly corrosive gases (like NH_3). Besides, the nitrogen doping content and configurations could be tuned by the annealing temperature and the growth time.

Figure 3.2 The synthesis of the nitrogen graphite foam by chemical vapor deposition.

3.2.2 Electrochemical deposition

Conducting polymers, like polyaniline (PANi), have high capacitance, good conductivity, excellent flexibility and low cost. [10] PANi and carbon material composites can be fabricated through chemical or electrochemical co-deposition. Compared to chemical deposition, electrochemical deposition is a fast and efficient way for material synthesis, especially for conducting polymers. Electrochemical deposition has advantages like, simple setup, fast generation, easy control and it is favorable for binder-free electrodes. Three routes could be used for co-deposition, i.e. galvanostatic, potentiostatic and potentiodynamic methods. Galvanostatic or potentiostatic method is performed at a

constant positive current or potential. Potentiodynamic is also known as cyclic voltammetry which is most commonly used for the electrochemical deposition.[11]

Figure 3.3 The schematic illustration of the co-deposition of polyaniline and carbon black composites.

As schematically illustrated in Figure 3.3, the electrochemical deposition is conducted in a three-electrode system, including the working electrode (graphite paper, graphite foam or stainless steel in this work), the counter electrode (a platinum plate) and a saturated calomel electrode (SCE) reference electrode. Under a driving force (potential/current), the monomer aniline will be oxidized and polymerized on the working electrode (current collector). In detail, the growth mechanism could be divided into two steps: the horizontal growth for a nucleation layer and the vertical growth for nanofibers.[12, 13]

Figure 3.4 The scheme of PANi growth on the graphite paper.[12]

As shown in Figures 3.3 and 3.4 with graphite paper as the deposition substrate, a PANi nucleation layer is formed at the surface of graphite paper at the initial stage. This step is vital for the morphologies of grown PANi nanofibers as a porous surface can afford a compact layer of nucleation, resulting in thin nanofibers during the following step. On the other hand, substrate with a plane surface is favor for thick nanofibers.[14] The horizontal growth stops once an intact nucleation layer is generated. And then, the vertical growth will start on the tips of nucleation formed during the first step. Subsequently, the nano-fibrillar PANi oligomers are grown on the nodes and the bottom-up growth of PANi nanofibers was finally stopped with the extinction of the extra voltage or current.[12] As a result, the thickness of the PANi nanofibers could be precisely controlled with changing the parameters.

3.2.3 Water bath method

Water bath method was employed in this work for the synthesis of tin sulfide. It is a facile method, which is suitable for uniform heating and low-temperature material deposition. A low growth temperature of 80 °C was used for homogeneous deposition of tin sulfide nanoflakes on graphite foam. This method is superior compared to those enquiring high temperature and high pressure, like hydrothermal method, which is widely used for tin sulfide synthesis.[15-17]

Figure 3.5 The scheme of water bath deposition of tin sulfide on graphite foam supported polyaniline nanofibers.

The growth mechanism of tin sulfide on polyaniline nanofibers could be described as follows. First the thioacetamide ($\text{C}_2\text{H}_5\text{NS}$) hydrolysis and the in-situ replacement reaction occur on polyaniline nanofibers: $\text{C}_2\text{H}_5\text{NS} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{NO} + \text{H}_2\text{S}$; $\text{Sn}^{4+} + 2\text{H}_2\text{S} \rightarrow \text{SnS}_2 + 4\text{H}^+$. [18] ii) And then, the self-assembly of tin sulfide will be promoted for nanoflakes. [19, 20] When the substrate (graphite foam supported polyaniline nanofibers) soaked in the mixed solution, the Sn^{4+} ions are more likely to absorb on the substrate surface other than in the solution, which makes the in-situ growth of tin sulfide on PANi much more favorable. Meanwhile, the thioacetamide hydrolysis in alkaline solution produces large amounts of H_2S , reacting with Sn^{4+} to form the nanocrystallites. The resulting SnS_2 has a unique hexagonal CdI₂-type layered structure, [21] which is in favor of layered nanoflake formation. In detail, this unique structure of SnS_2 gives rise to limited growth along the [001] direction, as the (001) layers are stacked by van der Waal forces. On the other hand, the ions (Sn, S) are bonded by strong ionic bonding in the (001) layer. Therefore, the stacking of (001) planes along [001] is suppressed by the weak interlayer forces and the in-plane growth of (001) layer is facilitated. [19, 22] Subsequently, the self-assembly of tin sulfide results in thin nanoflakes on polyaniline nanofibers.

3.3 Rationale for selection of characterizations

The electrochemical performance of energy storage devices, like supercapacitors and batteries, greatly depends on the morphologies, structures, components and oxidation states of the electrode materials. In order to optimize the electrochemical performance, various microscopic, spectroscopic and diffractive techniques were employed in this work to examine the morphological, structural and binding information. The Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) were used to study the morphology of the samples. Structural and bonding information were obtained by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and UV-visible spectroscopy. Moreover, the surface chemical states were examined by X-ray photoelectron spectroscopy (XPS). The pore structure/property and phase information

were obtained by Nitrogen adsorption-desorption method and X-ray powder diffraction (XRD). The working principles and functionalities of every technique and equipment are discussed in detail in the subsequent sections.

3.3.1 Scanning electron microscopy

The SEM used in this work is a field emission SEM (FE-SEM) (Model Jeol JSM 6700F). Normally, the operation voltage being chosen is 5, 10 and 15 kV. As the name implying, the electrons are used to scan the sample to get microscopy information. There is an electron gun at the top of the whole system, where the electron beam is emitted by a strong electric field. And then, the electron beam passes through a couple of magnetic lenses, condenser lens and objective lens for a focus beam. A focus electron beam is beneficial for high resolution images at high magnifications as a focus beam allows large numbers of electrons in a very small area. The focused beam, also known as incident electron beam, then hits the surface of the examined material, resulting in the emission of x-rays, primary backscattered electrons, secondary electrons, auger electrons ect. from the sample.

Figure 3.6 The simplified illustration of the interactions between the incident electron beam and the sample, with the emission of secondary electrons, backscattered electrons, auger electrons, transmitted electrons and characterized X-rays.

The primary backscattered electrons and secondary electrons are used to examine the material surface by scanning electron microscopy (Figure 3.6). The secondary electron has low energy, which is emitted from the sample after the inelastic scattering of the incident beam by the sample. It is suitable for the topological surface analysis of sample. The number of secondary electrons is related with the incident angle of electron beam. The emitted secondary electrons increase with the incident angle because the oblique incidence of electrons could induce larger interaction volume, resulting in longer escape distance of secondary electrons. Therefore, the bright edges (obliquely incident area) and dark flat centers (vertically incident area) are reflected on the screen via a specific secondary electron recorder.

The backscattered electrons are high energy electrons from the incident electron beam. When the beam hits heavy atoms, there is elastic scattering and a portion of incident electrons are rebounded as the backscattered electrons. The elastic scattering between the incident electrons and the heavy elements allows for large numbers of backscattered electrons and bright image. Therefore, the backscattered electrons could be used to examine the elementary and phase difference. By recording both the backscattered and secondary electrons, the texture of sample surface could be well-observed in the three-dimension images with different magnifications.

3.3.2 Transmission electron microscopy

The transmission electron microscopy (TEM) used in this work is performed on JEM-2010F, TEM, acceleration voltage: 200 kW) and JEOL-2100F, TEM, acceleration voltage: 200 kW. The working principle and setup of TEM are quite similar with SEM, consisting of the electron gun, magnetic (magnifying/objective/projector) lenses, specimen, electron recorders/analyzers and a fluorescent screen.

The most significant difference is the detected electrons, which is transmitted electrons (Figure 3.6) for TEM measurement, while for SEM, the scattered electrons (secondary/backscattered electrons) are examined. In view of this, several differences are

arising from SEM and TEM. i) In TEM system, the sample is placed between the condenser lens and objective lens to examine the transmitted electrons for high-resolution transmitted images. For SEM, the sample is placed at the bottom; ii) The sample for TEM test should be thin enough to allow for electrons transmitted. For SEM, the sample could be in any thickness; iii) Typically, TEM is suitable for small area and high-resolution examination while SEM could study large area of sample; iv) Both the inner structures and phase information could be obtained by TEM, while SEM could only be used for surface observations; v) Two-dimensional images could be obtained from TEM while three-dimensional images from SEM.

In this work, TEM were also employed for selected area electron diffraction (SAED) and Energy dispersive spectrum (EDS). The setups have little differences between the diffraction mode and image mode. The diffraction lens is placed between the objective and intermediate lens to obtained SAED patterns, which could be used to obtain crystalline information of small volume material. SAED can determine whether the material is monocrystalline (diffraction spots), polycrystalline (diffraction rings) or amorphous (diffuse rings). The high-energy electron has small wavelength, which is a hundred times smaller than the atom spacing in the solid sample. Therefore, the atoms act like the diffraction grating, which could diffract electrons hitting on. As the atoms are arranged in different orientation, the electrons could be diffracted in different directions. Determined by the crystal structure of the specific materials, different SAED pattern could be obtained for phase identification.

EDS analysis can be used to perform the small area elemental studies. It could be performed in the SEM or TEM system. As shown in Figure 3.6, the characterized x-ray from different elements will be collected for the EDS analysis. As each element has a unique atomic structure, which exhibits a unique set of peaks in the electromagnetic emission spectrum, the qualitative and semiquantitative analysis could be conducted by this technique. For qualitative analysis, it is fairly straightforward by identifying the spectrum of every elements. The quantitative study is based on the measurements of the line intensities for every element.

3.3.3 Fourier transform infrared spectroscopy

In order to obtain the bonding information of materials, the Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy are employed. In this part, the FTIR, which uses the IR source, will be discussed in detail.

The sample with different components has various vibration modes in different molecules. Normally, a molecular vibration happens with the periodic motion in the atoms and the constant translational/rotation motion of the whole molecule. The periodic motion of different atoms has different vibration frequency, corresponding to a wide wavenumber range ($300 - 3000 \text{ cm}^{-1}$ in IR range). For example, the stretching bonds in molecules have vibrational frequencies related to both the strength of the chemical bonds and the masses of the atoms. Therefore, only photon with certain energies can excite certain molecular vibrations and the photon could be absorbed by the molecule when a dipole moment change is caused by the vibrations. As certain frequencies of photons are absorbed by specific molecular bonds, the unique transmittance/absorbance IR spectrum is obtained, which could serve as a signature or fingerprint to identify the molecule.

Moreover, FTIR is a non-destructive technique, which is valuable in chemical analysis. However, one difficulty is the vibration modes in different molecules may have similar adsorption of a certain photon, resulting in overlapped peaks in the spectrum. Thereupon, the analysis of sample with more than one component becomes difficult by the infrared (IR) technique. Another difficulty is that some molecules have no dipole moment changes when the vibrations occurs. Then the FTIR technique is out of work as it is inactive for certain materials. Raman spectroscopy could also measure the vibration frequencies of materials directly and these two techniques are comparison and supplementary to distinguish the components on sample by different molecular vibrations.

3.3.4 Raman spectroscopy

Although FTIR and Raman can both be used for the test of the vibration and rotation level in the molecules, these two techniques have different principles. The IR spectra are obtained with certain photons absorbed while the Raman spectra are typically scattered spectra. The light source used in this work is 532 nm laser in the visible range. There are certain interactions between the laser light and the molecular vibrations, like inelastic scattering or Raman scattering (Stokes or anti-Stokes in Figure 3.7 b), with the release of photons or excitations. As a result, the energy in laser photons has a shift, namely Raman shift, which could give information about the vibrational modes in the materials.

Figure 3.7 Schematic illustration of interactions between photons and molecules. (a) Various interactions of the laser with a molecule, including Raman scattering (Stokes and anti-Stokes), Rayleigh scattering and Transmitted light. (b) Molecular energy diagram comparing these scattering interactions.[23]

Raman scattering can provide information on symmetry of Raman active vibration modes as it is polarization sensitive. Then Raman spectroscopy could detect the polarizability change of the electron cloud in the molecule via laser incident. Take the symmetric molecules as example, the IR is invisible as there is no dipole moment change during vibration in such molecules. But Raman could detect the polarizability changes to identify the symmetric molecule. Therefore, Raman spectroscopy could also be used to examine the vibration modes in different materials to determine the components. As schematically shown in Figure 3.7a, Raman spectroscopy is capitalizing on the inelastic scattering of photons from the tested sample via the activation of laser source. Figure 3.7b is the molecular energy diagram of Rayleigh scattering (elastic scattering, without energy change), small fraction of Stokes/Anti-stokes Raman scattering (inelastic

scattering). As the laser producing oscillating polarizations in the molecular when irradiates on the sample, the coupling of the polarizations could result in electronic excitations. The photons could gain or lose energy during the elastic scattering. After the transition of an activated photon from ground state to a virtual state, Stokes Raman scattering corresponds to the transition of the exited photon from a virtual state to some excited state, with lower energy compared to the incident photon; Anti-stokes scattering corresponds to the transition of the exited photon from a virtual state to ground state, with higher energy compared to the incident photon. The frequency difference is denoted as Raman shift. By studying the Raman peaks assigning to different components with characteristic Molecular vibrational, the chemical composition could be identified.

As some molecules have big changes of the dipole moment with vibrations, then the IR adsorption is strong, while some other molecules have big polarizability change (Raman scattering) and the Raman shift could be detected. The two techniques, together could provide a comprehensive and detailed study of the bonding information in the specific electrode materials.

3.3.5 UV visible spectroscopy

The Ultraviolet (UV)-visible spectroscopy is absorption (transmittance) or reflection spectroscopy in ultraviolet and visible range. As the ultraviolet and visible lights possess higher energy than infrared light used in FTIR, the UV-visible spectroscopy could be used to study the electronic transitions in the organic materials.

In the UV-vis spectroscopy system, the photons with characteristic energies are absorbed by the sample when they pass through or reflected by the sample, resulting in electronic transitions in materials. There are four possible types of transitions ($\sigma\text{-}\sigma^*$, $\pi\text{-}\pi^*$, $n\text{-}\sigma^*$ and $n\text{-}\pi^*$). Among them, electrons occupying an occupied molecule orbital of a sigma bond (σ) can get excited to the unoccupied molecule orbital of the corresponding antibonding (σ^*), which is denoted as a $\sigma\text{-}\sigma^*$ transition. Similarly, an electron excited from a π -bonding orbital to an antibonding π^* orbital can be described as the $\pi\text{-}\pi^*$ transition. There

could be also transitions from nonbonding orbital n to antibonding σ^* and π^* orbitals ($n\text{-}\sigma^*$ and $n\text{-}\pi^*$ transitions) in saturated compounds with lone pair electrons. As shown in Figure 3.8, possible electronic transitions in organic materials are schematically illustrated.

Figure 3.8 Possible electronic transitions of σ , π and n : $\sigma\text{-}\sigma^*$, $\pi\text{-}\pi^*$, $n\text{-}\sigma^*$ and $n\text{-}\pi^*$.

The unique spectrum for specific material is obtained after the data processing. The examination of the electronic transitions could be used to understand the electronic structures of the material and to qualify material conductivity, as illustrated in this work (Chapter 4). The electronic transition band of $n\text{-}\pi^*$ has a red shift in PANi based electrode materials. Here the n band is polaron band in PANi and the red shift indicates the decrease of the gap energy.[24, 25] Moreover, the electronic structure with polaron states in the band gap of the conjugated PANi samples were confirmed through UV-visible spectroscopy.

3.3.6 X-ray diffraction

X ray is an electromagnetic radiation in short wavelength range, typically 0.01 to 100 nm. It has high energy (0.124 keV~124 keV according to $E=hc/\lambda$), which is capable of high penetrating power. As it also possesses all properties of electromagnetic wave, like reflection, diffraction, refraction and polarization, it is suitable to study the crystalline structures and phases and elemental analysis.

X-ray diffraction technique is based on the diffraction of X-ray on the crystalline phase in detected materials. The wavelength of X-ray is similar with the interplanar spacing of the crystal planes. Then the crystal could act as the diffraction grating for X-ray. According to Bragg equation: $2d\sin\theta = n\lambda$, the crystalline structure could be identified by the interplanar spacing d (Figure 3.9).

Figure 3.9 The schematic illustration of bragg equation.

3.3.7 X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) with a monochromatic Al $K\alpha$ X-ray source is used in this work to quantify the ratio of different elements and the oxidation states of every element in the samples. X-ray with known high energy can excite the electrons of the sample. the photoelectrons from the sample are analyzed by measuring the kinetic energy of the photoelectrons. According to the equation, $E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)$, the XPS spectra, Intensity vs. E_{binding} could be graphed. Here the E_{photon} is 1486.6 eV of monochromatic Al $K\alpha$ X-ray source, ϕ is the work function in the system.

The XPS is a surface technique with a test depth less than several nanometers. To study the bulk materials, depth-profiling XPS has been employed in this work. An Argon ion gun has been employed to etch the sample layer by layer at a certain rate whilst XPS spectra are acquired after every cycle of ion gun etching. By analyzing the XPS spectra of every surface, the composition and elemental distribution of material across the bulk will

be obtained.

Figure 3.10 The schematic presentation of depth profiling XPS study on solid electrolyte interface (SEI).

3.3.8 Porosity measurement

The electrochemical performance is greatly dependent on the specific surface area and the pore size distribution. A high surface area of electrode material could allow enlarged electrode and electrolyte interface area, improving double layer and faradic capacity in energy storage devices. Moreover, the pore size distribution is also vital for energy storage as the suitable pore size in active material could allow more electrolyte ions in the pore. In particular, if the size of certain electrolyte ions (cations or anions) is larger than the average pore size in active material, the capacitive current is negligible in the corresponding part of the voltammetry curve, rather than regular rectangular shape.[26]

Therefore, it is important to study the pore size distribution, pore volume and specific surface area of the electrode materials. As the gas adsorption could allow probing of entire surface including pore interiors and irregularities, the nitrogen adsorption and desorption isotherms were employed in this work. As the isotherm is a function of gas/solid interactions, the pressure and the temperature, conducting the experiment at a fixed temperature with the controlled variable pressure could obtain the intrinsic

adsorption properties of the samples. In this work, the experiment is conducted on ASAP 2020 or ASAP 3020 at 77 K in the relative pressure range from 0 to 1.0 (P/P_0). Based on the adsorption and desorption isotherms, the pore size distribution and specific surface area could be calculated by Density functional theory (DFT) and Brunauer-Emmett-Teller (BET) methods.

3.4 Electrochemical test

The electrochemical performance of supercapacitor electrode is usually evaluated in a three-electrode system and full cell is examined in a two-electrode cell. In a three-electrode system, as shown in Figure 3.3, containing a working electrode (WE), a counter electrode (CE) and a reference electrode (RE). Current is passed between the WE and the CE, while the potential is measured between the WE and the RE. The circuit consists of WE and RE could be assumed as open circuit with RE at a constant potential to determine the potential of WE. WE and CE form another circuit, with CE used to realize the electrochemical equilibrium in the cell. In this work, the platinum sheet with stable electrochemical behaviors is chosen as the CE and the saturated calomel electrode (SCE) is RE. With the help of RE and CE, the electrochemical characteristics of WE (investigated electrode) could be obtained.

Supercapacitor electrodes can also be examined in a two-electrode full cell configuration. In the two-electrode systems, RE is not connected. WE and CE are the anode and cathode and the electrochemical behaviors of the whole device is investigated.

For battery test, the electrode material is evaluated in an assembled coin cell, CR2032. The tests are regularly performed in half-cell configuration, in which potassium foil is the anode, while the carbon material to be investigated is the cathode. Whatman grade GF/D glass microfiber filter separator is the membrane. Two different electrolytes are involved in this work, 0.6 M $\text{KN}(\text{SO}_2\text{F})_2$ (KFSI) in EC/DEC (1:1 in volume) electrolyte or and M KPF_6 in 1:1 EC/DEC (1:1 in volume) electrolyte. The is a two-electrode system, similar

with the full supercapacitor test. As shown in Figure 3.11, the active material, the separator with electrolyte and the K metal are sealed accordingly in a coin half-cell.

Figure 3.11 Coin cell assembly of the potassium ion half-cell.[27]

3.4.1 Cyclic voltammetry

Cyclic voltammetry (CV) is a potentiodynamic electrochemical technique with the current plotted versus applied voltage. A typical CV curve with a couple of cathodic and anodic peaks is shown in Figure 3.12. CV curves are efficient for identifying the redox reactions and phase changes. CV could also help to estimate the reversibility and the kinetic properties of the electrode material. The high symmetry of CV curves indicates good reversibility of electrode materials.

Figure 3.12 A typical CV curve with a couple of cathodic and anodic peaks.[28]

CV curves could be used to determine the specific capacity, which will be discussed in 3.3.4. Moreover, the CV curves could also evaluate the long-term cycling stability. Moreover, the oxidation/reduction peak potential difference in the CV curve could be used to estimate the electrochemical polarization effect in the system, which is related with the kinetic properties of the electrode materials. The peak current intensity also depends on potential scanning rate. A linear relationship between the peak current and the square root of rate indicates a diffusion-controlled process in the system. More details on the CV applications can be found in the following chapters.

3.4.2 Galvanostatic charge-discharge profiles

Similar to CV curves, the galvanostatic charge-discharge profiles are regularly used in supercapacitor and battery studies to evaluate their electrochemical performances, cycling stability and rate performance of electrodes. Besides, it is an efficient technique to determine the coulombic efficiency. As shown in Figure 3.13, the electrode species are oxidized or reduced during charge/discharge at a constant anodic or cathodic current. If there are irreversible electrochemical reactions during charge and discharge, the capacities obtained are different. The coulombic efficiency is lower than 100%. In both supercapacitor and battery systems, the coulombic efficiency is very important as the irreversible electrochemical reactions could lead to the continuous capacity fade, resulting in inferior cycling stability.

For a double layer capacitor, the galvanostatic charge and discharge curves are symmetric, indicating fully reversible behaviors. In a pseudocapacitor, the charge/discharge profiles are similar with that shown in Figure 3.13, where only a portion of charges stored during charge are released during discharge. This reveals that the electrode reaction is not fully reversible. In a battery, the coulombic efficiency is even more important as the high capacity and high energy density are the key advantages of batteries. Low coulombic efficiency will result in low capacity after long-term cycling test. Take the lithium ion battery as an example, low coulombic efficiency attributed to irreversible Li^+ intercalation and de-intercalation indicates the waste of anode materials as Li ions occupy

certain active sites in the anode. More importantly, it is waste of cathode material, as the Li ions are extracted from cathode during charge. Therefore, the capacity will be smaller and smaller with low coulombic efficiency. The calculations of capacity and energy density based on galvanostatic charge and discharge curves will be illustrated in 3.3.4 in detail.

Figure 3.13 A typical galvanostatic charge discharge curve of electrode materials with faradic reactions.[28]

3.4.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is an efficient way to examine electronic and ionic conductivity in the electrode material and the whole device. In this PhD thesis, the conductivity of electrodes in supercapacitors and batteries are characterized by Nyquist plots in the range of 0.1 to 100,000 Hz to study the ohmic resistance (R_s) at the ultra-high frequency range (>10 kHz), the charge transfer resistance (R_{ct}) in intermediate frequency and the solid diffusion (Z_w) of ions in the active materials in the low frequency.[29]

In detail, the ohmic resistance (R_s) in supercapacitor or battery systems is related with the resistance of ions across electrolyte, membrane (if applicable) and electrons across

electrode materials, current collectors and conductive wires. The charge transfer resistance (R_{ct}) is related with charge transfer in the electrode materials. For supercapacitors, it is mainly due to the pseudo capacitive behavior induced resistance, while for metal ion (Li^+/K^+) batteries, it originates from the Li^+ (K^+) intercalation/de-intercalation (for intercalation type anodes, like graphite). The solid diffusion resistance (Z_w) is attributed to the ion diffusion resistance in solid state electrode materials.[29-31]

In Figure 3.14a below, a simple equivalent circuit diagram is shown below. R_s , CPE, R_{ct} , Z_w represent the resistance from ohmic, double layer behavior, charge transfer and Warburg diffusion. As shown in Figure 3.14b, R_{SEI} is related with the resistance of K^+ transport through solid electrolyte interphase (SEI) in a battery. The equivalent circuit diagrams differ a lot in different electrochemical systems or different electrode materials. It should be simulated based on the components in a certain system, which is convincing and of great significance. The EIS is an important technique that can help to study the rate performances and the capacity fade mechanism during cycling stability.

Figure 3.14 Typical equivalent circuit diagrams used for Nyquist plots (a) For PANi based supercapacitors. (b) For potassium ion batteries. (may delete that in chapter 6,7)

3.4.4 Quantitative analysis based on electrochemical tests

Both the CV curves and galvanostatic profiles could be used for quantitative analysis of electrochemical performance, like capacity, energy and power density. However, CV curves could roughly evaluate the performance of supercapacitors while for batteries, this method is not accurate for batteries. The gravimetric specific capacity C_g ($F\ g^{-1}$ or $mA\ h\ g^{-1}$) calculated based on the charge/discharge curves for both batteries and supercapacitors following the equation:

$$C_g = I_{\Delta}t/(m_{\Delta}V)$$

where I (mA), Δt (s or h), m (mg), and ΔV (V) represent the charge/discharge current, total discharge time, mass of electrode materials and potential range during charge/discharge, respectively. For most battery test systems, the output of galvanostatic profiles is potential (V) vs capacity (mAh g^{-1}).

Similarly, the specific capacity ($F\ g^{-1}$ or $mA\ h\ g^{-1}$), energy density ($W\ h\ kg^{-1}$) and power density ($kW\ kg^{-1}$)

of the full cell could be determined by the following equation:

$$C_{cell} = It/(M_{\Delta}V)$$

$$E = C_{cell}\Delta V^2/2$$

$$P = E/t$$

where I (mA), t (s or h), M (mg), and ΔV (V) represent the discharge current, total charge/discharge time, mass of both electrode materials and potential range during the full cell test, respectively.

References

- [1] S. Agnoli, M. Favaro, *J. Mater. Chem. A*, **2016** 4 5002-5025.
- [2] C.H. Xu, B.H. Xu, Y. Gu, Z.G. Xiong, J. Sun, X.S. Zhao, *Energy Environ. Sci.*, **2013** 6 1388-1414.
- [3] X.S. Li, W.W. Cai, L. Colombo, R.S. Ruoff, *Nano Lett.*, **2009** 9 4268-4272.

- [4] Y.Z. Xue, B. Wu, Q.L. Bao, Y.Q. Liu, *Small*, **2014** 10 2975-2991.
- [5] X.W. Wang, G.Z. Sun, P. Routh, D.H. Kim, W. Huang, P. Chen, *Chem. Soc. Rev.*, **2014** 43 7067-7098.
- [6] Z. Jin, J. Yao, C. Kittrell, J.M. Tour, *ACS Nano*, **2011** 5 4112-4117.
- [7] Z.Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu, J.M. Tour, *Nature*, **2010** 468 549-552.
- [8] H. May, **1959** 9 340-344.
- [9] H.S. Zhai, L. Cao, X.H. Xia, *Chin. Chem. Lett.*, **2013** 24 103-106.
- [10] G.A. Snook, P. Kao, A.S. Best, *J. Power Sources*, **2011** 196 1-12.
- [11] A. Kellenberger, D. Ambros, N. Plesu, *Int. J. Electrochem. Sci.*, **2014** 9 6821-6833.
- [12] H.B. Zhang, J.X. Wang, Z. Wang, F.B. Zhang, S.C. Wang, *Synth. Met.*, **2009** 159 277-281.
- [13] N.T. Kemp, J.W. Cochrane, R. Newbury, *Synth. Met.*, **2009** 159 435-444.
- [14] H.H. Wang, J.L. Liu, Z. Chen, S. Chen, T.C. Sum, J.Y. Lin, Z.X. Shen, *Electrochim. Acta*, **2017** 230 236-244.
- [15] Y. Li, H.Q. Xie, J.F. Wang, *J. Solid State Electrochem.*, **2011** 15 1115-1119.
- [16] B. Luo, Y. Fang, B. Wang, J.S. Zhou, H.H. Song, L.J. Zhi, *Energy Environ. Sci.*, **2012** 5 5226-5230.
- [17] Y.C. Liu, H.Y. Kang, L.F. Jiao, C.C. Chen, K.Z. Cao, Y.J. Wang, H.T. Yuan, *Nanoscale*, **2015** 7 1325-1332.
- [18] O.M. Pesterev, C.J. De Ranter, **1976** 1062-1065.
- [19] D.L. Chao, P. Liang, Z. Chen, L.Y. Bai, H. Shen, X.X. Liu, X.H. Xia, Y.L. Zhao, S.V. Savilov, J.Y. Lin, Z.X. Shen, *ACS Nano*, **2016** 10 10211-10219.
- [20] Z.C. Wu, Y.J. Xue, Y.L. Zhang, J.J. Li, T. Chen, *RSC Adv.*, **2015** 5 24640-24648.
- [21] G. Wang, J. Peng, L.L. Zhang, J. Zhang, B. Dai, M.Y. Zhu, L.L. Xia, F. Yu, *J. Mater. Chem. A*, **2015** 3 3659-3666.
- [22] L.X. Yin, S.M. Chai, J.F. Huang, X.G. Kong, L.M. Pan, *Electrochim. Acta*, **2017** 238 168-177.
- [23] W.A. El-Said, H.-Y. Cho, J.-W. Choi, SERS Application for Analysis of Live Single Cell, in: *Nanoplasmonics-Fundamentals and Applications, InTech*, **2017**.
- [24] M. Mitra, C. Kulsi, K. Chatterjee, K. Kargupta, S. Ganguly, D. Banerjee, S. Goswamid, *RSC Adv.*, **2015** 5 31039-31048.

- [25] L. Shi, R.P. Liang, J.D. Qiu, *J. Mater. Chem.*, 2012 22 17196-17203.
- [26] F. Béguin, V. Presser, A. Balducci, E. Frackowiak, *Adv. Mater.*, **2014** 26 2219-2251.
- [27] C.R. Birkel, E. McTurk, M.R. Roberts, P.G. Bruce, D.A. Howey, *J. Electrochem. Soc.*, **2015** 162 A2271-A2280.
- [28] G.Z. Chen, *Prog. Nat. Sci.*, 2013 23 245-255.
- [29] E. Barsoukov, J.R. Macdonald, *Impedance spectroscopy: theory, experiment, and applications*, *John Wiley & Sons*, **2018**.
- [30] M.K. Liu, Y.E. Miao, C. Zhang, W.W. Tjiu, Z.B. Yang, H.S. Peng, T.X. Liu, *Nanoscale*, **2013** 5 7312-7320.
- [31] S.H. Ng, J. Wang, Z.P. Guo, G.X. Wang, H.K. Liu, *Electrochim. Acta*, **2005** 51 23-28.

Chapter 4

Synergistic capacitive behavior between polyaniline and carbon black

Polyaniline (PANI) is an excellent electrode material with high pseudocapacitance for supercapacitors. Here the binder-free supercapacitor electrodes with high specific capacitance (458 F g^{-1} at 2 mV s^{-1}) and Coulombic efficiency (100%) are successfully synthesized via a one-step potentialdynamic co-deposition of PANi and carbon black (CB). Significant synergistic effect between PANi and CB is demonstrated. Particularly, CB as the secondary dopant of PANi has been found to play an important role in producing higher conductivity, extended conformation structure, improved porosity, higher oxidation state and depressed hydrolysis effect, leading to superior capacitive performance. This promotes better understanding about synergistic effect between active materials and carbon additives and opens up new research and direction for high performance electrode design.

*This section published/submitted substantially as (H.H. Wang, J.L. Liu, Z. Chen, S. Chen, T.C. Sum, J.Y. Lin, Z.X. Shen, *Electrochim. Acta*, **2017** 230 236-244.).

4.1 Introduction

Supercapacitors with high power density, long-term cycling stability and high reversibility have been rising as promising energy storage devices. There are three main types of electrode materials for supercapacitors, namely, carbon species, metal compounds and conducting polymers.[1-3] The combination of carbonaceous materials, metal compounds and conducting polymers in a composite system usually results in improved performance due to the synergistic effect of every component.[4, 5]

Polyaniline (PANi) has been extensively studied as electrode materials for supercapacitors for its excellent properties, including high pseudocapacitance, high conductivity, high flexibility and low cost. Compared to other polymers, including polypyrrole or polythiophene, polyaniline exhibits highest theoretical and experimental specific capacity.[6-8] The excellent capacitive properties and fast charge transfer usually result in high energy/power density and good rate capability for supercapacitors. Moreover, the flexibility makes PANi promising to fabricate flexible electrodes. However, the pseudocapacitance of PANi is not always high and its capacitive behaviors is significantly dependent on its structural and chemical properties.[2] PANi can exist in three different oxidation states: fully reduced leucoemeraldine (LE), 50%-oxidized emeraldine base (EB) and fully oxidized pernigraniline (PE). EB is the most stable form of PANi, consisting of equal numbers of reduced amine ($-NH-$) and oxidized imine ($-N=$) units,[9] as shown in Figure 4.1a. Upon doping with acid, neutral EB, which is insulating with a wide band gap can be converted to protonated emeraldine salt (ES), which is electrically conducting. LE and PE are insulators, even when doped. PANi-ES with reduced amine and oxidized imine units possesses an asymmetric electronic structure in the energy band gap,[10] where the protonation of imine ($-N=$) sites and the subsequent internal redox reaction induce two asymmetric polaron bands. The upper polaron band (p^*) is narrow and nearly degenerated in the conduction band while the lower band (p) is broad. Hence the protonation results in the shift of Fermi level from the middle of the band gap to the middle of the half-occupied lower polaron band (as schematically shown in Figure 4.1b). The polaron bands facilitate the electron transition across the band gap,

resulting in significantly enhanced conductivity of PANi-ES.[11] When PANi-EB is protonated, the polymer backbone is positively charged and the negative counterions like SO_4^{2-} could sit in the vicinity of polymer chains, resulting in the so-called PANi-ES. It will cause the change of the conformation, conjugation length of PANi, which are significantly related to the conductivity, as well as the electrochemical performance.

Figure 4.1 (a) The polaron formation and conversion in PANi-ES. (b) the schematic energy band structure of PANi-ES with asymmetric upper (p^*) and lower polaron bands (p). CB (π^*) and VB (π) represent of conduction band and valence band, respectively.

Even the conductivity of PANi could be greatly increased by the doping of acid that increases the electrochemical performance, the inferior mechanical stability due to swelling, shrinkage or crack and the degradation due to side reactions during the polymerization and electrochemical test will restrict its application in supercapacitors. As mentioned above, PANi has three different forms based on the oxidation states. Besides, there are also unwanted side products like p-benzoquinone (BQ) and hydroquinone (HQ) due to the hydrolysis. The hydrolysis is unavoidable during the polymerization, which will affect the conductivity, reversibility and stability of PANi.[12, 13]

Carbon materials are common supercapacitor materials with high stability but low specific capacitance[14, 15]. Recently, many PANi based composites containing nanostructured carbon materials such as carbon nanotubes (CNTs), graphene and various porous carbon materials have been reported with enhance electrochemical performance for supercapacitors. The presence of nanostructured carbonaceous materials in hybrid PANi/C electrodes can significantly enhance the stability, conductivity and the dispersibility of PANi, resulting in enhanced electrochemical performance. Graphene and CNTs are popularly used in energy storage and show excellent intrinsic electronic, structural and mechanical properties [16, 17]. Many investigations have been conducted on PANi based composite electrodes involving graphene or CNTs, which show high specific capacitance over 500 F g^{-1} and good cycling stability of around 90% capacity retention after hundreds of electrochemical cycles [6-8, 18-20]. However, the syntheses of graphene normally follow the Hummer's method with complicated chemical process [7]. The resulting graphene oxide (GO) suffers from low conductivity, which needs to be reduced to reduced graphene oxide (rGO). Several works focused on functional-rGO, such as nitrophenyl-rGO and aminophenyl-rGO, which were found to further enhance the performance of PANi/functional rGO.[7] Besides, CNTs are usually obtained through the chemical vapor deposition and surfactant of dopant is introduced to modify the surface properties of CNTs to facilitate the combination with PANi.[18] Most of these works were time consuming or cost ineffective due to complicated chemical process and prohibitive cost of graphene and CNTs, which could hamper the commercial application.

In this paper, we adopt a facile electrochemical co-deposition method to achieve freestanding PANi/CB electrode on porous graphite substrates, using low cost precursors. The potentialdynamic polymerization is employed because it can produce binder-free electrode with uniform porous-network in short reaction time with a simple set-up (Figure 4.2a), allowing fine-tuning of mass loading of active materials. The hybrid composites exhibit improved electrochemical performance due to the addition of CB in terms of specific capacitance (458 F g^{-1} , 2 mV s^{-1}), cycling stability (74% retention after 300 cycles) and Coulombic efficiency (100%), which are among the best results in literature on PANi and commercial active carbon materials,[21-26] while the pure PANi only delivers a specific capacitance of 381 F g^{-1} with 70% retention after 300 cycles and 74% Coulombic efficiency. This is attributed to the significant synergistic effect between PANi and CB. Particularly, several roles of CB have been identified: (i) It promotes the formation of extended PANi chains to be much thinner, longer and more porous than pure PANi. This extended conformation is favorable for electron transfer and ion diffusion, thus enhancing the electric conductivity and ensuring high capacity resulting from more active sites exposed to the electrolyte. (ii) The CB nanoparticles can be well-wrapped in PANi chains without inducing any additional resistance. (iii) It can increase the doping level and decrease the defects density of PANi, facilitating the transfer of bipolarons to polarons and delocalization of polarons and ensuring the improved electric conductivity.[2] All these contribute to the enhanced electrochemical performance.

4.2 Synthesis and characterizations

4.2.1 Chemicals and instruments

The chemicals, Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) (ACS reagent, $\geq 99.5\%$), was purchased from SIGMA-ALDRICH and used as received. The sulfuric acid (98%) and ethanol involved in this work were bought from VWR CHEMICALS (PROLABO) and Fisher Chemical, respectively. The commercial carbon (xc-72 carbon black) was purchased from Shanghai Lisheng Industry CO., LTD. The deionized water (DIW, $18.2 \text{ M}\Omega$) was employed for

electrolyte and sample clean. A platinum plate (area 4 cm²) and a saturated calomel electrode (type, 217) purchased from Xuzhou Zhenghao Electronic Technology CO., LTD and Shanghai Leici Instrument Factory were used during the electrochemical deposition and tests.

4.2.2 Synthesis: Fabrication of PANi/CB composite electrode

The electrochemical co-deposition was carried out on the EC workstation (CHI 760D) with a three-electrode system, where graphite paper (GP), a Pt sheet and a saturated calomel electrode (SCE) acted as the working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively. Fresh distilled aniline (C₆H₅NH₂) and vulcan XC-72 carbon black with the concentration of 0.1 mol dm⁻³ and 1 g dm⁻³ respectively were dispersed in 0.5 mol dm⁻³ H₂SO₄ as the deposition electrolyte. The potentialdynamic deposition was cycled between -0.2 and 0.8 V under a stirring speed of 300 rpm to guarantee homogenous growth. Different scan rates of 10, 20 and 50 mV s⁻¹ were involved and the samples were denoted as PANi+CB-10, PANi+CB-20 and PANi+CB-50, respectively. For comparison, the control samples of PANi were also prepared in a 0.5 mol dm⁻³ H₂SO₄ containing 0.1 mol dm⁻³ aniline without CB named as PANi-10, PANi-20 and PANi-50, respectively. In order to study the effects of substrates, the GP was also replaced by stainless steel (SS) and the resultant electrodes obtained at 20 mV s⁻¹ was named as PANi+CB-20-SS. All electrodes were washed with deionized water to remove the residual reactants and sulfuric acid. The instruments for morphological, structural characterizations and electrochemical evaluations are illustrated in 3.1.

4.2.3 Morphological studies

SEM images shown in Figure 4.2b and Figure 4.2c reveal the nanofibrous structure of PANi samples. For PANi+CB-20, the PANi fibers exhibit diameter of 50-80 nm with length in the range of 1-2 μm, which is much longer and thinner than those (100-120 nm in diameter and ~1 μm in length) of PANi-20, indicating that the presence of CB can facilitate the growth of long and thin PANi nanofibers. This larger aspect ratio (L/D) for

PANi+CB-20 is in good agreement with previous studies that the addition of carbonaceous dopants or other additives could change the conformation and form extended chains of PANi by removing twist defects in the aromatic rings in PANi.[27] The extended feature is advantageous for enhancing the electronic conductivity due to the stronger interaction between adjacent bipolarons and the delocalization of polarons (see Figure 4.1a), and ensuring high capacity resulting from more active sites exposed to the electrolyte.

Figure 4.2 (a) Schematic illustration of the synthesis of PANi based samples deposited on the GP substrate (left). After electrochemical co-deposition (middle), PANi/CB nanofibers are coated on the GP substrate (right). (b), (c) FE-SEM images of PANi-20 and PANi+CB-20, respectively.

As shown in the TEM images, the spherical CB nanoparticles are well wrapped in the single stranded PANi nanofibers uniformly (Figures 4.2d, 4.2e). The intact electronic/physical contact between CB and PANi is favorable for electron transfer and ion diffusion, thus yielding high specific capacitance. This is further verified by N₂ adsorption and desorption results in Figure 4.2f, the negligible change of specific surface area (SSA) for two samples indicates CB well-encapsulated in the PANi chains. In Figure 4.2g, PANi+CB-20 exhibits more mesoporous sized at 3.0 nm and 4.5 nm than PANi-20. This pore size distribution feature is particularly favorable for supercapacitors.

The morphology of PANi/CB depends both on the scan rate and substrate of potentialdynamic deposition. As shown in Figure A.1a and A1b, PANi+CB-10 is composed of short nanorods while PANi+CB-50 mainly contains entangled and merged nanofibers, giving rise to a compact structure. These results are consistent with previous studies. The growth of PANi nanofibers through electrochemical deposition involves the horizontal growth of a compact nucleation layer and the following vertical growth of PANi nanofibers.[28] The amount of PANi nuclei is proportional to the deposition scan rates.[29] At lower scan rates, the oxidation time is longer for the growth of PANi on less amounts of nuclei, thus achieving shorter nanorods with larger horizontal dimensions. Higher scan rate is favorable for more PANi nuclei, so the nanofibers of PANi+CB-50 are much more compact compared with PANi+CB-10 and PANi+CB-20. In addition, the morphology of PANi is strongly dependent on substrate type. For PANi+CB-20-SS (Figure A.2c), the electrode materials consist of large-sized nanoparticles with large mesopores (average pore size around 8nm) and limited nanopores. The low specific surface area (19.491 m²/g) and low pore volume (Figures A2c, A2d) impede the ion diffusion in the electrode, which emphasizes the great effect of substrates in electrochemical polymerization of PANi. On the contrary, GP with higher porosity and larger surface area could promote vertical growth of PANi due to the good dispersibility of PANi nuclei on the surface of substrate, resulting in larger quantity and better structured PANi nanofibers.[30]

4.2.4 Structural analysis

Figure 4.3 FTIR spectra of CB, PANi-20 and PANi+CB-20. (b) The schematic representation of the formation mechanism of PANi/CB composite. (c) Raman spectra of CB, PANi and PANi/CB electrodeposited on GP. (d) UV-visible spectra of PANi-20 and PANi+CB-20 deposited on Graphite paper.

The FTIR, Raman and UV-visible spectra of PANi based samples are shown in Figure 4.3. The IR bands around 1105 cm^{-1} , 1240 cm^{-1} and 1300 cm^{-1} in the PANi-20 spectrum are assigned to the quinoid $\text{Q}=\text{N}$ stretching vibrations (Q represents of quinoid unit),[31] the $\text{C}-\text{N}^{+}$ stretching vibrations and the $\text{C}-\text{N}$ amine stretching vibrations, respectively.[32] The bands centered around 815 cm^{-1} , 1480 cm^{-1} and 1558 cm^{-1} are attributed to $\text{C}-\text{H}$ out of plane vibrations in aromatic ring deformation, $\text{C}-\text{C}$ stretching vibration in benzene and quinone ring, respectively.[32] Similar peaks are identified for PANi+CB-20. However, the peak intensity is much weaker for PANi+CB-20 due to the presence of CB. The broad

band around 3420 cm^{-1} and narrow band at 2912 cm^{-1} , which are respectively attributed to O–H and C–H stretching vibration in CB, disappear in PANi+CB-20 spectrum, corroborating the covalent interaction between CB and PANi via functional groups.[33] These interactions may include the hydrogen bonding between O–H/C–O groups of CB and –NH– sites of PANi as schematically illustrated in Figure 4.3b. Moreover, the π – π stacking between the aromatic rings of CB and PANi may also exist.[34] These interactions can not only stabilize the structure of the composite, but also improve the PANi backbone chain conformation, facilitating the transfer of bipolarons to polarons and the delocalization of polarons (refer to Figure 4.1a).

In Figure 4.3c, the Raman spectra of XC-72 CB show a D band at 1343 cm^{-1} and a G band at 1594 cm^{-1} , which represent the breathing modes of rings due to the defects and the in-plane stretching motion of C–C bond in carbon black,[31] and remain observable in PANi and PANi/CB spectra. For PANi-20, the peaks at 810, 1170, 1332, 1479 and 1598 cm^{-1} are attributed to the out of plane C–H motions, in-plane bending of C–H in semi-quinoid units, C–N⁺ stretching, N=Q=N stretching in quinonoid rings and C=C stretching in the semi-quinoid rings, respectively.[31, 32] These Raman peaks are characteristic of PANi and also observed in the PANi+CB-20 spectrum. Nevertheless, the peak intensity at 1170 and 1479 cm^{-1} is much stronger for PANi+CB-20 than that of PANi-20, indicating more imine sites connected with quinonoid rings due to the presence of CB, which corresponds to the enhanced bipolaron/polaron formation and hence the enhanced conductivity for PANi+CB-20 as compared with PANi-20 (refer to Figure 4.1a). These effects can be further verified by UV-visible measurements. In Figure 4.3d, the UV-visible band at 360 nm and 454 nm for PANi-20 are attributed to the transition between the valance band to the conduction band (π – π^*) of benzenoid rings and the lower polaron band to conduction band (p – π^*), respectively (refer to Figure 4.1b).[34, 35] CB shows maximum adsorption at 265 nm, which is attribute to the aromatic π – π^* transition of C–C bonds. In the case of the PANi+CB-20, the shoulder around 240 nm is blue-shifted compared with the spectrum of pure CB, which could be a result of interactions between PANi and CB. Moreover, the p – π^* transition band shifts from 454 nm to 460 nm for PANi+CB-20. This red shift corresponds to the decrease of the gap energy

between the lower polaron band (p) and the conduction band, from 2.73 eV to 2.69 eV. Moreover, the PANi+CB-20 spectrum shows a higher upward tendency above 600 nm, which is attributed to the excitation of valence electrons to the lower polaron band (p). This substantial enhancement of excitation in high wavelength range suggests the abundant delocalized polarons with the presence of CB.[36] As the transition of valence band to polaron band and polaron to conduction band are tremendously facilitated for PANi+CB-20, the transition between valence band and conduction band is negligible with the absence of absorption peak around 360 nm.

XPS analysis was conducted to shed more light on element information of PANi based electrodes. The S, C, N and O elements are identified for PANi-20 and PANi-CB-20 (Figure 4.4a). Sulfur comes from the doping of SO_4^{2-} during the polymerization process.[37] The atomic ratio of C to N is around 6 for PANi-20 (atomic ratio C: N: O = 73.4: 13.3: 13.2), which agrees well with the ratio for pristine PANi where each benzene/quinoid ring is connected to one N atom (either in amine or in imine). The much higher C to N ratio in PANi+CB-20 indicates the successful addition of CB in PANi+CB-20 (atomic ratio C: N: O = 79.8: 8.1: 12.1). The C 1s spectra of PANi-20 and PANi+CB-20 can both be fitted into four sub-peaks at 283.9 eV (C=C), 284.6 eV (C–C/C–H), 285.5 eV (C–O) and 286.9 eV (C=O), respectively (Figures 4.4b, 4.4d). The peak of C–C bond with a binding energy of 284.6 eV acts as the reference. The substantial increase of C=C peak intensity for PANi+CB-20 is due to the presence of CB, corresponding to the higher degree of oxidation and thus higher conductivity of PANi with the addition of CB. In the same spectra, the reduction in the C–O peak intensity at 285.5 eV (0.17 for PANi+CB-20 vs. 0.41 in PANi-20) appears to mean a lower defect density due to the incorporation of carbon particles. The XPS N 1s core-level spectra in Figure 4.4c and Figure 4.4e are deconvoluted into four Gaussian–Lorentzian sub-peaks centered at 398.2 eV (=N–), 399.0 eV (–NH–), 400.1 eV (–N⁺H–), 401.6 eV (=N⁺H–), respectively. Similarly, the ratio of imine to amine, i.e. [=N–]/[–NH–] is indicative of the oxidation/polymeric level of PANi chain.[38] The value is 0.23 for PANi+CB-20, larger than the value of 0.16 for PANi-20, corresponding to a higher polymeric level in PANi+CB-20.[35, 38] These results are

coherent with FTIR, Raman and UV-visible results, corroborating the higher oxidation level and enhanced electronic properties with the presence of CB.

Figure 4.4 (a) Wide scan XPS spectra of PANi-20 and PANi+CB-20. C 1s regions of (b) PANi-20 and (d) PANi+CB-20. N 1s regions of (c) PANi-20 and (e) PANi+CB-20, respectively.

4.3 Electrochemical results

The electrochemical properties of as obtained green-colored PANi on substrates were studied on a CHI760D Electrochemical workstation (CHENHUA, Shanghai, China) to

study the electrochemical properties. The cyclic voltammetry (CV) and galvanostatic charge-discharge were both conducted in the potential range from 0 to 0.9 V with the scan rates of 2 to 20 mV s^{-1} and current densities of 0.1 to 5 A g^{-1} , respectively. The electrochemical impedance spectroscopy (EIS) characterization was performed in the frequency range of 100 kHz to 0.01 Hz for the samples. All tests were conducted in 0.5 M H_2SO_4 electrolyte.

Figure 4.5 (a) CV curves at a scan rate of 2 mV s^{-1} and (b) galvanostatic charge and discharge curves obtained at 0.1 A g^{-1} . (c) Cycling stability at a scan rate of 20 mV s^{-1} for PANi-20 and PANi+CB-20. (d) Nyquist plots for PANi-20 and PANi+CB-20. The inset is the equivalent circuit used for impedance spectra fitting. R_{el} is the equivalent series resistance (ESR), Qdl is the element related with double layer capacitance, R_{ct} is the charge transfer resistance and W is Warburg impedance.

Electrochemical properties of PANi based electrodes were investigated in a three-electrode system containing 0.5 M H₂SO₄ solution. Typical cyclic voltammetry curves for PANi+CB-20 and PANi-20 are shown in Figure 4.5a. The CV curve of the PANi+CB-20 exhibits much larger area than that of PANi-20, indicating that the addition of CB is favorable for the enhancement of specific capacitance. Three redox pairs have been identified in the CV curves of PANi+CB-20. The first redox pair ($O_1/R_1 \sim 0.2V$) is attributed to the transition between semiconducting leucoemeraldine (LE) form and the conducting polaronic emeraldine salt (ES), the second one ($O_2/R_2 \sim 0.45V$) is corresponding to the transition between p-benzoquinone (BQ) and hydroquinone (HQ). The BQ produced during the polymerization of PANi is a side product of the hydrolysis.[13] The third one ($O_3/R_3 \sim 0.75V$) represents the transition between ES state and the fully oxidized (per) nigraniline (PE), respectively.[39, 40] For PANi-20, the first and third pairs of redox peaks are substantially suppressed (almost negligible) because of the excessive formation of BQ. Although BQ and HQ as the side-products from hydrolysis can still contribute to the specific capacitance, they may affect the electronic properties of PANi and the stability of the electrode.[12, 41] Interestingly, the second redox pair (BQ/HQ) is depressed in PANi+CB-20 compared with that of PANi-20 and hence can enhance the conductivity and stability of the composite. This is probably because the attachment of CB nanoparticles partially protects the active sites ($-NH-$) in PANi from being attacked by water.

Besides the protective effect of the dopant (CB), the hydrolysis was found to be affected by the morphology of PANi. As shown in Figure A.3, PANi+CB-10 and PANi+CB-50 both show high intensity of BQ/HQ. For PANi+CB-10, short nanorods mainly consist of short PANi chains, which can be easily attacked by water, leading to high hydrolysis effect. As for PANi+CB-50, higher scan rate means the reduced oxidation time and thus hydrolysis effect is promoted since the chain growth and hydrolysis of PANi are competing to each other.[13, 29] The potential separation of the second pair of redox peaks for PANi+CB-50 is evidently larger than PANi+CB-10 and PANi+CB-20, indicating inferior reversibility. The specific capacitance was calculated based on cyclic voltammetry (CV) curves. A specific capacitance of 458 F g⁻¹ is obtained for PANi+CB-

20 at 2 mV s^{-1} , which is higher than 381 F g^{-1} of pure PANi-20 (see Figure 4.5a). In order to study the effect of substrates for the electrochemical deposition of PANi, we synthesized the electrode materials with same method on stainless steel (SS) substrate and test the electrochemical performance. The CV curve for PANi+CB-20-SS in Figure A.3 is of triangular and narrow shape with much lower specific capacitance 231 F g^{-1} vs. 458 F g^{-1} of PANi+CB-20. This triangular shape may be caused by small effective pore size of electrode materials on SS, which inhibits the access of large anions (SO_4^{2-}) into the pores for double layer capacitance.[42] The low specific surface area and poor porous structure (Figure A.2) of PANi+CB-20-SS lead to less accessible surface area, which will restrain the ions adsorption and transportation, resulting in low specific capacitance.[30]

The specific capacitance was also calculated based on galvanostatic discharge curves. At 0.1 A g^{-1} , PANi+CB-20 also shows higher capacitance of 382 F g^{-1} vs. 288 F g^{-1} of PANi-20 (see Figure 4.5b). Furthermore, the Coulombic efficiency increases from 74% for PANi-20 to 100% for PANi+CB-20, indicating significantly enhanced reversibility. The cycling stability of PANi+CB-20 is also greatly improved by the presence of CB in the composite (Figure 4.5c). PANi+CB-20 can maintain specific capacitance at 180 F g^{-1} with 74% capacitance retention after 300 cycles, which is higher than that of PANi-20 (140 F g^{-1} with 70% capacitance retention). Even after 650 cycles, PANi+CB-20 shows 63% capacity retention, which is comparable to those in literature for rGO-PANi composites.[43] The capacity degradation is mainly due to (i) the hydrolysis effect and (ii) the structural change. The former one will result in side products with low conductivity and stability. Consequently, the specific capacity will drop, especially at high scan rates. In addition, the hydrolysis of PANi may damage the initial fiber-like structure of PANi, resulting in poor conductivity and decreased surface area. Besides the hydrolysis, the latter one, structural change is also related with the doping and dedoping of ions in the electrolyte. All these, together, lead to sluggish electrochemical kinetics, reduced exposure surface area of active materials and poor contact between the electrode/electrolyte, and thus, a capacity fade. The capacity of PANi-20 decays in the initial cycles and then increase to the maximum at around 300 cycles (Figure 4.5c). The

initial capacitance fade for PANi-20 may be due to the degradation of PANi (e.g. via hydrolysis side reaction), while the increase from 200 to 300 cycles may result from the improved wettability via sufficient soaking of electrolyte during previous charge-discharge process. The results in Figure 4.5c indicate that the presence of CB can improve the wettability of electrodes to the electrolyte solution and thus the electrochemical performance.

The electrochemical impedance spectra (EIS) for PANi-20 and PANi+CB-20 are compared in Figure 4.5d. The slope of the Warburg tail in low frequency region is smaller than 45° from horizontal axis for PANi-20 while the PANi+CB-20 electrode exhibits an almost vertical straight line, which reveals faster Warburg ion diffusion and better capacitive behavior in PANi+CB-20. The lower ion diffusion resistance can be correlated to the larger aspect ratio of polymer chains measured by SEM in Figure 4.2, which is in favor to the ion diffusion from the electrolyte to the pore structure of the PANi/CB composites.[44, 45] In the high-frequency region, the equivalent series resistance (ESR) and charge transfer resistance (R_{ct}) are estimated to be ESR=1.5 Ω , 2 Ω and R_{ct} =1.5 Ω , 6.4 Ω for PANi+CB-20 and PANi-20, respectively. The enhanced electric conductivity as well as the improved specific capacitance and cycling stability are attributed to the addition of CB: (i) It has improved the conformation structure to form extended chains, resulting in longer and thinner PANi fibers with more mesopores of 3.0 - 4.5 nm. This confirmative structure provides more active sites exposed to the electrolyte. (ii) CB is embedded in PANi fibers with intact contact. The presence of CB as the second dopant in PANi promotes the formation and delocalization of polarons, substantially improving the conductivity. (iii) The doping of CB increases the polymeric level, suppresses hydrolysis side reaction, and decreases the defects density. All these contribute to higher specific capacitance, better reversibility and longer cycle life.

4.4 Conclusions

The binder-free supercapacitor electrodes with high specific capacitance (458 F g⁻¹), good cycling stability (74% retention after 300 cycles) and high coulombic efficiency (100%),

are designed based on PANi and CB composites. Significant synergistic effect between PANi and CB is demonstrated. The addition of CB is found: (i) to promote the formation of extended PANi chains that are much thinner, longer and more porous than CB-free PANi, (ii) to ensure better wettability of PANi to the electrolyte and thus better electrochemical contact, and (iii) to induce higher doping level of PANi, facilitating the transfer of bipolarons to polarons and delocalization of polarons and thus ensuring the improved electric conductivity and capacity. In addition, the facile synthesis method adopted here is superior over conventional chemical synthesis route in terms of simpler procedure, lower cost and improved performance. It can also be expanded to many other fields such as anticorrosion,[46] rechargeable batteries,[47] electrochemical energy conversion [38] and capacitive de-ionization(CDI) for water purification,[48] where PANi based systems have attracted increased attention. This displays great practical significance of our facile work.

References

- [1] H. Jiang, J. Ma, C.Z. Li, *Adv. Mater.*, **2012** 24 4197-4202.
- [2] G.A. Snook, P. Kao, A.S. Best, *J. Power Sources*, **2011** 196 1-12.
- [3] R.R. Salunkhe, Y.V. Kaneti, J. Kim, J.H. Kim, Y. Yamauchi, *Acc. Chem. Res.*, **2016** 49 2796-2806.
- [4] J.L. Liu, L.L. Zhang, H.B. Wu, J.Y. Lin, Z.X. Shen, X.W. Lou, *Energy Environ. Sci.*, **2014** 7 3709-3719.
- [5] R.R. Salunkhe, J. Tang, N. Kobayashi, J. Kim, Y. Ide, S. Tominaka, J.H. Kim, Y. Yamauchi, *Chem. Sci.*, **2016** 7 5704-5713.
- [6] G.Q. Ning, T.Y. Li, J. Yan, C.G. Xu, T. Wei, Z.J. Fan, *Carbon*, **2013** 54 241-248.
- [7] L.F. Lai, H.P. Yang, L. Wang, B.K. Teh, J.Q. Zhong, H. Chou, L.W. Chen, W. Chen, Z.X. Shen, R.S. Ruoff, J.Y. Lin, *ACS Nano*, **2012** 6 5941-5951.
- [8] J.L. Liu, J. Sun, L.A. Gao, *J. Phys. Chem. C*, **2010** 114 19614-19620.
- [9] D. Li, J.X. Huang, R.B. Kaner, *Accounts Chem. Res.*, **2009** 42 135-145.
- [10] J. Kim, S. Park, N.F. Scherer, *J. Phys. Chem. B*, **2008** 112 15576-15587.
- [11] C.H.B. Silva, N.A. Galiote, F. Huguenin, E. Teixeira-Neto, V.R.L. Constantino, M.L.A. Temperini, *J. Mater. Chem.*, **2012** 22 14052-14060.

- [12] N. Gospodinova, P. Mokreva, L. Terlemezyan, *Polymer*, **1994** 35 3102-3106.
- [13] C.Q. Cui, L.H. Ong, T.C. Tan, J.Y. Lee, *Electrochim. Acta*, **1993** 38 1395-1404.
- [14] B.L. Xing, J.L. Cao, Y. Wang, G.Y. Yi, C.X. Zhang, L.J. Chen, G.X. Huang, B. Xu, *Funct. Mater. Lett.*, **2015** 8 4.
- [15] J. Tang, Y. Yamauchi, *Nat. Chem.*, **2016** 8 638-639.
- [16] A.A. Balandin, *Nat. Mater.*, **2011** 10 569-581.
- [17] A.K. Geim, K.S. Novoselov, *Nat. Mater.*, **2007** 6 183-191.
- [18] Y. Yang, Y. Hao, J. Yuan, L. Niu, F. Xia, *Carbon*, **2014** 78 279-287.
- [19] J. Yan, T. Wei, Z. Fan, W. Qian, M. Zhang, X. Shen, F. Wei, *J. Power Sources*, **2010** 195 3041-3045.
- [20] R.R. Salunkhe, S.H. Hsu, K.C.W. Wu, Y. Yamauchi, *ChemSusChem*, **2014** 7 1551-1556.
- [21] M.J. Bleda-Martinez, E. Morallon, D. Cazorla-Amoros, *Electrochim. Acta*, **2007** 52 4962-4968.
- [22] D. Salinas-Torres, J.M. Sieben, D. Lozano-Castello, D. Cazorla-Amoros, E. Morallon, *Electrochim. Acta*, **2013** 89 326-333.
- [23] W.C. Chen, T.C. Wen, H.S. Teng, *Electrochim. Acta*, **2003** 48 641-649.
- [24] C.C. Hu, W.Y. Li, J.Y. Lin, *J. Power Sources*, **2004** 137 152-157.
- [25] C. Tran, R. Singhal, D. Lawrence, V. Kalra, *J. Power Sources*, **2015** 293 373-379.
- [26] A. Olad, H. Gharekhani, *Prog. Org. Coat.*, **2015** 81 19-26.
- [27] Y.N. Xia, J.M. Wiesinger, A.G. Macdiarmid, A.J. Epstein, *Chem. Mat.*, **1995** 7 443-445.
- [28] H.B. Zhang, J.X. Wang, Z. Wang, F.B. Zhang, S.C. Wang, *Synth. Met.*, **2009** 159 277-281.
- [29] S.L. Mu, Y.F. Yang, *J. Phys. Chem. B*, **2008** 112 11558-11563.
- [30] S. Mondal, K. Barai, N. Munichandraiah, *Electrochim. Acta*, **2007** 52 3258-3264.
- [31] X.N. Chen, F.C. Meng, Z.W. Zhou, X. Tian, L.M. Shan, S.B. Zhu, X.L. Xu, M. Jiang, L. Wang, D. Hui, Y. Wang, J. Lu, J.H. Gou, *Nanoscale*, **2014** 6 8140-8148.
- [32] A. Janosevic, G. Ciric-Marjanovic, B. Marjanovic, P. Holler, M. Trchova, J. Stejskal, *Nanotechnology*, **2008** 19 1-8.

- [33] S.H. Tang, L.P. Sui, Z. Dai, Z.T. Zhu, H.X. Huangfu, *RSC Adv.*, **2015** 5 43164-43171.
- [34] M. Mitra, C. Kulsi, K. Chatterjee, K. Kargupta, S. Ganguly, D. Banerjee, S. Goswamid, *RSC Adv.*, **2015** 5 31039-31048.
- [35] L. Shi, R.P. Liang, J.D. Qiu, *J. Mater. Chem.*, **2012** 22 17196-17203.
- [36] C. Dhand, M. Das, G. Sumana, A.K. Srivastava, M.K. Pandey, C.G. Kim, M. Datta, B.D. Malhotra, *Nanoscale*, **2010** 2 747-754.
- [37] L. Shi, R.-P. Liang, J.-D. Qiu, *J. Mater. Chem.*, **2012** 22 17196-17203.
- [38] G. Wu, L. Li, J.H. Li, B.Q. Xu, *Carbon*, **2005** 43 2579-2587.
- [39] C.C. Hu, J.Y. Lin, *Electrochim. Acta*, **2002** 47 4055-4067.
- [40] L. Wang, Y.J. Ye, X.P. Lu, Z.B. Wen, Z. Li, H.Q. Hou, Y.H. Song, *Sci Rep*, **2013** 3 1-9.
- [41] R. Mazeikiene, A. Malinauskas, *Eur. Polym. J.*, **2002** 38 1947-1952.
- [42] F. Béguin, V. Presser, A. Balducci, E. Frackowiak, *Adv. Mater.*, **2014** 26 2219-2251.
- [43] B.L. Liang, Z.Y. Qin, T. Li, Z.J. Dou, F.X. Zeng, Y.M. Cai, M.F. Zhu, Z. Zhou, *Electrochim. Acta*, **2015** 177 335-342.
- [44] M.K. Liu, Y.E. Miao, C. Zhang, W.W. Tjiu, Z.B. Yang, H.S. Peng, T.X. Liu, *Nanoscale*, **2013** 5 7312-7320.
- [45] Q. Wu, Y.X. Xu, Z.Y. Yao, A.R. Liu, G.Q. Shi, *ACS Nano*, **2010** 4 1963-1970.
- [46] C.H. Chang, T.C. Huang, C.W. Peng, T.C. Yeh, H.I. Lu, W.I. Hung, C.J. Weng, T.I. Yang, J.M. Yeh, *Carbon*, **2012** 50 5044-5051.
- [47] G.C. Li, G.R. Li, S.H. Ye, X.P. Gao, *Adv. Energy Mater.*, **2012** 2 1238-1245.
- [48] C.J. Yan, L. Zou, R. Short, *Desalination*, **2012** 290 125-129.

Chapter 5

Nanoengineering of 2D Tin Sulfide Nanoflake Arrays Incorporated on Polyaniline Nanofibers with Boosted Capacitive Behavior

Nanoscale engineering plays an important role in designing novel electrode architecture and boosting energy storage in supercapacitors. Herein, we demonstrate the fabrication of freestanding tin sulfide-based supercapacitor electrode using facile nucleation substrate control, i.e. polyaniline network. This is the first time that tin sulfide-based material is fabricated as a binder-free electrode for supercapacitors. The first combination of tin sulfide and polyaniline also evokes synergistic effect to enhance the performance as the polyaniline nanofibers facilitate the growth of tin sulfide flakes in nanosize which is further proved helpful for improving the capacity and stability of the electrode. The significantly improved pseudocapacitive and diffusive contributions of polyaniline nanofibers incorporated electrode are identified by quantitative kinetics analysis due to greatly decreased particle size and introduced mesopores, nanoclusters, and exposed edges. Profited from effective nanostructure engineering, a Na^+ intercalation mechanism is also pointed out in boosting the electrochemical performance.

*This section published/submitted substantially as (H.H. Wang, D. L. Chao, J.L. Liu, J.Y. Lin, Z.X. Shen, *2D Materials*, **2018** 5 1-10).

5.1 Introduction

Supercapacitor has been playing a great role in portable devices and hybrid electric vehicles due to the high power density, fast charge process, long cycling life and high safety, which bridges the gap between batteries with sluggish kinetics and traditional capacitor with low capacitance.[1] However, the energy density of commercialized double layer capacitors is still limited. In order to settle this issue, electrode materials with pseudocapacitive behavior have been widely studied, which could be divided into two main types, metal oxide/hydroxide/chalcogenide based compounds and conducting polymers.[2]

Transition metal oxides (RuO_2 , MnO_2 , Co_3O_4 , NiO , Fe_2O_3 , Fe_3O_4 , and etc.), which have been comprehensively studied due to their high specific capacitance.[3-5] Nevertheless, metal chalcogenides, such as CoS nanowires,[6] NiS nanowalls,[7] and MoS_2 nanospheres,[8] possess better conductivity and stability than corresponding metal oxides/hydroxides and have been attracting researchers interests in the last few years. Tin sulfide with unique 2D layered metal chalcogenide structure, good conductivity and high redox reversibility exhibits high cycling stability, while its specific capacitance and especially rate capability still cannot fulfill its application in capacitive energy storage.[9] Strategies have been proposed to enhance the overall electrochemical performances. For one thing, doped tin sulfide composites have been investigated with improved capacitance. Among them, molybdenum (Mo) doped flower-like tin sulfide demonstrates superior performance compared with undoped one.[10, 11] The specific capacitance is improved from 89.4 F g^{-1} to 213.2 F g^{-1} due to the mesoporous structure and Mo-induced rich dislocations.[11] For another, combination of tin sulfide with other conductive materials is also proposed.[12-14] Flower-like tin sulfides decorated $\text{g-C}_3\text{N}_4$ sheets deliver a high specific capacitance around 210 F g^{-1} owing to its high surface area, unique 3D structure and nitrogen-rich skeleton.[12] Nevertheless, the potential range ($\sim 0.5 \text{ V}$) of these investigated composites is quite narrow and the rate capability remains poor, resulting in inferior energy density and power density.[11, 12, 15, 16] Moreover, the reported tin sulfide based electrode materials exist in powder form, with extra weight of

additives, polymer binders, and current collectors, which could further decrease the energy and power density of the whole devices. Therefore, we designed the self-supported tin sulfide-based electrode for flexible supercapacitor with improved electrochemical performances. Besides the material design, rare reports have revealed the redox reaction mechanisms on tin sulfide based supercapacitor electrodes.[11, 13] Chauhan, et. al. proposed that the Na^+ ions in the electrolyte may intercalate into and de-intercalate from the tin sulfides during the charge/discharge process.[13, 17] However, the storage mechanism of tin sulfide based aqueous supercapacitors remains unclear till now. As the energy storage mechanism is very important for the improvement of supercapacitor performances. Only a clear understanding on the hidden mechanism can help to fabricate an excellent supercapacitor device, including the design of material, the selection of electrolyte, and the full cell assembly. Hence, we further studied the ion intercalation feature of tin sulfide as supercapacitor electrode.

Here we report the fabrication of tin sulfide nanoflake arrays which were anchored on graphite foam-supported polyaniline nanofiber network ($\text{SnS}_2@\text{PANI@GF}$) as flexible supercapacitor electrode for the first time. Following the electrochemical deposition of polyaniline (PANI) nanofibers, the tin sulfide nanoflake arrays were incorporated on the PANi network by a hot-bath method. PANi as an attractive electrode material for supercapacitors,[18] acting not only as a conductive support, but also facilitating the growth of nano-sized tin sulfide. Verified by the kinetic studies, PANi supported SnS_2 nanoflake electrode exhibits superior pseudocapacitive and diffusion-controlled capacitance compared to micro-sized SnS_2 without PANi ($\text{SnS}_2@\text{GF}$). Simultaneously, the tin sulfide nanoflakes acting as a protective coating can prevent PANi from the structural change and electrochemical degradation, thus greatly enhancing the cycling stability. As proved by the *ex-situ* TEM studies, the significantly improved performance is related with the facilitated Na^+ diffusion and intercalation into tin sulfide nanoflakes. Therefore, the nanosized tin sulfides could evoke an enhanced Na^+ intercalation owing to successfully introduced mesopores and exposed edges by the nanoengineering approach. As a result, our $\text{SnS}_2@\text{PANI@GF}$ electrode exhibits the best rate capability (75% retention from 0.1 A g^{-1} to 10 A g^{-1}) and voltage tolerance (0.95V) among reported

tin sulfide supercapacitors. [10-12, 19, 20] The assembled asymmetric supercapacitor (ASC) with wide potential range of 1.5 V also exhibits good performance, with energy density (E) of 29.25 Wh kg⁻¹ and power density (P) of 0.75 kW kg⁻¹. To the best of our knowledge, this is the first report of ASC based on tin sulfide, demonstrating tin sulfide composites as promising electrode for full-cell application.

5.2 Synthesis and characterizations

5.2.1 Chemicals and instruments

The chemicals, Tin chloride (SnCl₄·5H₂O) (98%), Aniline (C₆H₅NH₂) (ACS reagent, ≥99.5%), Thioacetamide (C₂H₅NS) (ACS reagent, ≥99.0%) and poly(vinylidene fluoride) (PVDF) were purchased from SIGMA-ALDRICH and used as received. The hydrochloride acid (37%), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5 %) and ethanol, absolute (analytical reagent grade) involved in this work were bought from VWR CHEMICALS (PROLABO), Alfa Aesar and Fisher Chemical, respectively. The commercial carbon for negative electrode fabrication was purchased from Shanghai Lisheng Industry CO., LTD. Through the synthesis and electrode fabrication, deionized water (DIW, 18.2 MΩ) was employed for electrolyte and sample clean. A platinum plate (area 4 cm²) and a saturated calomel electrode (type, 217) purchased from Xuzhou Zhenghao Electronic Technology CO., LTD and Shanghai Leici Instrument Factory were used during the electrochemical deposition and tests.

5.2.2 Fabrication of SnS₂@PANi@GF composite electrode

The tin sulfide nanoflake arrays anchored on polyaniline nanofiber network were synthesized through a two-step method. Firstly, PANi was electrochemically deposited on graphite foam (GF) using a three-electrode system on the electrochemical workstation (CHI 760D). The GF fabricated by chemical vapor deposition was served as the working electrode,[21] while platinum plate and saturated calomel electrode were the counter and reference electrodes, respectively. 0.3 M double distilled aniline dispersed in 1.0 M HCl

was used as the deposition electrolyte. The PANi network was obtained after the potentiostatic deposition at 0.8 V for 5 mins. Secondly, the as-obtained PANi@GF and another piece of bare GF were immersed into a solution with 0.1 M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.3 M thioacetamide in 50 ml ethanol. Then, the hot-bath growth of tin sulfide was conducted at 80 °C for 30 mins. The as-obtained SnS_2 @PANi@GF and SnS_2 @GF electrodes were cleaned and dried thoroughly for further characterization and electrochemical test. The instruments for morphological, structural characterizations and electrochemical evaluations are illustrated in 3.1.

5.2.3 Morphological studies

As schematically illustrated in Figure 5.1, the PANi nanofibers were deposited on a pre-synthesized graphite foam (GF) by a potentiostatic process (Figures 5.1a to 5.1b) and the tin sulfide nanoflake arrays were grown on the PANi network via low temperature hot-bath (Figures 5.1b to 5.1c). The SEM image of GF substrate in Figures 1d and S1a clearly reveal the micro-sized porous structure which could facilitate the growth of PANi nanofibers through electrochemical deposition.[22] A compact nucleation layer was formed on the GF first. Then the vertical growth of PANi nanofibers (several μm in length, ~ 80 nm in diameter) resulted in the PANi network on GF (Figure 5.1e). The hot-bath deposition of SnS_2 involves the hydrolysis of the precursor (tin tetrachloride & thioacetamide), the replacement reaction of Cl^- by S^{2-} , and the self-assembly and oriented crystallization processes, forming interlaced nanoflakes.[9] The nanoscale size of PANi network (Figure 5.1e) leads to more nucleation sites and the formation of much smaller SnS_2 nanoflakes with more exposed edges and surfaces.[23] As shown in Figures 5.1f and 5.1g, the nanoflakes on PANi nanofibers exhibit a lateral size around 50 nm, while the size of SnS_2 flakes on PANi-free GF is around 1 μm . In Figure 5.1h, the color of the samples changes uniformly from silver gray (GF) to atrovirens (PANi@GF) and claybank (SnS_2 @PANi@GF), indicating the entire coverage and homogeneous distribution of PANi nanofibers and SnS_2 nanoflakes on the substrate. Figure 5.1i reveals the porous feature, robust flexibility and freestanding configuration (inset of Figure 5.1i) of SnS_2 anchored PANi network on GF.

Figure 5.1 Synthesis and morphology of the electrode materials. (a-c) Schematic illustration of the synthesis of SnS₂@PANI@GF. Schematic and typical SEM image of (a, d) GF, (b, e) PANi@GF and (c, f) SnS₂@PANI@GF. (g) FESEM image of micro-sized SnS₂@GF. (h) Representative photographs of (h1) the GF in black, (h2) PANi@GF in atrovirens, and (h3) SnS₂@PANI@GF in claybank. (i) Low magnification SEM of as obtained SnS₂@PANI@GF. Inset of (i): photograph showing flexibility of SnS₂@PANI@GF electrode.

The morphologies and detailed structures of tin sulfide-based electrode materials were further verified by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). As shown in Figure 5.2a, the PANi nanofibers are well wrapped by the SnS₂ nanoflakes with much smaller size compared with that of SnS₂@GF in Figure 5.2d, which is consistent with the SEM results. In particular, Van der Waals interaction along the [001] orientation assisted in the formation of the interlaced tin sulfide nanoflakes with a periodic stacking of fringes corresponding to the four layers of (001) plane (total

thickness of 2.4 nm), as shown in Figure 5.2b. The selected area electron diffraction (SAED) image in inset of Figure 5.2b further confirms the related crystallographic nature. As shown in Figure 5.2c, the clear lattice fringes with spacing of 0.32, 0.27 and 0.18 nm, correspond respectively to the (100), (101) and (-1-10) planes of hexagonal SnS_2 for $\text{SnS}_2@\text{PANi}$ network. For SnS_2 grown on GF, the thickness of microflakes is about 15 nm, corresponding to ~ 25 stacking layers (Figure 5.2e). [9, 24] In the aerial-view TEM image in Figure 2f, the SnS_2 microflakes are composed of large crystalline particles. By contrast, numerous nanoclusters and nanopores are observable in PANi supported SnS_2 nanoflakes (Figure 5.2c), which allow for larger surface area, shorter ion diffusion path, and more active sites in SnS_2 nanoflakes and contribute to superior energy storage, especially for high rate performance. Figure 5.2g depicts the energy-dispersive X-ray spectroscopy (EDS) elemental mapping of $\text{SnS}_2@\text{PANi}@GF$, revealing homogeneous distribution of N, C in PANi core and Sn, S in SnS_2 branches.

Figure 5.2 TEM and HRTEM images of $\text{SnS}_2@\text{GF}$ and $\text{SnS}_2@\text{PANi}@\text{GF}$. (a, d) TEM images of $\text{SnS}_2@\text{PANi}@\text{GF}$ and $\text{SnS}_2@\text{GF}$. Inset of (b): SAED pattern of SnS_2 . (b, e) HRTEM images displaying the lateral view and (c, f) the aerial view of tin sulfide nanoflakes and microflakes for $\text{SnS}_2@\text{PANi}@\text{GF}$ and $\text{SnS}_2@\text{GF}$, respectively. (g) EDX elemental mapping of Sn, S, N, and C of $\text{SnS}_2@\text{PANi}@\text{GF}$.

5.2.4 Structural analysis

The N_2 adsorption-desorption isotherms are obtained on ASAP Tri-star II 3020 and the specific surface area and pore size distribution are calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. Structural and phase information were obtained by X-Ray Diffraction (XRD) and Raman spectroscopy which were performed on Bruker D8 Advance XRD and Renishaw (laser wavelength: 532 nm), respectively.

Figure 5.3 Morphological and Structural characterization of SnS₂@GF and SnS₂@PANi@GF. (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of SnS₂@GF and SnS₂@PANi@GF. (c) The Raman spectra and (d) XRD patterns of SnS₂@GF and SnS₂@PANi@GF.

As shown in Figure 5.3a, both SnS₂@GF and SnS₂@PANi@GF illustrate a type IV isotherm, indicating mesoporous feature. The result is aligned with other tin sulfide based materials.[11, 13, 25, 26] Correspondingly, the pore size distribution of both samples calculated by BJH method in Figure 5.3b exhibits high intensity around 20 nm. Besides, SnS₂@PANi@GF contains micropores around 1.2 nm and mesopores around 4.6 nm compared with SnS₂@GF, which could be the reason of much higher BET specific surface area of SnS₂@PANi@GF (100.2 m² g⁻¹ versus 46.0 m² g⁻¹ for SnS₂@GF). Figure 5.3c compares the Raman spectra of SnS₂@GF and SnS₂@PANi@GF. For SnS₂@GF, a strong Raman peak located at 1581 cm⁻¹ represents the in-plane stretching motion of C-C bond in graphite foam.[27] Besides, an obvious peak around 313 cm⁻¹ and a weak shoulder around 230 cm⁻¹ are also observed, which are assigned to the A_{1g} mode and E_u mode of hexagonal SnS₂, respectively.[24, 28, 29] The A_{1g} mode for SnS₂@PANi@GF is much weaker compared with SnS₂@GF, which is a significant evidence for the decreased layer number of SnS₂ nanoflake.[30] The additional peaks at 1179, 1235, 1335, and 1398 cm⁻¹ are characteristic of PANi in the form of protonated emeraldine salt (PANi-ES), corresponding to the in plane C-H bending of quinoid, the vibration mode of C-N, the C-N⁺ vibration and the C-N⁺ stretching modes,[31, 32] the presence of which indicate good conductivity of as-obtained PANi nanofibers.

The phase structures of the SnS₂@GF and SnS₂@PANi@GF heterostructures were further examined by XRD patterns. As illustrated in Figure 5.3d, both samples display obvious diffraction peaks which support the assignment of hexagonal SnS₂ (JCPDS 23-0677) except for a distinct diffraction peak around 26°, which is assigned to the crystal plane of the graphite foam (JCPDS 75-1621).[11, 17, 24, 28] Significantly, the diffraction pattern of tin sulfide on bare GF exhibits sharper and higher peak intensity compared with tin sulfide grown on PANi networks. This reveals the higher degree of crystallinity

for SnS₂@GF, which is in contrast with the nanoporous and nanocluster feature of SnS₂@PANi@GF. The additional dislocations or defects induced from the nanoclusters, nanopores, and exposed edges in SnS₂@PANi@GF could act as new sites for ion adsorption and pseudo-redox reactions, which is envisioned that the as-obtained tin sulfide nanoflakes can exhibit higher specific capacitance and superior rate capability in comparison with the bare micro-sized SnS₂. [11]

5.3 Electrochemical results

The electrochemical performance of tin sulfide-based electrodes was characterized in a three-electrode system consisting of a working electrode (GF-based electrodes), a platinum plate counter electrode and a saturated calomel electrode reference electrode in 2 M Na₂SO₄ electrolyte. The cyclic voltammetry (CV) and galvanostatic charge-discharge were tested on a CHI760D Electrochemical workstation in the potential range from -0.2 to 0.75 V. The area of the electrode is ~4 cm². The areal mass of GF was ~0.8 mg cm⁻², and that of PANi, SnS₂ and PANi+SnS₂ were ~0.8, 1.1, and 2.4 mg cm⁻², respectively. The gravimetric specific capacitance C_g (unit of F g⁻¹) was calculated based on the active materials of PANi, SnS₂ and PANi+SnS₂ for PANi@GF, SnS₂@GF and SnS₂@PANi@GF, according to: $C_g = I_{\Delta t} / (m_{\Delta} V)$, where I (mA), Δt (s), m (mg), and ΔV (V) represent the discharge current, total discharge time, mass of electrode materials and potential range during discharge, respectively.

Figure 5.4 (a-d) Electrochemical performance of SnS₂@GF and SnS₂@PANI@GF. (a) Galvanostatic charge and discharge curves obtained at 0.1 A g⁻¹. (b) Cyclic Voltammetry curves at a scan rate of 10 mV s⁻¹. (c) Specific capacitances at different current density and (d) cycling stability tested at 1 A g⁻¹. (e) Galvanostatic charge-discharge curves of SnS₂@PANI@GF at various current density. (f) The comparison of rate capability for the preliminary studied tin sulfide-based electrodes for supercapacitors.

The electrochemical performance of SnS₂@PANi@GF and the control sample SnS₂@GF is evaluated in a three-electrode system in 2 M Na₂SO₄ electrolyte. As shown in Figure 5.4a, PANi supported SnS₂ nanoflake electrode delivers much higher electrochemical capacitance compared with the SnS₂ microflake electrode. At constant current 0.1 A g⁻¹, the specific capacitance of SnS₂@PANi@GF is 325 F g⁻¹, around 7 times that of SnS₂@GF (48 F g⁻¹). Similarly, at scan rate 10 mV s⁻¹, the specific capacitance of SnS₂@PANi@GF is 11 times that of SnS₂@GF (365 vs. 32 F g⁻¹). Broad redox peaks appearing at around 0.45 V/0.20 V in the CV curve of SnS₂@PANi@GF is due to a combination of redox reactions of PANi and the excited sequential reversible pseudocapacitance originated from tin sulfide nanoflakes,[33] which will be discussed in the following part.[11, 14, 33] As shown in Figure 5.4c, SnS₂@PANi@GF exhibits excellent rate performance. A specific capacitance of 244 F g⁻¹ was measured at 10 A g⁻¹, achieving 75% capacitance maintenance as compared to that tested at low current density of 0.1 A g⁻¹ (see Figures 5.4c, 5.4e). As clearly depicted in Figure 5.4f, our SnS₂@PANi@GF electrode shows superior rate performance when compared to the recent investigated tin sulfide based supercapacitor electrodes.[10-12, 14, 19] Long-term stability test was further conducted. As illustrated in Figure 5.4d, SnS₂@PANi@GF exhibits 73% capacitance retention after 5,000 cycles at 1 A g⁻¹, while PANi@GF network without SnS₂ protection tends to swell and agglomerate after around 650 cycles with some small grains emerging on the nanofibers due to the side products, such as p-benzoquinone and hydroquinone oligomers, [34] as shown in chapter 4.

5.4 Quantitative capacitive analysis and *ex* TEM studies

To better understand the greatly enhanced capacitance and the synergetic effect between the tin sulfide nanoflakes and PANi nanofibers, the kinetic analysis was conducted to distinguish contributions arising from two different mechanisms, i.e. the accesible surface related capacitance and the diffusion-controlled capacitance.[9, 35] The distinguished capacitances arising from surface-controlled and diffusion-controlled of RuO₂ were proposed as early as 1990, which were donoted as the contribution from less accessible inner surface and more accessible outer surface by S Trasatti.[36] The dependence of

current origin from capacitive and diffusive contributions is then elucidated according to $i(V) = k_1 v + k_2 v^{1/2}$, where i is the total current at certain potential (V), which could be divided into the capacitive effect ($k_1 v$) and diffusion-controlled process ($k_2 v^{1/2}$). By determining k_1 , k_2 using voltammetric scan rates (v), the current fractions from two different mechanisms could be obtained.[35] Based on the CV curves obtained from various scan rates (Figure A.4), the deconvoluting charge storage contributions of SnS₂@GF, PANi@GF and SnS₂@PANi@GF are calculated (Figures 5.5a, 5.5b, 5.5c).[37, 38]

Figure 5.5 Quantitative capacitive analysis of charge storage behavior. (a, b, c) Capacitive contribution (Shaded area) calculations of SnS₂@GF, PANi@GF and SnS₂@PANi@GF at 10 mV s⁻¹. (d) Capacitive and diffusive contributions of SnS₂@GF, PANi@GF, and SnS₂@PANi@GF, respectively.

It is clearly shown that the surface capacitive behavior of the nanoflakes SnS₂@PANi@GF is predominant (77%, 281 F g⁻¹, Figure 5.5c) among the total capacitance, which is distinguished from the micro-scaled SnS₂@GF (38%, 12 F g⁻¹).

Compared to both $\text{SnS}_2@\text{GF}$ and $\text{PANi}@\text{GF}$, $\text{SnS}_2@\text{PANi}@\text{GF}$ exhibits both improved diffusive and surface accessible capacitances (Figures 5.5d), suggesting a special synergistic effect between SnS_2 nanoflakes and PANi nanofibers. It is notable that $\text{PANi}@\text{GF}$ exhibits largest diffusive contribution among all electrodes, 91% of total capacitance, which is originating from the anion (SO_4^{2-}) and proton intercalating into PANi chain.[39] This is a surface controlled charge-transfer process. For tin sulfide nanoflakes in this work, the faradaic contributions arising from charge-transfer process at the surface are dominated the total capacitance. On the other hand, the diffusion controlled capacitance has also been greatly improved due to the decreasing of particle size to nanoscale, promoting the ion diffusion in the electrode. Therefore, $\text{SnS}_2@\text{PANi}@\text{GF}$ exhibits the best electrochemical performance, including Na^+ insertion involved diffusion-controlled capacitance and surface-controlled pseudo and double-layer capacitance.

Herein, PANi acts not only as a conductive network, which provides abundant nucleation sites and facilitates the growth of nanoscale SnS_2 flakes. The resulting SnS_2 nanoflakes contribute to high specific capacitance compared with microflakes due to the more exposed edges and the introduce of large amounts of mesopores. On the other hand, PANi itself can also hold electrolyte ions, contributing substantially to the total capacitance. Synergistically, the SnS_2 nanoflakes anchored on PANi can in turn prevent PANi networks from degrading especially in long-term cycles. The high specific surface area and high conductivity of nanoscaled SnS_2 are beneficial for the pseudocapacitive process on the PANi network beneath it. Thus nanosized tin sulfide with mesopores, nanoclusters, and exposed edges promotes the surface controlled energy storage, including the fast surface/subsurface charge-transfer and the double layer process of $\text{SnS}_2@\text{PANi}@\text{GF}$, resulting in high specific capacitance, good rate performance and long cycle life.[40, 41] Moreover, the enhancement in diffusion-controlled capacitance is also ascribed to the shortened diffusion distance for Na^+ insertion/desertion in the much smaller tin sulfide nanoflakes.

Figure 5.6 SAED patterns of SnS₂ nanoflakes at different states. (a) At initial stage, (b) after charge and (c) after discharge.

As illustrated in Figure 5.5d, both the capacitive pseudocapacitance and diffusion controlled capacitance improved in SnS₂@PANi@GF. In order to disclose the charge storage mechanism of tin sulfide electrode, we conducted the *ex-situ* TEM of the electrode materials at different states. SnS₂ keeps the original morphologies and phases after the charge and discharge processes from Figures 5.6a to 5.6c. Moreover, the d spacings between adjacent (100) and (101) lattice planes in hexagonal SnS₂ crystal lattice are enlarged after discharge, indicating an intercalation mechanism involved. As shown in Figure 5.6, the d spacing of the discharge SnS₂ exhibits a much larger d_{100} spacing, $3.34 \text{ \AA}$ compared with that of original one, $3.15 \text{ \AA}$, while the charged SnS₂ show similar value ($3.19 \text{ \AA}$) with the original one, indicating the reversible Na⁺ insertion and extraction between the lattice planes. Herein, the possible redox reactions involved in the system could be assigned as: $\text{SnS}_2 + x\text{Na}^+ + xe^- \leftrightarrow \text{Na}_x\text{SnS}_2$. When incorporating with PANi nanofibers, high capacitance is thus obtained owing to the facilitated electron transfer and Na⁺ ion transport during the charge and discharge process due to the dramatically reduced size, layers and more exposed edges.

5.5 Full cell assembly

In order to explore the performance of SnS₂@PANi@GF in a full cell, the asymmetric supercapacitor (ASC) was assembled with the as-obtained SnS₂@PANi@GF as the positive electrode, Black Pearls 2000 (BP2000) pasted onto graphite paper as the negative

electrode and 2 M Na₂SO₄ as the electrolyte. The negative electrode was fabricated by mixing 80 wt. % of Black Pearls 2000, 15 wt. % Super carbon and 5 wt. % PVDF in NMP and pasting onto the graphite paper (GP) using a blade. After throughout drying, the BP2000@GP with $\sim 3 \text{ mg cm}^{-2}$ active material is ready to use. The cyclic voltammetry (CV) and galvanostatic charge-discharge were tested in the potential range from -0.75 to 0.05 V vs SCE. As a result, the ASC SnS₂@PANi@GF//BP2000@GP works stable and well in a potential window of 0 - 1.5 V. The mass ratio of positive electrode and negative electrode is determined by $m_-/m_+ = (C_+ \times V_+)/ (C_- \times V_-)$. m_+ and m_- (g) are the active mass loading of each electrode. C_+ and C_- (F g⁻¹) are the specific capacitance of each electrode. V_+ and V_- (V) are the potential range during charge or discharge of each electrode. The mass ratio (m_-/m_+) was 2.1 for the assembled ASC. The specific capacitance (F g⁻¹), energy density (W h kg⁻¹) and power density (kW kg⁻¹) of the ASC are calculated following the equations: $C_{\text{cell}} = It/(M\Delta V)$, $E = C_{\text{cell}}\Delta V^2/2$ and $P = E/t$, where I (mA), t (s), M (mg), and ΔV (V) represent the discharge current, total discharge time, mass of both electrode materials and potential range during the full cell test, respectively.

Figure 5.7 (a) The Cyclic Voltammetry curves of SnS₂@PANi@GF and BP2000@GP at 10 mV s⁻¹. (b) The Cyclic Voltammetry curves of SnS₂@PANi@GF// BP2000@GP asymmetric supercapacitor at varied scan rates. (c) The galvanostatic charge discharge profiles of SnS₂@PANi@GF// BP2000@GP asymmetric supercapacitor at varied current density and (d) The long-term cycle stability test of SnS₂@PANi@GF// BP2000@GP ASC at 1 A g⁻¹. Inset of (d): the photograph of the full cell configuration.

An asymmetric supercapacitor (ASC) was fabricated in order to investigate the performance of SnS₂@PANi@GF in full cell. The commercial porous carbon Black Pearl 2000 (BP2000) and the as-obtained SnS₂@PANi@GF were employed as the negative electrode and positive electrode. As shown in Figure 5.7a, both the positive electrode SnS₂@PANi@GF (-0.2 ~ 0.75 V) and negative electrode BP2000@GP (-0.75 ~ 0.05 V) show wide potential range. As a result, the assembled cell works stably in a voltage range of 0 to 1.5 V, which ensures high energy density of the full cell according to $E = C_{\text{cell}}\Delta V^2/2$. The potential range is much larger compared to the tin sulfide and graphene hybrid nanosheets published recently, with ~0.5 V for the full-cell assembly.[14] The CV curves at different speed rates and the charge-discharge profiles at various current density of the assembled ASC are shown in Figure 5.7b and 5.7c. The rectangular shape of the ASC indicates highly reversible capacitive behavior and fast charge discharge process. The charge-discharge profiles in Figure S6b exhibit small IR drop, around 0.08 V, indicating good electronic properties of the assembled ASC. The specific capacitance (C_{cell}) of ASC is calculated as 93.6 F g⁻¹ at 1 A g⁻¹ based on the total mass of 8.9 mg, including the cathode and anode. And the corresponding energy density (E) and power density (P) are 29.25 Wh kg⁻¹ and 0.75 kW kg⁻¹, respectively. As shown in Figure 5.7d, the ASC can still deliver 72 F g⁻¹ after long-term cycling test, around 79% retention compared with the initial capacitance.

5.6 Conclusions

In summary, a self-supported electrode composed of tin sulfide nanoflake arrays incorporated on robust polyaniline network is fabricated, via a facile process, for the flexible supercapacitor application. The SnS₂@PANi@GF nanocomposites show high

specific capacitance (365 F g^{-1} at 10 mV s^{-1}) and long cycle life (73% retention after 5000 cycles), outperform two-component electrodes, microscaled SnS_2 @GF or SnS_2 -free PANi@GF. Notably, the SnS_2 @PANi@GF electrode delivers superior rate capability of 244 F g^{-1} even at 10 A g^{-1} , which is the best rate performance reported for SnS_x ($x=1, 2$)-based electrodes. The quantitative kinetic study reveals the synegetic effect between SnS_2 and PANi that conducting PANi network facilitates the growth of nanostructured SnS_2 while SnS_2 coating stabilizes PANi and boosts the capacitive behaviors. The nanoengineering of the architecture here promotes surface accessible and diffusion-controlled Na^+ ion intercalation, leading to greatly enhanced specific capacitance and high rate capability as compared to microscaled SnS_2 microflake electrode. The facile designed SnS_2 and PANi composites could also be used in other applications as both PANi and tin sulfides are good electrode materials for energy storage and conversion devices. The success of the combination may evoke numbers of investigations in this area. Furthermore, the use of neutral electrolyte in this system is encouraging which could simplify device manufacturing for further development of high performance capacitors.

References

- [1] M.R. Lukatskaya, B. Dunn, Y. Gogotsi, *Nat. Commun.*, **2016** 7 1-13.
- [2] A.S. Arico, P. Bruce, B. Scrosati, J.M. Tarascon, W. Van Schalkwijk, *Nat. Mater.*, **2005** 4 366-377.
- [3] Z.L. Ma, X.B. Huang, S. Dou, J.H. Wu, S.Y. Wang, *J. Phys. Chem. C*, **2014** 118 17231-17239.
- [4] J. Eskusson, P. Rauwel, J. Nerut, A. Janes, *J. Electrochem. Soc.*, **2016** 163 A2768-A2775.
- [5] M.J. Zhi, C.C. Xiang, J.T. Li, M. Li, N.Q. Wu, *Nanoscale*, **2013** 5 72-88.
- [6] S.J. Bao, C.M. Li, C.X. Guo, Y. Qiao, *J. Power Sources*, **2008** 180 676-681.
- [7] X.H. Xia, C.R. Zhu, J.S. Luo, Z.Y. Zeng, C. Guan, C.F. Ng, H. Zhang, H.J. Fan, *Small*, **2014** 10 766-773.
- [8] M.S. Javed, S.G. Dai, M.J. Wang, D.L. Guo, L. Chen, X. Wang, C.U. Hu, Y. Xi, *J. Power Sources*, **2015** 285 63-69.

- [9] D.L. Chao, C.R. Zhu, P.H. Yang, X.H. Xia, J.L. Liu, J. Wang, X.F. Fan, S.V. Savilov, J.Y. Lin, H.J. Fan, Z.X. Shen, *Nat. Commun.*, **2016** 7 1-8.
- [10] L.N. Wang, Y. Ma, M. Yang, Y.X. Qi, *RSC Adv.*, **2015** 5 89059-89065.
- [11] L. Ma, L.M. Xu, X.P. Zhou, X.Y. Xu, L.L. Zhang, *RSC Adv.*, **2015** 5 105862-105868.
- [12] S.A. Ansari, M.H. Cho, **2017** 1 510-519.
- [13] H. Chauhan, M.K. Singh, S.A. Hashmi, S. Deka, *RSC Adv.*, **2015** 5 17228-17235.
- [14] C.Y. Liu, S.L. Zhao, Y.N. Lu, Y.X. Chang, D.D. Xu, Q. Wang, Z.H. Dai, J.C. Bao, M. Han, *Small*, **2017** 13 1-9.
- [15] Y. Li, H.Q. Xie, J.F. Wang, *J. Solid State Electrochem.*, **2011** 15 1115-1119.
- [16] R.K. Mishra, G.W. Baek, K. Kim, H.-I. Kwon, S.H. Jin, *Appl. Surf. Sci.*, **2017** 425 923-931.
- [17] H. Chauhan, M.K. Singh, P. Kumar, S.A. Hashmi, S. Deka, *Nanotechnology*, **2017** 28 1-11.
- [18] G.A. Snook, P. Kao, A.S. Best, *J. Power Sources*, **2011** 196 1-12.
- [19] G. Hatui, G.C. Nayak, G. Udayabhanu, Y.K. Mishra, D.D. Pathak, *New J. Chem.*, **2017** 41 2702-2716.
- [20] X.H. Rui, H.T. Tan, Q.Y. Yan, *Nanoscale*, **2014** 6 9889-9924.
- [21] J.L. Liu, L.L. Zhang, H.B. Wu, J.Y. Lin, Z.X. Shen, X.W. Lou, *Energy Environ. Sci.*, **2014** 7 3709-3719.
- [22] H.H. Wang, J.L. Liu, Z. Chen, S. Chen, T.C. Sum, J.Y. Lin, Z.X. Shen, *Electrochim. Acta*, **2017** 230 236-244.
- [23] J.A. Gursky, S.D. Blough, C. Luna, C. Gomez, A.N. Luevano, E.A. Gardner, **2006** 128 8376-8377.
- [24] D.L. Chao, P. Liang, Z. Chen, L.Y. Bai, H. Shen, X.X. Liu, X.H. Xia, Y.L. Zhao, S.V. Savilov, J.Y. Lin, Z.X. Shen, *ACS Nano*, **2016** 10 10211-10219.
- [25] Z.C. Wu, Y.J. Xue, Y.L. Zhang, J.J. Li, T. Chen, *RSC Adv.*, **2015** 5 24640-24648.
- [26] A. Patil, A. Lokhande, P. Shinde, H. Shelke, C. Lokhande, *Int. J. Eng.*, 10 914-922.
- [27] X.N. Chen, F.C. Meng, Z.W. Zhou, X. Tian, L.M. Shan, S.B. Zhu, X.L. Xu, M. Jiang, L. Wang, D. Hui, Y. Wang, J. Lu, J.H. Gou, *Nanoscale*, **2014** 6 8140-8148.
- [28] B. Luo, Y. Fang, B. Wang, J.S. Zhou, H.H. Song, L.J. Zhi, *Energy Environ. Sci.*, **2012** 5 5226-5230.

- [29] J.F. Chao, Z. Xie, X.B. Duan, Y. Dong, Z.R. Wang, J. Xu, B. Liang, B. Shan, J.H. Ye, D. Chen, G.Z. Shen, *Crystengcomm*, **2012** 14 3163-3168.
- [30] Y.C. Liu, H.Y. Kang, L.F. Jiao, C.C. Chen, K.Z. Cao, Y.J. Wang, H.T. Yuan, *Nanoscale*, **2015** 7 1325-1332.
- [31] C.H.B. Silva, N.A. Galiote, F. Huguenin, E. Teixeira-Neto, V.R.L. Constantino, M.L.A. Temperini, *J. Mater. Chem.*, **2012** 22 14052-14060.
- [32] X. Peng, K.F. Huo, J.J. Fu, X.M. Zhang, B. Gao, P.K. Chu, *Chem. Commun.*, **2013** 49 10172-10174.
- [33] K. Zhang, L.L. Zhang, X.S. Zhao, J.S. Wu, *Chem. Mat.*, **2010** 22 1392-1401.
- [34] C.Q. Cui, L.H. Ong, T.C. Tan, J.Y. Lee, *Electrochim. Acta*, **1993** 38 1395-1404.
- [35] T. Brezesinski, J. Wang, S.H. Tolbert, B. Dunn, *Nat. Mater.*, **2010** 9 146-151.
- [36] S. Ardizzzone, G. Fregonara, S. Trasatti, *Electrochim. Acta*, **1990** 35 263-267.
- [37] J. Wang, J. Polleux, J. Lim, B. Dunn, *J. Phys. Chem. C*, **2007** 111 14925-14931.
- [38] J. Liu, J. Wang, C. Xu, H. Jiang, C. Li, L. Zhang, J. Lin, Z.X. Shen, *Adv. Sci.*, **2017** 1 1-19.
- [39] C. Peng, S. Zhang, D. Jewell, G.Z. Chen, **2008** 18 777-788.
- [40] C.R. Zhu, L. Yang, J.K. Seo, X. Zhang, S. Wang, J. Shin, D.L. Chao, H. Zhang, Y.S. Meng, H.J. Fan, *Mater. Horizons*, **2017** 4 415-422.
- [41] G.P. Wang, L. Zhang, J.J. Zhang, *Chem. Soc. Rev.*, **2012** 41 797-828.

Chapter 6

Passivation study on potassium storage mechanism in doped graphite foam

Other than supercapacitors with high power density, I also studied Potassium-ion batteries (KIBs) with high energy density, which is a promising alternative metal ion battery beyond lithium ion battery, in terms of high storage capacity of K^+ ions for traditional graphite anode. No matter for supercapacitors or batteries, the redox reactions are involved. The predominant difference for these two different popular devices is phase change during charge and discharge. For batteries, there is always phase change accompanied during energy storage. As a result, batteries usually exhibit inferior reversibility and cycling stability, especially for potassium ion batteries with large K^+ size. Herein, the dependency of battery coulombic efficiency and cycling stability on solid electrolyte interface (SEI) formation in two different electrolytes, KPF_6 and $KN(SO_2F)_2$ (KFSI)-based, were carefully studied to unravel the K^+ ion storage mechanism. Experimental results including depth-profiling XPS study, ex-situ TEM, SEM, and FTIR analysis, reveal that KFSI salt contributes to a thin, uniform and intact SEI layer with less unstable alkyl carbonates ($ROCO_2K$) compared to KPF_6 induced SEI layer. All these features, together, ensure good cycling stability and high reversibility in KFSI-based electrolyte.

6.1 Introduction

Lithium ion batteries (LIBs) with high energy density and long cycling life are playing an important role in commercial power supply. They have been widely used to power up the portable devices. Furthermore, they infiltrate into the transportation to supply pure or hybrid power to the electric vehicles like electric bicycles, motors, automobiles and trains.[1] However, the limited earth resource (0.0017 wt. %) and the uneven distribution of lithium make it an expensive metal so as with the high price of LIBs.[2] As the energy demand increases due to the economic prosperity, the scarce lithium could not afford a sustainable future.[3] Accordingly, the exploration of the alternatives is highly desirable. Sodium is attractive due to its large crust reserves (2.3 wt. %).[2] However, its storage in graphite is rather poor, with an electrochemical capacity of less than 35 mAh g⁻¹ via forming NaC₆₄. [4, 5] This signifies that the commercialized and mature graphite based technology for LIBs could not be transferred to the sodium ion batteries.[6, 7]

Interestingly, a specific capacity of 279 mAh g⁻¹ can be achieved for reversible K⁺ storage in graphite, via the formation of stage 1 K-intercalated graphite intercalation compounds (K-GICs).[8-12] This demonstrates the practical feasibility of graphite anode for KIBs. However, the development of KIBs is lagging probably due to the large atomic weight and large ionic radius (vs. Li⁺), which may lead to decreased gravimetric and volumetric energy. Nonetheless, recent study shows that the molar mass of potassium containing cathode is analogous to lithium containing cathode due to the slightly lower molar ratio of potassium in the cathode material, which indicates that the relatively large atomic weight of potassium is not a problem when evaluating the performance of whole batteries.[13] Besides, the much weaker Lewis acidity of K⁺ compared with other alkalis ions could result in faster transport and higher mobility of K⁺ due to smaller solvated ions, which are critical for rate capability.[9] Furthermore, K⁺/K redox couple delivers the lowest standard reduction potential (vs. SHE) in polyacetylene carbonate (PC) compared with Li⁺/Li and Na⁺/Na, ensuring high energy densities of KIBs.[9, 13, 14] All these features, together, make KIB a promising alternative of LIBs.

Graphite, a commercial anode material for LIBs has first been studied for KIB applications in 2015.[10, 11] A high specific capacity of 273 mAh g⁻¹ was obtained at C/10 (27.9 mAh g⁻¹) during the first depotassiation process.[10] In addition to graphite, other carbonaceous materials and metal based anodes have been studied and significant progresses have been made over the past few years.[15, 16] Among all the carbon based electrodes, heteroatom doping, especially for nitrogen doped carbon materials, exhibit superior electrochemical performance, including high specific capacity and excellent rate performance. However, the coulombic efficiency and cycling stability are still not satisfactory for practical applications. Analogy to LIBs and NIBs, an intact and stable solid electrolyte interface (SEI) is essential to the long-term performance and high coulombic efficiency of KIBs. The formation and growth of SEI in terms of chemical composition, morphology, thickness and stability are greatly dependent on the electrode structure/morphology, electrolyte constituents and electrochemical conditions, etc.[17-20] To date, intense research has been focused on the optimization of the micro/nanostructures of the carbon-based anodes or composites. However, the electrolyte effect on the formation and growth of SEI and the influence of SEI layer on electrochemical performance are poorly understood for KIBs. Therefore, we studied the electrolyte effect on solid electrolyte interphase in nitrogen doped carbon-based cells.

Herein, a comprehensive investigation of different potassium salts on the formation and/or growth of the SEI on binder free carbon-based anodes for KIBs has been conducted via a combination of spectroscopic and microscopic techniques. KPF₆ and KFSI in organic solvent are selected as the electrolytes for comparative studies. KPF₆ is the analog to typical electrolyte salt LiPF₆ in LIB while KFSI has been shown as the most appropriate conductive salt due to high solubility (as compared to KPF₆ and KClO₄ etc.).[21] The SEI features such as chemical composition, morphologies and thickness are well identified and correlated with electrolyte types. Experimental results including depth-profiling XPS study, *ex-situ* TEM, SEM, and FTIR analysis, reveal that KFSI salt contributing to a better SEI layer compared to KPF₆, in terms of i) a smooth and intact surface, ii) a homogenous distribution of segments across the SEI layer and iii) more stable species (organic esters/alkoxides/polycarbonates) and less soluble/unstable alky

carbonates (ROCO_2K). All these contribute to high coulombic efficiency and good cycling stability.

6.2 Synthesis and characterizations

6.2.1 Chemicals and instruments

Nickel foams (NFs) (Pore size, 0.1-10 mm) were bought from Shanghai Zhongwei New Material Co., Ltd. Chemicals including melamine ($\text{C}_3\text{H}_6\text{N}_6$) (ACS reagent, $\geq 99\%$), Iron (III) chloride (FeCl_3) (reagent grade, 97%) and reagents Ethylene carbonate (EC, 98%)/Diethyl carbonate (DEC, 99%), potassium hexafluorophosphate (KPF_6) ($\geq 99\%$, Sigma-Aldrich) were purchased from Sigma and used as received. The potassium bis(fluorosulfonyl)imides (KFSI) (Cica-Reagent) was bought from Kanto chemical CO., INC, Japan. The reagents hydrochloric acid (37%) and ethanol (analytic reagent grade) were purchased from VWR CHEMICALS (PROLABO) and Fisher Chemical. The deionized water (18.2 M Ω , DIW) was used for cleaning samples.

6.2.2 Fabrication of nitrogen doped graphene foam

Nitrogen doped graphene foam which was used as the self-supported electrode in this study was prepared via chemical vapor deposition as described in Section 3.1.1. The CVD set up is schematically shown in Figure 3.2. Nickel foams (NFs) with the areal size of $\sim 20\text{ cm}^2$ and thickness $\sim 1\text{ mm}$, which were pretreated in 5 wt.% hydrochloric acid for 3 hours to remove the oxide surface, were placed in the center of quartz tube as the template and catalyst for the fabrication of NGFs. A quartz container with $\sim 1.5\text{ g}$ melamine which was used as the sole source containing both N and C, was placed at the streaming side of the horizontal quartz tube. The NFs were first annealed to $1000\text{ }^\circ\text{C}$ in a 20 sccm N_2 with a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ and preserved for 20 mins. Thereafter, the as obtained NGF-NF was soaked in 0.5 M FeCl_3 solution to remove the NF skeletons and denoted as NGF-5.12.

6.2.3 Characterizations and tests

Besides the common morphological and structural characterizations summarized in 3.1, the *ex-situ* SEM/TEM images, FTIR spectra, XPS depth profiles of discharged electrodes are also acquired to examine the SEI layers. Discharged electrodes were rinsed with diethyl carbonate in glovebox prior to all analysis. And then, the resulting electrode materials were transferred into the holders in the glovebox with argon protection. The depth-profiling XPS was conducted with an Ar^+ ion gun (beam energy 1.5 eV, pressure 2×10^{-5} Torr) in the XPS chamber. Via etching by argon ion beam, the surfaces across SEI layer were examined layer by layer (etching time $t = 0$ min, 2mins, 7mins, 17mins, 40mins and 100mins). Calibration of the binding energy scale was set using the reference of C-C at 284.6 eV.

KIB half-cells with self-supported NGFs and K metal foil electrodes were assembled/sealed accordingly in a coin cell in a glovebox with Ar atmosphere. Whatman grade GF/D glass microfiber filter was used as the separator while 0.6 M $\text{KN}(\text{SO}_2\text{F})_2$ (KFSI) in EC/DEC (1:1 in volume) or 0.6 M KPF_6 in 1:1 EC/DEC (1:1 in volume) was the electrolyte. Cyclic voltammetry curves from 0.01 V to 1.5 V (vs K^+/K) and Nyquist plots in the frequency range of 100 kHz to 0.01Hz were performed on CHI760D Electrochemical workstation (CHENHUA, Shanghai, China). The galvanostatic rate and cycling tests were conducted on Neware Technology testing system in the voltage range of 0.01-1.0 V versus K^+/K .

6.3 The effect of different salts, KFSI and KPF_6 on electrochemical performance

The binder-free NGFs without any conductive additive were employed to study the SEI components for the sake of obtaining precise information to identify the role of electrolyte in SEI structure and function. The HRTEM, XRD, Raman and XPS are employed to characterize the as-obtained NGF. In Figure 6.1, TEM images and XRD pattern reveal that the as-obtained NGF has a graphitic structure, with lattice planes (002),

(101) and (100) are well identified. NGFs are the stacking of few-layer graphene along c axis direction. It consists about 20 layers of graphene. The D band around 1350 cm^{-1} in Raman spectroscopy indicates defective properties of as-obtained NGF, which is favorable for K ion storage.[22] The nitrogen doping content is $\sim 5.12\text{ at. \%}$ determined from XPS.

Figure 6.1 Characterizations of as-obtained NGF. (a) HRTEM image and corresponding fast Fourier transform (FFT) pattern. (b, c, d) XRD pattern, Raman spectra and XPS spectra of NGF-5.12.

The electrochemical properties of NGFs were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge tests. As shown in Figures 6.2 a-d, the CV curves obtained at 0.1 mV s^{-1} during the initial 10 cycles and the corresponding Nyquist plots are illustrated to study the difference of formed SEI in different electrolytes. Meanwhile, the galvanostatic charge-discharge tests are conducted to check the reversibility and cycling stability (Figures 6.2e-h). NGFs in both electrolytes show broad peaks during first potassiation (cathodic sweep). These broad peaks disappear in the subsequent 2-10 cycles, corresponding to the electrolyte

decomposition and irreversible SEI formation. There remains a broad cathodic peak from 0.4 to 0.02 V in the subsequent 2-10 cycles, which is assigned to the formation of potassium-intercalated graphite compounds (K-GICs) with various stages.[10] It is also noted that this peak in KFSI cell is stronger (Figure 6.2b) than that in KPF₆ cell (Figure 6.2a), which means that KFSI is more favorable for the complete K⁺ ion intercalation. The broad and overlapped anodic peaks from 0.3 V to 0.6 V indicate the high reversibility of K⁺ storage in NGF, which are ascribed to the corresponding depotassiation processes. For KFSI cell, the anodic peak around 0.5 V is clearly distinguishable, which may correspond to interstage transition within different K-GICs stages. This is probably due to the improved electronic/ionic conductivity of KFSI-based cell with respect to KPF₆-based cell. Little change is observed in Figure 6.2b between 2-10 cycles, exhibiting good stability for the KFSI cell.

The advantages of the KFSI cell over the KPF₆ cell is further identified from the galvanostatic charging/discharging profiles (Insets of Figure 6.2e, 6.2f). During the first potassiation of NGF electrodes to 0.01 V, the specific capacities reach up to 430.5 and 446.7 mAh g⁻¹ for KPF₆ and KFSI cells, corresponding to the sequent staging process.[10-12] In the following charge process, a clear platform appears around 0.25 V, corresponding to stable and continuous depotassiation of K ions. However, the charging capacity could be recovered to 180.4 and 217.0 mAh g⁻¹ for the KPF₆ and KFSI cell respectively, giving rise to the 1st columbic efficiency of 41% for KPF₆ and 49% for KFSI-based cells. Furthermore, the columbic efficiency in KFSI-based electrolyte is almost 100% since the subsequent cycles (Figure 6.1f), while that of KPF₆-based cell reaches to 100% after about 30 cycles (Figure 6.1e). The lower columbic efficiency of the KPF₆ electrode could be a consequence of much more severe electrolyte consumption in forming SEI. These reveal that an intact and stable SEI layer is formed during the first cycle for KFSI-based electrolyte, whereas continuous electrolyte decomposition occurs during the subsequent cycles in KPF₆-based electrolyte. The gradual thickening of the SEI layer further consumes K⁺ ions and salts, increase cell resistance, and degraded coulombic efficiency and cell performance.

Figure 6.2 Electrochemical evaluations of KPF₆ and KFSI-based cells. (a), (b) CV curves obtained at 1st, 2nd, 3rd, 5th and 10th cycle at 0.1 mV s⁻¹. (c), (d) Nyquist plots acquired after 1st, 2nd, 3rd, 5th and 10th cycle's test. Insets are atomic structures of two salts, KPF₆ and KFSI. (e), (f)

Coulombic efficiency during the first 30 cycles' test. Insets are the 1st charge-discharge profiles at 40 mAh g⁻¹, respectively. (g) Galvanostatic cycling test.

As exhibited in Figure 6.2c and Figure 6.2d, Nyquist plots of the two half cells with KPF₆ and KFSI based electrolytes were obtained during CV cycling tests, which are vital for electrochemical impedance analysis. Typically, all Nyquist plots include a depressed semicircle in high-frequency range, identified as a complex of interface resistance related with SEI layer and the charge transfer resistance, and a straight line at low-frequency, corresponding to Warburg solid state ion diffusion.[23] Based on equivalent circuit diagram in Figure 3.14b,[23, 24] the impedance parameters of Nyquist plots are fitted and shown in Table 6.1. When compare Figure 6.2c and Figure 6.2d, KPF₆-based battery exhibits higher impedance resistance and inferior diffusion during cycling tests compared to KFSI-based cell, verified by the much larger semicircle in high-frequency range and less vertical line in low-frequency range. Particularly, the interface resistance for KPF₆-based cell increases rapidly upon cycling, probably originating from the continuous degradation of electrolyte and formation of SEI layer. This is also in good line with both CV and galvanostatic testing results.[25] For KFSI-based cell, the interface resistance is small and quite stable since the first cycling process.

The cycling stability tests is shown in Figure 6.2g. After 100 cycles' test, the specific capacity retention is 84% (175.6 mAh g⁻¹ at 40 mA g⁻¹) for KFSI-based cell, which is much higher than that of KPF₆-based electrolyte (69%, 137.3 mAh g⁻¹ at 40 mA g⁻¹). Even after 200 cycles, a specific capacity of 166.0 mAh g⁻¹ can be delivered for NGF in KFSI-based electrolyte, with 81% of the initial capacity. The distinct difference of the cycling stability and coulombic efficiency in two different electrolytes could be well explained by the SEI formation during the first passivation process as the initial quality of SEI layer can greatly affect the electrochemical performance.[26] To verify the hypothesis, depth-profiling XPS, ex-situ FTIR analysis in combination with HRTEM and SEM characterizations were carried out to study the SEI layer chemistry and constituents in KPF₆ and KFSI-based electrolytes.

Table 6.1 Influence of electrolyte on impedance parameters at different test conditions.

Cells	Test condition	Impedance parameters			
		R_s (ESR) (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)	Z_w -P
KPF ₆ -based cell	After 1 st cycle	9.6	115.8	789.6	0.72
	After 2 nd cycle	7.8	201.4	878	0.64
	After 3 rd cycle	7.8	215.4	932	0.61
	After 5 th cycle	8.0	298.9	997	0.61
	After 10 th cycle	7.2	443	1130	0.61
KFSI-based cell	After 1 st cycle	6.3	26.6	1070	0.84
	After 2 nd cycle	5.2	32.5	760.4	0.79
	After 3 rd cycle	5.0	29.6	880.9	0.85
	After 5 th cycle	4.8	42.7	855.8	0.81
	After 10 th cycle	5.0	55.9	830.2	0.77

* ESR: Equivalent series resistance; R_{SEI} : Interface resistance; R_{ct} : Charge transfer resistance; Z_w : Warburg impedance.

6.4 Morphological and structural studies of SEI layer

The morphology and structure of the electrodes were studied by SEM, TEM and FTIR. The SEM images of as-obtained NGF-5.12 are shown in Figure A5 as the reference to compare the morphological changes after the charging/discharging cycles. Figure 6.3a displays the morphology of the KPF₆-induced SEI layer on cycled NGF-5.12 surface, which is quite rough and ruptured. The smooth and intact surface feature of NGF is well preserved of KFSI-based cell electrodes, as compared with the as-obtained NGF image in Figure A5a. This indicates an integrated and smooth KFSI-induced SEI layer is completely formed even during the first discharge (Figure A5c), while dozens of cycles are required for the synthesis of intact KPF₆-induced electrolyte, agreeing with electrochemical characterizations. This is further supported by TEM images (Figures 6.3c & 6.3d), in which the KFSI-induced SEI layer is uniform with a thickness of about 20 nm, whereas the KPF₆-induced SEI layer is interlaced with different thickness ranging from

10 to 60 nm. The lattice fringe of NGF in KPF₆ cell is not obvious and the interface of SEI and NGF is not so clear compared to KFSI cell, probably due to the large thickness of KPF₆-induced SEI on the electrode surface. It is known from LIBs that the cathodic reduction reactions between the graphitic anode and organic electrolyte happen in potential range of 0.8 - 0.2 V in the first charge/discharge cycle, resulting in multicomponent SEI layer. Below 0.2 V, the intercalation of Li⁺ in graphite is promoted and the Li-intercalated graphite intercalation compounds (Li-GICs) formed above 0 V.[20] In the case of K, the situation is similar as shown in the CV curves and charge-discharge profiles (Figures 6.2a, 6.2b).[10] However, the decomposition of electrolytes will continue if the SEI layer is not fully developed above 0.2 V, when the solvent and K⁺ co-intercalation would take place and result in large volume expansion.[20] In addition, the SEI layer may break due to the huge volume change, and regenerate every cycle, as happened in KPF₆ case. This explains why the surface morphologies of NGF change so much via continuous charge/discharge in KPF₆-based electrolytes. All these may account for the poor cycling stability and low coulombic efficiency in KPF₆-based cell .[27] The corresponding Energy-Dispersive X-ray Spectrometry (EDS) mappings of two cycled electrodes are illustrated in Figure A6. The elements C, N, O, F, K, P (or S) are uniformly distributed on NGF anode surface after cycling in both electrolytes. Interestingly, KFSI-induced SEI is rich in F and S, and the KPF₆-induced SEI is rich in F and P. This indicates the inorganic segments, like fluorides and sulfites or phosphates are generated in the KFSI-induced and KPF₆ -induced SEI layers. Moreover, all the elements are uniformly distributed, revealing the homogenous feature of SEI layers.[28]

Figure 6.3 *Ex-situ* SEM and TEM images of NGF-5.12 anodes in (a, c) KPF₆-based and (b, d) KFSI-based electrolytes after 20th discharge to 0.01 V. Insets of (a), (b) are the corresponding low magnification images. (e) FTIR spectra of NGF-5.12 anodes after discharge in above two electrolytes.

More details about the SEI chemical components can be discerned from FTIR spectra. In Figure 6.3e, the transmittance peaks at 2949, 1659, 1387, 1300, 1078 and 835 cm⁻¹ in both electrolytes are attributed to the stretching mode of C-H (ν C-H), the asymmetric stretching of C=O (ν_{as} C=O), the bending of -CH₂ (δ -CH₂), the symmetric stretching of C=O (ν_s C=O), the stretching of C-O (ν C-O) and the bending of -OCO₂ (δ -OCO₂), respectively.[29] They originate from the alkyl carbonates ROCO₂K ((CH₂OCO₂K)₂, C₂H₅OCOOK) in the SEI layer, which are reduction products of ethylene carbonate (EC) and diethyl carbonate (DEC).[30-33] Notably, the peak around 835 cm⁻¹ assigned to the bending mode of -OCO₂, is much stronger in KPF₆-induced SEI layer than that in KFSI-induced SEI. Similar trend is also identified for KPF₆-induced SEI layer with stronger symmetric and asymmetric stretching modes of C=O around 1300 and 1659 cm⁻¹. These imply more ROCO₂K in KPF₆-induced SEI layer due to the severe reduction reactions of solvents (EC&DEC) during the first 20 cycling test. This consists well with the SEM and

electrochemical results and corroborates the hypothesis that the KPF_6 -induced SEI is not completely developed in the first discharge process (Figure A5), and continuous electrolyte consumption and irreversible feature (Figure 6.1e) are identified during initial dozens of cycling test. Generally, the segmental ROCO_2K is quite unstable, and easily decomposes into RCH_2OK and K_2CO_3 upon electrochemical cycling. This feature results in poor protection of anode from electrolyte attack and giving rise to the inferior stability for KPF_6 containing cells.[30-32] The stronger peaks at 1190 and 1387 cm^{-1} for KFSI-induced SEI (Figure 6.3e) is probably originating from the O-S-O symmetric/asymmetric stretching modes in KFSI and the decomposition products, like KFSO_2 , KNSO_2 . [34, 35] The relatively weak band at 1176 cm^{-1} for KPF_6 -induced SEI is attributed to the stretching mode of $\text{P}=\text{O}$ in K_xPOF_y species from the degradation of KPF_6 . [36] As there are some remaining electrolytes on the surface, a pair of peaks at 1778 and 1808 cm^{-1} is identified for both SEI layer. It is assigned to the stretching modes of $\text{C}=\text{O}$ in the solvents (EC&DEC). [36, 37]

6.5 XPS depth-profiling studies

The XPS depth profiling method is an effective way to examine spatial distribution of elements and chemical states, particularly suitable for evaluating the SEI layer in a qualitative and semi-quantitative manner. Here we employ it to monitor the component evolution across the SEI film formed in KPF_6 and KFSI based electrolytes besides the outmost surface detection. The $\text{C}1\text{s}$ spectra of KPF_6 -based NGF anode (Figure 6.4a) display a broad peak around 285 eV assigned to many possible carbon contributions. Four components can be distinguished based on detailed analysis, C-C (284.6 eV), C-O (~285.8 eV), $\text{C}=\text{O}$ (~287.5 eV) and $\text{poly}(\text{CO}_3)$ (~291 eV). [33] The C-C bonding originates from the graphitic anode materials and C-O/ $\text{C}=\text{O}$ are attributed to the oxygen containing inorganic and organic species, like ether oxygen ($\text{R-O-R}'$), alkoxides (RCH_2OK), alkyl carbonates (ROCO_2K) and K_2CO_3 . The notable peak around 290.5 eV at the outermost surface is assigned to the polycarbonates, denoted as $\text{poly}(\text{CO}_3)$. [31, 33, 38] This indicates the polymerization of solvent molecules or alkyl carbonates, resulting in $\text{poly}(\text{EC/DEC})$ or $\text{poly}(\text{alkyl carbonate})$ during the SEI formation. [38] The outermost

surface ($t = 0$ min) of tested electrode has a low C-C ratio of 9.6% for KPF₆-based SEI. As expected, upon Ar⁺ ion sputtering (from $t=0$ min to $t=100$ mins), the C-C peak increases in intensity, indicating the continuous stripping of the SEI layer. The gradual change of signal intensity reveals that the SEI film formed in KPF₆ is quite thick.[39, 40]

Figure 6.4 Depth-profiling XPS spectra of SEI layer in KPF₆ and KFSI-based electrolytes. (a) C1s, (b) O1s for KPF₆-based and (c) C1s, (d) O1s for KFSI-based) at different time of Ar⁺ bombardment of discharged electrodes. The outmost surface of SEI is $t = 0$ min.

Different trends have been identified in KFSI-induced SEI (Figure 6.4c). For instance, the C-C peak (284.6 eV) is hard to be detected (4.2%) at the outmost surface of SEI ($t=0$

min), indicating the formation of a compact SEI layer. It appears after 2 mins' Ar^+ bombardment and does not change much in intensity with sputtering time increasing. This indicates that i) the NGF electrode is almost exposed after 2 min-sputtering, and ii) the KFSI-induced SEI layer is thin[41]. This agree quite well with SEM, TEM and FTIR results and again, corroborating the thin and uniform features of KFSI-induced SEI layer. Furthermore, although oxygen containing organic and inorganic products (285–291 eV) are found, their amounts are much less than that in KPF_6 -induced SEI, indicating the less degradation of KFSI-based electrolyte. All these contribute to the higher initial Coulombic efficiency (ICE) and better cycling stability of KFSI-based cell compared with KPF_6 -based cell.

In order to quantify the ratio difference of oxygen containing species, the O1s spectra are fitted and analysis in detail. The O1s spectra for KPF_6 (Figure 6.4b) and KFSI (Figure 6.4d) containing SEI layers could be fitted into three sub-peaks, C-O, C=O and the C~O in poly(CO_3), originating from the decomposition products of EC and DEC. The C-O (~533.5 eV) might be traced to the ether oxygen (R-O-R')/alkoxides (RCH_2OK) and the carbonyl C=O (~531.5 eV) could be attributed to the alkyl carbonates (i.e., $(\text{CH}_2\text{OCO}_2\text{K})_2$, $\text{C}_2\text{H}_5\text{OCO}_2\text{K}$). [33, 42, 43] The peak around 534 eV is assigned to polycarbonates (poly(CO_3)) polymerized from the solvents and alkyl carbonates. The poly(CO_3) is beneficial for high mechanical and electrochemical stability of SEI layer. i) Mechanically, it could act as a polymer binder holding each component in the SEI layer together; ii) Electrochemically, it could well protect the electrode from attacking by the electrolyte without scarifying the fast ion diffusion.[33, 41] For KPF_6 -based cell, the portion percentage of C-O at the outermost surface ($t=0$ min) in KPF_6 -induced SEI is 34.8% (Table A.1), which is smaller than that of C=O (43.4%), implying that C=O containing instable alkyl carbonates (ROCO_2K) dominate the SEI surface.

Furthermore, the portion of C-O keeps lower compared to C=O, as evidenced by their peak intensity evolution upon Ar^+ sputtering, indicating ROCO_2K as the main component across the SEI layer. As mentioned above, ROCO_2K is generally unstable, which could decompose into RCH_2OCK and K_2CO_3 during electrochemical cycling test.[44] Thus the

substantial amounts of ROCO_2K across the whole KPF_6 -induced SEI layer may lead to inferior cycling stability. In contrast, the portion ratio of C-O is mainly higher than C=O from the outer to inner surfaces (t=0 to t=100 mins) for KFSI-induced SEI as illustrated in Table A.1, indicating small portion of instable ROCO_2K . Meanwhile, the polymerized $\text{poly}(\text{CO}_3)$ exhibits an increasing trend from the inner to outer layers in both electrolytes, resulting in high atomic ratio of 21.8% for KPF_6 -induced SEI and 45.5% for KFSI-induced SEI at the outer most surface. More importantly, the $\text{poly}(\text{CO}_3)$ is larger in portion across the whole KFSI-induced SEI than that in to KPF_6 -induced SEI. As mentioned above, the $\text{poly}(\text{CO}_3)$ could be beneficial for high mechanical and electrochemical stability. Therefore, the higher portion of $\text{poly}(\text{CO}_3)$ and the lower portion of ROCO_2K , together contribute to high stability of SEI layer, as well as the cycling stability of whole system.

Figure 6.5 Depth-profiling XPS spectra of (a) F1s, (b) P2p for KPF_6 -based and (c) F1s, (d) S2p for KFSI-based electrolytes at different time of Ar^+ bombardment of discharged electrodes.

To further evaluate the SEI composition, the salt-related spectra for F 1s, P2p, and S 2p are shown in Figure 6.5. In F 1s spectrum of the KPF_6 induced SEI (Figure 6.5a), a clear peak corresponding to the salt anion $-\text{PF}_6$ at 688.1 eV can be observed at the outmost surface ($t=0$ min). This is supported by the appearance of a strong peak at ~138 eV in P2p spectrum, which is traced from KPF_6 -salt Figure 6.5b). The coverage of salts also makes the oxygen-containing decomposition products (~134 eV), like K_xPOF_y , difficult to be identified. After 2-min Ar^+ bombardment, two distinct peaks at 684.5 eV and 688.5 eV appear, indicating large amounts of KF and P-F containing species (like K_xPF_y , K_xPOF_y)

in the SEI layer. The peak intensity of KF, K_xPF_y and K_xPOF_y in F1s and P2p spectra decreases gradually with the Ar^+ bombardment, clearly suggesting the continuous SEI exfoliation.[39, 45] The case in KFSI induced SEI layer is quite different. As shown in Figure 6.5c, two peaks at 684.5 eV and 688.3 eV are separated in F1s spectra, corresponding to KF and S-F bonding originates from the decomposition products of KFSI (like $KFSO_2$, $KNSO_2$), respectively.[46] Additionally, three components can be distinguished from the S2p spectra (Figure 6.5d): K_2SO_3 (166.9 eV, 20.2%), KSO_2F (168.3 eV, 37.5%), and $KNSO_2$ (169.4 eV, 42.3%).[47] The sulfites are believed to be more active than oxygen containing species and they could easily accept electrons from the solvents, like EC, DEC, thus preventing the co-intercalation of solvents and K^+ into graphite. As a result, the structural changes and volume expansion of the anode are alleviated, which are beneficial to the electrochemical performances when coated on graphitic anodes.[48]

6.6 Conclusions

Summarizing the findings on the SEI layers, both KPF_6 -induced and KFSI-induced SEI are mainly composed of oxygen containing organic species, including alkyl carbonates ($ROCO_2K$)/alkoxides, (RCH_2OCK) /ethers, $(R-O-R')$ /poly(CO_3) and inorganic segments like KF and K_2CO_3 . However, the KFSI induced SEI layer contributes to better coulombic efficiency and cycling stability in terms of i) Morphologically, a thin, smooth and intact SEI surface was obtained upon the first discharge process; ii) Structurally, the produced SEI layer exhibits uniform distribution of different elements and species; iii) Less instable alkyl carbonates ($ROCO_2K$) and larger amounts of stable poly(CO_3) are present across the whole KFSI-induced SEI layer. Our results may evoke numbers of investigations in this area for more clear understanding in KIB system.

References

- [1] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.*, **2011** 4 3243-3262.
- [2] J.C. Pramudita, D. Sehrawat, D. Goonetilleke, N. Sharma, **2017**.

- [3] T.C. Wanger, *Conserv. Lett.*, **2011** 4 202-206.
- [4] R. Asher, S. Wilson, **1958** 181 409-410.
- [5] Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cumings, C. Wang, **2014** 5 4033.
- [6] S.W. Kim, D.H. Seo, X. Ma, G. Ceder, K. Kang, **2012** 2 710-721.
- [7] P. Ge, M. Fouletier, **1988** 28 1172-1175.
- [8] Y. Mizutani, T. Abe, K. Ikeda, E. Ihara, M. Asano, T. Harada, M. Inaba, Z. Ogumi, *Carbon*, **1997** 35 61-65.
- [9] S. Komaba, T. Hasegawa, M. Dahbi, K. Kubota, *Electrochem. Commun.*, **2015** 60 172-175.
- [10] Z.L. Jian, W. Luo, X.L. Ji, *J. Am. Chem. Soc.*, **2015** 137 11566-11569.
- [11] W. Luo, J.Y. Wan, B. Ozdemir, W.Z. Bao, Y.N. Chen, J.Q. Dai, H. Lin, Y. Xu, F. Gu, V. Barone, L.B. Hu, *Nano Lett.*, **2015** 15 7671-7677.
- [12] K. Share, A.P. Cohn, R.E. Carter, C.L. Pint, *Nanoscale*, **2016** 8 16435-16439.
- [13] A. Eftekhari, Z.L. Jian, X.L. Ji, *ACS Appl. Mater. Interfaces*, **2017** 9 4404-4419.
- [14] Y.N. Chen, W. Luo, M. Carter, L.H. Zhou, J.Q. Dai, K. Fu, S. Lacey, T. Li, J.Y. Wan, X.G. Han, Y.P. Bao, L.B. Hu, *Nano Energy*, **2015** 18 205-211.
- [15] I. Sultana, M.M. Rahman, Y. Chen, A.M. Glushenkov, *Adv. Funct. Mater.*, **2018** 28 18.
- [16] H. Kim, J.C. Kim, M. Bianchini, D.H. Seo, J. Rodriguez-Garcia, G. Ceder, *Adv. Energy Mater.*, **2018** 8 19.
- [17] S.H. Lee, H.G. You, K.S. Han, J. Kim, I.H. Jung, J.H. Song, *J. Power Sources*, **2014** 247 307-313.
- [18] M.Y. Nie, B.L. Lucht, *J. Electrochem. Soc.*, **2015** 162 X1-X1.
- [19] J.M. Zheng, J.A. Lochala, A. Kwok, Z.Q.D. Deng, J. Xiao, *Adv. Sci.*, **2017** 4 19.
- [20] S.J. An, J.L. Li, C. Daniel, D. Mohanty, S. Nagpure, D.L. Wood, *Carbon*, **2016** 105 52-76.
- [21] C. Vaalma, G.A. Giffin, D. Buchholz, S. Passerini, *J. Electrochem. Soc.*, **2016** 163 A1295-A1299.
- [22] Y.H. Xie, Y. Chen, L. Liu, P. Tao, M.P. Fan, N. Xu, X.W. Shen, C.L. Yan, *Adv. Mater.*, **2017** 29 9.

- [23] J.C. Guo, A. Sun, X.L. Chen, C.S. Wang, A. Manivannan, *Electrochim. Acta*, **2011** 56 3981-3987.
- [24] Z.C. Ju, S. Zhang, Z. Xing, Q.C. Zhuang, Y.H. Qiang, Y.T. Qian, *ACS Appl. Mater. Interfaces*, **2016** 8 20682-20690.
- [25] M. Gaberscek, J. Moskon, B. Erjavec, R. Dominko, J. Jamnik, *Electrochem. Solid State Lett.*, **2008** 11 A170-A174.
- [26] X.B. Cheng, R. Zhang, C.Z. Zhao, F. Wei, J.G. Zhang, Q. Zhang, *Adv. Sci.*, **2016** 3 20.
- [27] E. Peled, S. Menkin, *J. Electrochem. Soc.*, **2017** 164 A1703-A1719.
- [28] P. Verma, P. Maire, P. Novak, *Electrochim. Acta*, **2010** 55 6332-6341.
- [29] H. Ota, Y. Sakata, A. Inoue, S. Yamaguchi, *J. Electrochem. Soc.*, **2004** 151 A1659-A1669.
- [30] J.Z. Li, H. Li, Z.X. Wang, L.Q. Chen, X.J. Huang, *J. Power Sources*, **2002** 107 1-4.
- [31] H. Ota, Y. Sakata, X.M. Wang, J. Sasahara, E. Yasukawa, *J. Electrochem. Soc.*, **2004** 151 A437-A446.
- [32] A. Naji, J. Ghanbaja, P. Willmann, B. Humbert, D. Billaud, *J. Power Sources*, **1996** 62 141-143.
- [33] J.M. Zheng, M.H. Engelhard, D.H. Mei, S.H. Jiao, B.J. Polzin, J.G. Zhang, W. Xu, *Nat. Energy*, **2017** 2 8.
- [34] J.H. Huang, A.F. Hollenkamp, *J. Phys. Chem. C*, **2010** 114 21840-21847.
- [35] L.J. Hardwick, J.A. Saint, I.T. Lucas, M.M. Doeff, R. Kostecki, *J. Electrochem. Soc.*, **2009** 156 A120-A127.
- [36] D. Ostrovskii, F. Ronci, B. Scrosati, P. Jacobsson, *J. Power Sources*, **2001** 94 183-188.
- [37] H.L. Pan, X. Lu, X.Q. Yu, Y.S. Hu, H. Li, X.Q. Yang, L.Q. Chen, *Adv. Energy Mater.*, **2013** 3 1186-1194.
- [38] J.M. Zheng, P.F. Yan, D.H. Mei, M.H. Engelhard, S.S. Cartmell, B.J. Polzin, C.M. Wang, J.G. Zhang, W. Xu, *Adv. Energy Mater.*, **2016** 6 10.
- [39] D. Ensling, M. Stjerndahl, A. Nyten, T. Gustafsson, J.O. Thomas, *J. Mater. Chem.*, **2009** 19 82-88.

- [40] D. Liu, W.W. Lei, D. Portehault, S. Qina, Y. Chen, *J. Mater. Chem. A*, **2015** 3 1682-1687.
- [41] G.G. Eshetu, T. Diemant, S. Grugeon, R.J. Behm, S. Laruelle, M. Armand, S. Passerini, *ACS Appl. Mater. Interfaces*, **2016** 8 16087-16100.
- [42] M. Onuki, S. Kinoshita, Y. Sakata, M. Yanagidate, Y. Otake, M. Ue, M. Deguchi, *J. Electrochem. Soc.*, **2008** 155 A794-A797.
- [43] D. Aurbach, *J. Power Sources*, **2000** 89 206-218.
- [44] D. Aurbach, B. Markovsky, A. Shechter, Y. EinEli, H. Cohen, *J. Electrochem. Soc.*, **1996** 143 3809-3820.
- [45] M.A. Munoz-Marquez, M. Zarrabeitia, E. Castillo-Martinez, A. Eguia-Barrio, T. Rojo, M. Casas-Cabanas, *ACS Appl. Mater. Interfaces*, **2015** 7 7801-7808.
- [46] H. Kim, F.X. Wu, J.T. Lee, N. Nitta, H.T. Lin, M. Oschatz, W.I. Cho, S. Kaskel, O. Borodin, G. Yushin, *Adv. Energy Mater.*, **2015** 5 8.
- [47] S. Zhang, W.J. Li, S.G. Ling, H. Li, Z.B. Zhou, L.Q. Chen, *Chin. Phys. B*, **2015** 24 8.
- [48] R.J. Chen, F. Wu, L. Li, Y.B. Guan, X.P. Qiu, S. Chen, Y.J. Li, S.X. Wu, *J. Power Sources*, **2007** 172 395-403.

Chapter 7

Nitrogen doping induced holey active sites for potassium storage

Based on the optimized electrolyte, the nitrogen doping effect on K ion storage was also explored, which includes: i) the induced holey active sites for accommodating large amounts of K^+ , ii) the enlarged interlayer spacing for facilitated K^+ intercalation and iii) the improved electronic conductivity for fast kinetics. The high nitrogen doping level (8.47 at. %), the enlarged interlayer spacing (0.346 nm), the improved pore volume ($0.212 \text{ cm}^3 \text{ g}^{-1}$) and enhanced electronic properties together lead to the highest specific capacity, best cycling stability and rate performances of NGF-8.47 compared to NGF-1.03 and NGF-2.22. Particularly, the high pyridinic/pyrrolic nitrogen doping ratio, 89% out of the total doping for NGF-8.47, could create holey structures via high doping intensities, which contributes to large amounts of K^+ adsorption. This indicates that the electrochemical performance is dependent on both nitrogen concentrations and configurations. Our investigations promote better understanding of K^+ ion storage mechanism in doped graphite and provide invaluable guidance for optimized carbon-based electrode design for high-performance potassium ion batteries.

7.1 Introduction

In last chapter, different electrolyte induced solid electrolyte interphases are investigated and the SEI layers are found to play great role in the electrochemical performance, especially for reversibility and cycling stability. In addition to electrolyte, the electrode material modifications are also very important. The much larger radius of K^+ (1.38 Å) compared to Li^+ (0.76 Å) makes it difficult for K^+ intercalation.[1]. Moreover, the intercalation/de-intercalation of K^+ could cause large volume change (61% for graphite) and structural distortion/collapse. This will induce the loss of active sites and poor reversibility/stability upon long cycling.[2] To overcome these limitations of carbon based KIBs, i.e., low capacity, inferior cycling stability and poor coulombic efficiency, the structural and morphological modifications of electrode materials, including the tuning of interlayer spacing,[3] specific surface area[1] and the creation of new active sites for K^+ storage,[4] are highly desired.

A variety of carbonaceous based anode materials have been investigated for KIBs since 2010s. They are roughly divided into modified graphite,[5, 6] biomass derived carbon materials,[7-9] versatile designed carbon nanostructures[3, 10-12] and heteroatom (N, O, S, F) doped carbon materials.[13-18] The well-designed, modified or doped carbon materials usually have improved surface area or enriched active sites for K^+ storage and enhanced electronic conductivity, resulting in large specific capacity and good rate capability for KIBs. The modified graphite, like expanded graphite[6] and activated carbon,[19] exhibit enlarged interlayer distance in (002) crystal planes, contributing to high reversibility and long cycling life. Besides modified graphite, the short-range ordered mesoporous carbon with large interlayer spacing and unique structure has been also proved to be beneficial to high rate capability and good cycling stability. The volume expansion was reduced to 7% via K^+ intercalation, indicating the effective enhancement of electrochemical performance by enlarging the interlayer space.[3] Large surface area of carbon based electrode materials, like hierarchical porous hard carbon,[16] is favorable for high specific capacity due to the massive surface defects introduced for K^+ storage.

The heteroatom doping is another promising strategy to improve K^+ storage. Specifically, nitrogen-doping is of particular interest benefiting from the following merits: i) the doping N could enlarge the interlayer space of carbon materials, thus facilitating the intercalation/de-intercalation of K ions.[14] ii) The introduction of structural defects and disorders upon N-doping may alleviate the volume expansion to a certain extent, ensuring long cycling life.[13-15, 20] And iii) the conductivity could be greatly enhanced, beneficial for good rate performances.[21] The *in-situ* Raman spectra have been used to study the K^+ storage mechanism in nitrogen doped graphene. It was concluded that the nitrogen doping not only promotes the fully K^+ intercalation process, but also introduce more active sites for efficient K^+ storage, boosting the specific capacity significantly.[13],[16] Meanwhile, the enlarged interlayer spacing via doping is also beneficial for K^+ intercalation, contributing to improve capacity and stability.[22] To the best of our knowledge, there is no comprehensive study on the effects of doping concentration and configurations on K^+ storage. Besides, it is generally considered that the remarkable enhancement in capacity of N-doped carbonaceous materials is owing to large amounts of K^+ adsorption on N doped sites. However, there is no solid evidence to support it.

Here the self-supported graphene foam with different nitrogen concentrations and configurations have been prepared. It is found that the percentage of PD and PL nitrogen increase with the increasing of nitrogen content. This provides more holey structures with more active sites for efficient K^+ storage. For instance, at a nitrogen doping level of 8.47 at. % (NGF-8.47), the PD and PL, together reaches 89 % in total doping, with a large total pore volume of $0.212 \text{ cm}^3 \text{ g}^{-1}$, which is much higher than that of NGF-1.03 and NGF-2.22 (0.085 and $0.118 \text{ cm}^3 \text{ g}^{-1}$, respectively). The increased pore volume originates from large amounts of mesopores (around 10.9 and 14.6 nm), which could accommodate more K ions and facilitate contact between electrolyte and electrode. Meanwhile, the interlayer spacing is also enlarged to 0.346 nm, favorable for reversible K^+ intercalation. The improved pore volume and interlayer distance according to large N doping intensities, together contribute to a high specific capacity (247 mAh g^{-1} at 10 mA g^{-1}) and good cycling stability (86% capacity retention after 200 cycles' test). The large amounts N

doping also ensures considerable enhancement in conductivity, beneficial for superior rate performances.

7.2 Experimental

As illustrated in chapter 6.2. nitrogen doped foams (NGF-1.03, NGF-2.22 and NGF-8.47) with nitrogen doping concentration of 1.03 at. %, 2.22 at. % and 8.47 at. % respectively were synthesized via CVD using melamine as sole C/N source, as shown in Figure 3.2. They are employed to study the nitrogen doping effect. The electrochemical tests were conducted with the half cells consisting of self-supported NGF electrode, K foil and potassium bis(fluorosulfonyl)imides (KFSI) (Cica-Reagent) based electrolyte.

7.3 Morphological and structural studies

The low magnitude SEM images in Figure 7.1 (a-c) reveal that the branch structure of NGFs is well preserved in NGFs after the NF etching. In the high-resolution SEM images (Figure 7.1d-f), rough and rugged surfaces are observed, which could be favorable for electrolyte accommodation. As typically shown in Figure 7.1g, the Energy-Dispersive X-ray Spectrometry (EDS) mapping illustrates a uniform distribution of C, N and O, indicating homogenous incorporation of nitrogen in carbon matrix. Further investigations on the morphologies and structures were performed by HRTEM and selective area electron diffraction (SAED) patterns. As shown in Figures 7.2a, 7.2b and 7.2c, the high-resolution transmission electron microscopy (HRTEM) images of NGFs with different nitrogen doping concentrations reveal the highly graphitic structure. All NGFs are the stacking of dozens layer graphene along crystal plane (002) with a thickness around 10 nm. This few-layer structure is quite promising for K ion intercalation.[13, 18] All NGFs exhibit expanded interlayer distance compared to graphite (0.335 nm),[23] owing to the nitrogen doping effect. Specifically, the interlayer spacing is enlarged at high N doping level, with an interlayer spacing of 0.346 nm for NGF-8.47 (Figure 7.2c), which is larger than both NGF-1.03 (0.340 nm, Figure 7.2a) and NGF-2.22 (0.342 nm, Figure 7.2b). NGF-8.47 exhibits a curved and open lattice structure compared to NGF-1.03 and NGF-

2.22, thus creating abundant edges.[15] The XRD pattern in Figure 7.2d exhibits a sharp peak around $26.05^{\circ} \pm 0.1^{\circ}$, which is identified as (002) plane in graphitic structure (JCPDS 75-1621). In the inset of the figure, NGF-8.47 exhibits a largest interlayer spacing compared to NGF-1.03 and NGF-2.22, which is in agreement with the TEM study.

Figure 7.1 SEM images of (a, d) NGF-1.03, (b, e) NGF-2.22 and (c, f) NGF-8.47. (g) The EDX mapping of NGF-8.47.

Figure 7.2 Morphological and structural characterizations of NGFs. HRTEM images of (a) NGF-1.03, (b) NGF-2.22 and (c) NGF-8.47. Inset of (a, b, c): The corresponding FFT patterns. (d) XRD patterns and (e) Raman spectra of NGF-1.03, NGF-2.22 and NGF-8.47. Inset of (f): XRD spectra centered at the characteristic peak of (002) crystal plane. (g) Nitrogen adsorption and desorption isotherms and (h) pore size distribution of NGF-1.03, NGF-2.22 and NGF-8.47.

The Raman spectra of NGFs in Figure 7.2e exhibit two distinct peaks, D band (1350 cm^{-1}) and G band (1580 cm^{-1}).^[24] The intensity ratios of D band to G band (I_D/I_G) are calculated to be 0.83, 1.25 and 1.41 for NGF-1.03, NGF-2.22 and NGF-8.47,

respectively.[25, 26] The high intensity of D band indicates highly defective structures, arising from nitrogen doping, which is favorable for K^+ storage.[14, 25-30] To further examine the surface porosity originating from defective structures, the nitrogen adsorption-desorption isotherms were conducted. As shown in Figure 7.2g, all NGFs exhibit a type IV isotherm, revealing high mesoporosity.[31] The specific surface area of NGF-1.03, NGF-2.22 and NGF-8.47 were calculated by Brunauer-Emmett-Teller (BET) method to be 16.1, 22.6 and 45.6 $m^2 g^{-1}$, with corresponding total pore volume 0.085, 0.118 and 0.212 $cm^3 g^{-1}$, respectively. The pore size distribution curves in Figure 7.2h indicates that NGFs have a large portion of mesopores around 10.9 and 14.6 nm. It is clearly observed that NGF-8.47 contains more mesopores, i.e., 10.9 nm, compared to NGF-1.03 and NGF-2.22. The mesoporous structure could promote the K^+ mobility, in favor to the K^+ access to active sites during charge and discharge process,[9] Additionally it could accommodate the structural changes via K^+ intercalation and de-intercalation and enhance the cycling stability.[12]

Figure 7.3 High-resolution XPS test of NGFs. N1s spectra (a) NGF-1.03, (b) NGF-2.22 and (c)

NGF-8.47, respectively. (d) The schematic illustration of PD, PL and graphitic nitrogen contents in different NGFs. Inset of (d) Three typical nitrogen doping types, Graphitic, Pyrrolic and Pyridinic nitrogen doping (grey atom: carbon; blue atom: nitrogen; hydrogen atoms are not shown).

The nitrogen doping concentrations and configurations of NGFs were determined by XPS analysis, as illustrated in Figure 7.3. The N1s can be fitted into three sub-peaks, assigned to PD (~398.8 eV), PL (~400.2 eV) and graphitic nitrogen (~401.9 eV) respectively.[32, 33] As schematically illustrated in the histograms (Figure 7.3d), the ratio of three bonding configurations (PD, PL and Graphitic N) in whole electrode materials are elucidated based on the XPS results. The PD/PL nitrogen doping increases rapidly with the increasing of total nitrogen doping from 0.72 at. % to 7.54 at. %, while graphitic nitrogen increases much slower (0.31 at. % to 0.94 at. %), indicating that large doping intensity favors for PD/PL doping as well. The PD and PL nitrogen (7.54 at. % in NGF-8.47) are believed to be more effective to improve the reversible capacity by creating large intensities of holey structures and active sites for K ion storage.[4, 13, 34] Meanwhile, graphitic nitrogen located at the center and bonded with three sp³ carbon atoms could effectively enhance the conductivity of the graphitic carbon matrix as the electron-donor characteristic could be change significantly via this graphitic N doping.[16] Thereinto, NGF-8.47 with the highest graphitic N doping should confirm best electronic properties among all NGFs. The narrow scan C1s spectra in Figures 7.4a-c further demonstrate that nitrogen, as well as oxygen are doped in carbon matrix with bonding identifications around 285.3 eV (C-N), 286.2 eV (C-OH), 287.1 eV (C=O) and 288.7 eV (COOH).[16] It is clearly shown that the C-N portion increases with increasing nitrogen doping concentration. It is 30.7 % in C1s for NGF-8.47, and 22.7 %, 24.0 % for NGF-1.03, NGF-2.22, respectively. Figure 7.4d-f illustrate the O1s spectra of NGF-1.03, NGF-2.22 and NGF-8.47, respectively. All NGFs have highest amounts of hydroxyl groups (C-OH) and carboxy oxygen (C=O), which could improve the wetting of graphitic carbons in electrolytes, resulting in better contact of electrode and electrolyte.[35] The surface species concentrations of different elements and bonding types are summarized in Tables A.2-A.5.

Figure 7.4 High resolution XPS spectra, C1s and O1s for (a, d) NGF-1.03, (b, e) NGF-2.22 and (c, f) NGF-8.47, respectively.

7.4 Electrochemical tests

The electrochemical performances are illustrated in Figure 7.5. The CV curves in Figure 7.5a show a broad peak cathodic peak for all three NGF samples, starting around 0.70 V vs K/K⁺ during the first potassiation, which corresponds to the electrolyte decomposition and irreversible SEI formation. Cathodic peaks from 0.5 to 0.02 V are assigned to the formation of K-GICs with different stages.[36] During depotassiation, the broad and overlapped anodic peak around 0.43 V indicates high reversibility of the NGF electrode, which are ascribed to the corresponding deintercalation processes of K ions from graphite. There is an additional peak around 0.49 V for NGF-8.47, assigning to the K⁺ storage in nitrogen induced active sites.[13] However, the peak around 0.49 V is not obvious for NGF-1.03 and NGF-2.22, with a faint shoulder instead, as exhibited in Figure 7.5b.

Figure 7.5 Electrochemical test of NGF-1.03, NGF-2.22 and NGF-8.47. (a) cyclic voltammetry at 0.1 mV s⁻¹. (CV) curves, (b) selected range CV curves, (c) 1st discharge, (d) 1st charge and 2nd

discharge of the galvanostatic profiles. (e) Rate performance evaluations, (f) cycling stability test at 40 mA g⁻¹ and (g) Nyquist plots after 10 cycles' test of NGFs. (h) The corresponding equivalent circuit diagram and pictorial model of the affiliated impedance elements, the fitted results are exhibited in Table A.6.

The charge/discharge profiles of the NGF-cells are displayed in Figures 7.5c, 7.5d. The three NGF electrodes store almost the same amount of K⁺ ions during the first discharging (potasiation) process. However, the 1st charge capacities vary a lot, giving rise to the increase of ICE from 40%, 49% to 59%, with increasing N doping level. Reversible specific capacities of 201.6, 212.3 and 231.4 mAh g⁻¹ are obtained in the following charging (de-potasiation) process for NGF-1.03, NGF-2.22 and NGF-8.47, respectively. The highest value of NGF-8.47 is owing to increased nitrogen induced holey active sites. K ion starts to insert into NGF around 0.3 V (Figure 7.5c), accompanied by the formation of stage 3 K-GIC. Upon continuous intercalation below 0.2 V, a stage 2 K-GIC could be formed. The stage 1 K-GIC (KC₈) could be formed when the battery is fully discharged to 0.01 V.[37] During charge, K⁺ extracts from graphite and KC₈ converts back to graphite, with a main platform around 0.25 V as shown in Figure 7.5d. Compared to NGF-1.03 and NGF-2.22, NGF-8.47 exhibits more sloping charge-discharge curves (Figure 7.5d). This could be explained by the XRD and Raman results that NGF-8.47 has the lowest degree of graphitization and highest disordered/defective structures,[38, 39] which are account for best cycling stability and highest reversibility. In particular, the K⁺ desertion platform around 0.25 V (1st platform) is shortened and a longer sloping platform from 0.40 (2nd platform) arises during charging process.

Rate performance and cycling stability are further evaluated. The rate capability test results in Figure 7.5e show that the specific capacity of low N-doping samples decays rapidly to 36 and 87 mAh g⁻¹ whereas it remains relatively high at 112 mAh g⁻¹ for NGF-8.47 at discharging rate of 200 mA g⁻¹ that with increasing the charge/discharge rate from 10 to 200 mA g⁻¹. This is ascribed to the enhancement of porosity, active site and conductivity with increased nitrogen contents and fast kinetics of K ion transportation in

stable solid electrolyte interface and the electrode material.[40] Cycling stability test data of all NGFs are illustrated in Figure 7.5f, where NGF-1.03, NGF-2.22 and NGF-8.47 exhibit 76%, 80% and 86% retention of initial capacity after 200 cycles at 40 mA g^{-1} , respectively. Obviously, the cycling stability of NGFs increases with nitrogen increasing, which could be well explained by the reduced volume change and the increased chemical stability via nitrogen doping.[20]

In order to understand the underlying principles of improved performance, Nyquist plots are displayed in Figure 7.5g. All of the Nyquist plots contain a depressed semicircle (high/medium frequency range) and a sloping line (low frequency range), which present the resistance of contact/charge transfer and ion diffusion impedance, respectively.[41] Here, R_s , R_{SEI} , R_{ct} and Z_W in Figure 7.5h represent of the intrinsic ohmic resistance related with electrode, electrolyte and separator, the interphase contact resistance, the charge transfer resistance and ion diffusion impedance in electrode materials.[18, 42] It is obvious NGF-8.47 has the lowest charge transfer resistance (826.7, 466.4 and 393.1Ω for NGF-1.03, NGF-2.22 and NGF-8.47), indicating fast intercalation kinetics. [18] Besides, the most vertical line of NGF-8.47 in low frequency indicates good capacitive behavior with fast diffusion of K^+ in electrode materials. Meanwhile, the similar interphase resistances (34.9 , 26.6 and 28.5Ω for NGF-1.03, NGF-2.22 and NGF-8.47) reveal well formed SEI layer in all batteries, which is in agreement with CV curves and electrochemical impedance tests (Figure 7.5 and Figure 7.6). All these results verify the significant effect of high intensity nitrogen doping on conductivity improvement.

Figure 7.6 *In-situ* kinetic diagnosis during charge and discharge. (a) A typical potential vs time profile collected during EIS test. Nyquist plots of (b-d) NGF-1.03, (e-g) NGF-2.22 and (h-j) NGF-8.47 at different states of charge (SOCs).

In Figure 7.6, we focus on the high/medium frequency range to diagnosis the kinetics during potassiation and de-potassiation of all NGF anodes during first 2 cycles.[42] Figures 7.6b-j illustrates Nyquist plots acquired at different states (SOCs) of charge as indicated in Figure 7.6a. The semicircles in high/medium frequency are prolonged and the Nyquist plots are flattened in low frequency at 0.6 V during first discharge for all NGFs, which could be endowed by the formation of SEI at this voltage, resulting in

restricted K^+ ion diffusion and charge transfer.[43] As evidenced in second discharge process in Figures. 7.6d, 7.6g and 7.6j, there is no sharp variation at 0.6 V and the changing of resistance is progressive, which is indicative of successful SEI formation during first discharge. Moreover, all batteries exhibit lower resistance during 2nd discharge compared to 1st discharge process. This may originate from the electrode active process.[44]

As we can observe from the Nyquist plots in Figures. 7.6c, 7.6f and 7.6i, NGF-1.03 and NGF-2.22 exhibit high contact/charge transfer resistances from 0.1 V to 0.3 V during discharge, while for NGF-8.47, the semicircle becomes much smaller since charged to 0.3 V. This is coincident with charge profiles in Figure 7.5d, K^+ fully de-intercalates from NGF-8.47 before charged to 0.3 V. The 2nd platform originates from K^+ desertion from nitrogen induced holey structures, which is much more notable for NGF-8.47 compared to NGF-1.03 and NGF-2.22 owing to high doping intensity. Besides, a more sloping curve from 0.52 V to 1.0 V during charge and the corresponding sloping discharge curve for NGF-8.47 further indicate a capacitive behavior and fast kinetics.[16, 22] Meanwhile, as the charge transfer resistance is greatly dependent on the amounts of K^+ intercalated, all batteries have a large semicircle at the fully discharged state (0.01 V) during 2nd discharging (Figures. 7.6d, 7.6g, 7.6j).[44]

7.5 Conclusions

In conclusion, the reversible capacity, the rate performance and cycling stability of NGF as KIB electrodes could be improved with the nitrogen doping content increasing, owing to i) the induced holey active sites and increased pore volume for K ion storage, ii) the improved electronic conductivity and iii) the favorable structural change (enlarged interlayer spacing~ 0.346 Å). Particularly, the presence of nitrogen atoms in the carbon matrix, especially the pyridine-like and pyrrole-like nitrogen dopants at the edge sites, could induce holey active sites for K ion storage on every graphene layers without interrupting the formation of K-GIC, resulting in higher capacity for high intensity nitrogen doped anodes. Moreover, the volume changes due to the K^+ intercalation is well

accommodated due to the favorable structural change by high intensity nitrogen doping. When the nitrogen doping concentration increases to 8.47 at. % (PD/PL nitrogen takes 89% out of all nitrogen content), a high initial coulombic efficiency (59%), a reversible capacity of 247 mAh g⁻¹ and a superior cycling stability (89% retention after 200 cycles) are obtained.

References

- [1] M. Chen, W. Wang, X. Liang, S. Gong, J. Liu, Q. Wang, S. Guo, H. Yang, **2018** 1800171.
- [2] Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cumings, C. Wang, **2014** 5 4033.
- [3] W. Wang, J.H. Zhou, Z.P. Wang, L.Y. Zhao, P.H. Li, Y. Yang, C. Yang, H.X. Huang, S.J. Guo, *Adv. Energy Mater.*, **2018** 8 8.
- [4] Y.H. Xie, Y. Chen, L. Liu, P. Tao, M.P. Fan, N. Xu, X.W. Shen, C.L. Yan, *Adv. Mater.*, **2017** 29 9.
- [5] Z. Tai, Q. Zhang, Y. Liu, H. Liu, S. Dou, **2017** 123 54-61.
- [6] Y.L. An, H.F. Fei, G.F. Zeng, L.J. Ci, B.J. Xi, S.L. Xiong, J.K. Feng, *J. Power Sources*, **2018** 378 66-72.
- [7] S.J.R. Prabakar, S.C. Han, C. Park, I.A. Bhairuba, M.J. Reece, K.S. Sohn, M. Pyo, *J. Electrochem. Soc.*, **2017** 164 A2012-A2016.
- [8] Z. Tai, Y. Liu, Q. Zhang, T. Zhou, Z. Guo, H.K. Liu, S.X. Dou, **2017** 2 278-284.
- [9] Y. Li, R.A. Adams, A. Arora, V.G. Pol, A.M. Levine, R.J. Lee, K. Akato, A.K. Naskar, M.P. Paranthaman, **2017** 164 A1234-A1238.
- [10] Z.L. Jian, S. Hwang, Z.F. Li, A.S. Hernandez, X.F. Wang, Z.Y. Xing, D. Su, X.L. Ji, *Adv. Funct. Mater.*, **2017** 27 6.
- [11] D.S. Bin, Z.X. Chi, Y.T. Li, K. Zhang, X.Z. Yang, Y.G. Sun, J.Y. Piao, A.M. Cao, L.J. Wan, *J. Am. Chem. Soc.*, **2017** 139 13492-13498.
- [12] X.X. Zhao, P.X. Xiong, J.F. Meng, Y.Q. Liang, J.W. Wang, Y.H. Xu, *J. Mater. Chem. A*, **2017** 5 19237-19244.
- [13] K. Share, A.P. Cohn, R. Carter, B. Rogers, C.L. Pint, *ACS Nano*, **2016** 10 9738-9744.
- [14] Y. Xie, Y. Chen, L. Liu, P. Tao, M. Fan, N. Xu, X. Shen, C. Yan, **2017**.

- [15] P.X. Xiong, X.X. Zhao, Y.H. Xu, *ChemSusChem*, **2018** 11 202-208.
- [16] J.L. Yang, Z.C. Ju, Y. Jiang, Z. Xing, B.J. Xi, J.K. Feng, S.L. Xiong, *Adv. Mater.*, **2018** 30 11.
- [17] M. Chen, W. Wang, X. Liang, S. Gong, J. Liu, Q. Wang, S. Guo, H. Yang, **2018**.
- [18] Z.C. Ju, S. Zhang, Z. Xing, Q.C. Zhuang, Y.H. Qiang, Y.T. Qian, *ACS Appl. Mater. Interfaces*, **2016** 8 20682-20690.
- [19] Z.X. Tai, Q. Zhang, Y.J. Liu, H.K. Liu, S.X. Dou, *Carbon*, **2017** 123 54-61.
- [20] X.Y. Wu, D.P. Leonard, X.L. Ji, *Chem. Mat.*, **2017** 29 5031-5042.
- [21] X. Zhao, Y. Tang, C. Ni, J. Wang, A. Star, Y. Xu, **2018** 1 1703-1707.
- [22] R.A. Adams, J.M. Syu, Y.P. Zhao, C.T. Lo, A. Varma, V.G. Pol, *ACS Appl. Mater. Interfaces*, **2017** 9 17872-17881.
- [23] Z.Q. Li, C.J. Lu, Z.P. Xia, Y. Zhou, Z. Luo, *Carbon*, **2007** 45 1686-1695.
- [24] Z.H. Sheng, L. Shao, J.J. Chen, W.J. Bao, F.B. Wang, X.H. Xia, *ACS Nano*, **2011** 5 4350-4358.
- [25] D. Yan, C.Y. Yu, X.J. Zhang, W. Qin, T. Lu, B.W. Hu, H.L. Li, L.K. Pan, *Electrochim. Acta*, **2016** 191 385-391.
- [26] C.H. Jiang, J.X. Wang, Z.H. Chen, Z.Y. Yu, Z.Y. Lin, Z.M. Zou, *Electrochim. Acta*, **2017** 245 271-278.
- [27] Z. Luo, J. Zhou, X. Cao, S. Liu, Y. Cai, L. Wang, A. Pana, S. Liang, **2017**.
- [28] C. Qian, P. Guo, X. Zhang, R.F. Zhao, Q.H. Wu, L. Huan, X. Shen, M. Chen, *RSC Adv.*, **2016** 6 93519-93524.
- [29] F.C. Zheng, Y. Yang, Q.W. Chen, *Nat. Commun.*, **2014** 5 10.
- [30] J.N. Gu, Z.G. Du, C. Zhang, S.B. Yang, *Adv. Energy Mater.*, **2016** 6 7.
- [31] X.S. Zhao, G.Q. Lu, *J. Phys. Chem. B*, **1998** 102 1556-1561.
- [32] D. Liu, W.W. Lei, D. Portehault, S. Qina, Y. Chen, *J. Mater. Chem. A*, **2015** 3 1682-1687.
- [33] B.P. Vinayan, N.I. Schwarzburger, M. Fichtner, *J. Mater. Chem. A*, **2015** 3 6810-6818.
- [34] X. Liu, D. Chao, Q. Zhang, H. Liu, H. Hu, J. Zhao, Y. Li, Y. Huang, J. Lin, Z.X. Shen, **2015** 5 15665.

- [35] C.Q. Yuan, X.H. Liu, M.Y. Jia, Z.X. Luo, J.N. Yao, *J. Mater. Chem. A*, **2015** 3 3409-3415.
- [36] W. Luo, J.Y. Wan, B. Ozdemir, W.Z. Bao, Y.N. Chen, J.Q. Dai, H. Lin, Y. Xu, F. Gu, V. Barone, L.B. Hu, *Nano Lett.*, **2015** 15 7671-7677.
- [37] Z.L. Jian, W. Luo, X.L. Ji, *J. Am. Chem. Soc.*, **2015** 137 11566-11569.
- [38] A.D. Roberts, X. Li, H.F. Zhang, *Chem. Soc. Rev.*, **2014** 43 4341-4356.
- [39] D.L. Chao, C.R. Zhu, P.H. Yang, X.H. Xia, J.L. Liu, J. Wang, X.F. Fan, S.V. Savilov, J.Y. Lin, H.J. Fan, Z.X. Shen, *Nat. Commun.*, **2016** 7 8.
- [40] F.A. Soto, P.F. Yan, M.H. Engelhard, A. Marzouk, C.M. Wang, G.L. Xu, Z.H. Chen, K. Amine, J. Liu, V.L. Sprenkle, F. El-Mellouhi, P.B. Balbuena, X.L. Li, *Adv. Mater.*, **2017** 29 10.
- [41] J. Zhao, X.X. Zou, Y.J. Zhu, Y.H. Xu, C.S. Wang, *Adv. Funct. Mater.*, **2016** 26 8103-8110.
- [42] J.C. Guo, A. Sun, X.L. Chen, C.S. Wang, A. Manivannan, *Electrochim. Acta*, **2011** 56 3981-3987.
- [43] M. Holzapfel, A. Martinet, F. Alloin, B. Le Gorrec, R. Yazami, C. Montella, *J. Electroanal. Chem.*, **2003** 546 41-50.
- [44] Y.C. Chang, H.J. Sohn, *J. Electrochem. Soc.*, **2000** 147 50-58.

Chapter 8

Conclusions and recommendations for future works

In this chapter, the results of all works are briefly summarized. Besides, explanations on how the methods and solutions meet up with the initial motivation and obstacles are included. Other than the conclusions of completed works, future explorations on carbon-based potassium ion batteries are involved. Several undressed issues on potassium ion batteries are discussed.

8.1 Conclusion

In this dissertation, investigations on energy storage devices with high power density, supercapacitors and high energy density, batteries are involved. Supercapacitors and batteries each have advantages and disadvantages to meet different energy demands. The low energy density is a critical factor that impedes the development of supercapacitors, whereas the low power density and low lithium abundance hinder the progress of lithium ion batteries. In chapters 4 and 5, investigations on material design and underlying principles of energy storage mechanism in carbon supported polyaniline-based composites were involved. In chapters 6 and 7, potassium ion battery as an ideal alternative to lithium ion battery was studied. Thereinto, carbonaceous electrode modifications and solid electrolyte interphase were studied to obtain potassium ion battery with high capacity, superior reversibility and good cycling stability. In the following sections, brief conclusions and inspirations of every separate work is include.

In chapter 4, graphite paper supported polyaniline and carbon black composite was fabricated as supercapacitor electrode. Here, a facile one-step electrochemical co-deposition method was developed to synthesis polyaniline and carbon composites, which could realize rational design of conducting polymer-based composites with accurate thickness and loading mass via precise control of deposition parameters. In this work, the positive effect of carbon black was discussed in detail, including the improvement of conductivity and polyaniline polymeric level via the co-deposition process. Carbon black with functional groups like carboxyl groups (-COO) and hydroxy groups (-OH) has interactions with active sites, -NH- in polyaniline chain, to suppress the side reactions, like hydrolysis. Owing to enhanced electronic properties, high polymeric level, low defect intensity and improved structural/chemical stability of polyaniline, the electrochemical performance of the supercapacitor was greatly improved. However, carbon black could not contribute to the specific capacitance with increasing of total mass. Thus, the motivation on developing a polyaniline-based electrode with improved capacity and stability is stimulated.

In chapter 5, the self-supported tin sulfide anchored polyaniline network was designed as supercapacitor electrode. Here the tin sulfide nanoflakes and polyaniline nanofibers have synergistic effect. On one hand, polyaniline nanofiber could facilitate the growth of tin sulfide in nanosized. On the other hand, tin sulfide nanoflake could act as a protective layer to prevent polyaniline from degradation and accommodate structural changes during long term cycling test. Meanwhile, the nanosized tin sulfides could also make great contribution to specific capacity, in terms of promoted capacitive behaviors and shortened ion diffusion paths for improved diffusion-controlled capacity. Polyaniline nanofibers contribute to capacity via the transition of polyaniline among different oxidation states and the corresponding salts. The quantitative analysis was also conducted to distinguish the capacity originated from surface induced capacitive behavior and diffusion-controlled effect. The inferior cycling stability of polyaniline was greatly improved with tin sulfide nanoflakes.

In above two chapters, the structural and morphological design of polyaniline-based supercapacitor electrode were conducted. Compared to batteries, the energy density of polyaniline-based supercapacitor is still not high enough to meet long-term requirements. According to the scarce of lithium metal, the exploration of low-cost and high energy density alternatives to lithium ion batteries is urgent. As an ideal alternative to LIB, potassium ion battery is still at the early stage, which needs a lot of fundamental studies to acquire comparable performance to LIBs.

In chapter 6, the investigations on electrolytes for potassium ion batteries with high reversibility and good cycling stability were carried out. Two electrolyte salts, KPF_6 and $\text{KN}(\text{SO}_2\text{F})_2$ (KFSI) were chosen to study the effect on cycling stability and coulombic efficiency. *Ex-situ* SEM, TEM and depth profile XPS were employed to provide morphological, structural and elemental information of the solid electrolyte interface (SEI) generated in both electrolytes. KFSI containing electrolyte contributed to a uniform, thin and stable SEI layer with homogeneously distributed species. Besides, the stable SEI completely formed during first cycle, which distinguished from KPF_6 -based electrolyte, which led to a thick and interlaced SEI layer, generated cycle by cycle with low

coulombic efficiency in around 30 cycles' test. Particularly, the KFSI-induced SEI layer contains more insoluble organic esters/alkoxides/polycarbonates and less unstable alkyl carbonates (ROCO_2K) compared to KPF_6 -induced SEI layer. All these features, together, ensure good cycling stability and high reversibility in KFSI-based electrolyte.

In chapter 7, the nitrogen doping effect on electrochemical performance was also explored based on the optimized KFSI containing electrolyte. With the nitrogen content increasing, the reversible capacities, rate performances and cycling stability are improved. Particularly, pyridinic and pyrrolic nitrogen doping contribute most to the high capacity owing to the induced holey structures for K^+ storage, the greatly enhance conductivity and the favorable structural changes, like enlarged interlayer spacing for facilitated K^+ intercalation and large pore volume for electrolyte accommodation. When the nitrogen doping concentration increases to 8.47 at. % (PD/PL nitrogen takes 89% out of all nitrogen content), large amounts of additional active sites appeared for more K storage, resulting in highest reversible capacity. Moreover, the volume changes due to the K^+ intercalation is well accommodated due to the favorable structural change, resulting in greatly enhanced with the increasing of nitrogen contents.

In this dissertation, investigations on electrode and electrolyte modifications were conducted for supercapacitors and batteries. The morphological/structural features are important for electrode materials with good performance, in terms of hybridizations of different species and heteroatom doping of carbon materials. Other than electrode material modifications, SEI chemistry and constituent studies are also emphasized due to the significant importance on the stability and coulombic efficiency of batteries. The modifications of electrode and electrolyte, together lead to improved performance in energy storage devices.

8.2 Future plans

Based on preliminary results, more works on carbonaceous electrodes for KIBs, like other heteroatom (B, P, S, etc) doped free-standing carbon substrates and

morphological/structural modifications for KIB anodes for facilitated large-sized K^+ intercalation, are significant to understand K^+ storage mechanism. In order to realize the practicability, the assembly of full cell will be included in the following work.

8.2.1 Heteroatom doping effect on carbon-based potassium ion batteries

Investigations show that the nitrogen, boron, sulfur or phosphorous functionalized carbon materials have outstanding behaviors in energy storage devices.[1] As verified in above works, the nitrogen doping is found to promote enhanced electronic conductivity and induce active sites for K^+ ion storage in carbonaceous electrode. The boron-doping can also induce pseudocapacitive behavior and improve the wettability of the doped materials for an enhanced capacity. The sulfur functionalities contribute to high specific capacity and good cycling stability as proven by Kanamori.[2] Phosphorous doping is found to be beneficial to increase the voltage range tolerance, resulting in high energy densities and power densities.[3]

Objectives: To study the boron, phosphorus and sulfur doping effect on K^+ storage behavior in carbon materials and identify the dependency of K^+ storage on different doping types.

Proposal: Explore efficient doping agents for facile doping methods.

In preliminary study, nitrogen was doped in graphene foam via a one-step *in-situ* doping method, which could guarantee homogenous doping across the whole graphene foam. In order to realize *in-situ* doping of other heteroatoms, doping agents with low pyrolysis point or sublimation temperature were employed. Along this line, the *in-situ* doping of boron (B) and nitrogen (N) was conducted and considerable doping level was obtained, with 7.4 at. % and 9.5 at. % of B and N, respectively. The B, N co-doping is achieved via a facile one-step method. The melamine and boric acid were grinded to a mixture, acting as the precursor. The precursor was then placed at the low temperature range and the nickel foam at the high temperature zone. Via temperature increasing, boric acid could decompose into B_2O_3 vapor, HBO_3 (heating) $\rightarrow B_2O_3$ (vapor) + H_2O , to implement the

in-situ B doping.[4] The melamine provides the carbon/nitrogen source for efficient N-doping simultaneously, as illustrated in Figure 3.2.

In addition to B-N co-doped graphene foam, the sulfur and phosphorus will also be prepared to investigate the K^+ storage behavior. Sulfur containing amino acid, like L-cysteine, is a green agent for sulfur doping. Amino acid could be subjected to desulfuration and deamidization via heating, resulting in the release of sulfur containing vapor, like H_2S , which is ideal for sulfur doping in carbon materials. Phosphorous doping agents, like phosphoric acid, phytic acid and triphenylphosphine, have been widely used for carbon material modifications.[3, 5, 6] However, these agents are usually employed for post doping, not *in-situ* doping. In order to find a suitable phosphorous doping agent for self-supported graphene foam fabrication, more efforts need to be put in the future.

8.2.2 Investigations on K^+ based hybrid cell

In order to explore carbon-based potassium based full cells, several issues need to be addressed, including the match of anode and cathode, the optimization of working window, the selection of electrolyte to guarantee high capacity of both electrodes, etc. Here the carbon-based electrode materials will be discussed for different types of K^+ including cells.

Potassium ion batteries (KIBs) or potassium ion capacitors (KICs) involve the intercalation of K^+ into electrode materials. The energy storage mechanisms of KIBs have been explained in chapter 2, 6, 7. KICs have higher power density compared to KIBs. For one thing, the fast kinetics could be obtained via nanoscale material fabrication; For another, the hybrid cell with a capacitive positive electrode and intercalation negative electrode could be fabricated. In order to obtain high power density without impacting the energy density, the hybrid KICs could be fabricated. The strategies and underlying principles are summarized below.

Strategy 1: Carbon Cathode//Carbon anode configuration. Porous carbon materials as cathode and layered/porous carbon as anode.

Porous carbon materials derived from biomass are environmentally friendly and low cost. Moreover, biomass derived carbon materials usually possess high specific capacity and good cycle stability owing to high surface area, favorable pore structure and high chemical/mechanical stability.[7] The pyrolysis of cellulose in biomass could create large amounts of mesopores to enlarge the specific surface area. Owing to different structures and hardness, the biomass derived carbon materials could act as cathode or anode. Up to now, the effects of physical/chemical properties of carbonaceous anode in terms of pore-size distribution, specific surface area, graphitization degree on K^+ storage is still unclear. The pore size and pore volume of porous carbons will be studied to investigate ideal electrodes.

Typically, carbon materials with rough and porous surface features are favorable for ion adsorption due to high surface area and large pore volume, which are suitable as cathodes for anions (like PF_6^-) accumulation on the porous surface or in the carbon pores. Meanwhile, the porous carbon materials could also be anode based on multiple energy storage mechanisms, including K^+ intercalation and adsorption of ions. The layered carbon materials usually act as ion intercalation anodes, which are superior for lithium, sodium or potassium ion intercalation.[8]

Strategy 2: Polyaniline (polymer) Cathode//Carbon anode configuration. Polyaniline as a low-cost conducting polymer exhibits high specific capacity in supercapacitors. It is also promising for energy storage in metal batteries as anion-insertion cathode.[9]

The energy storage mechanism of polyaniline as a battery cathode is quite similar as supercapacitors. During charging and discharging, polyaniline is subject to transitions from different oxidation states, the anions (like PF_6^-) in electrolyte would be held at the active $-NH-$ sites to keep the neutrality. In the first part of the dissertation, the electrochemical synthesis of polyaniline has been intensively studied and a facile method

has been developed for the co-deposition of polyaniline-based composites with superior performance. Based on the optimized electrolyte, carbonaceous anodes and polyaniline cathodes, the potassium ion full cell could be fabricated. Moreover, the underlying energy storage mechanism of this hybrid cell could be studied to give suggestions on this new topic.

References

- [1] J.P. Paraknowitsch, A. Thomas, **2013** 6 2839.
- [2] G. Hasegawa, M. Aoki, K. Kanamori, K. Nakanishi, T. Hanada, K. Tadanaga, *J. Mater. Chem.*, **2011** 21 2060-2063.
- [3] D. Hulicova-Jurcakova, A.M. Puziy, O.I. Poddubnaya, F. Suarez-Garcia, J.M.D. Tascon, G.Q. Lu, *J. Am. Chem. Soc.*, **2009** 131 5026-+.
- [4] T.R. Wu, H.L. Shen, L. Sun, B. Cheng, B. Liu, J.C. Shen, *New J. Chem.*, **2012** 36 1385-1391.
- [5] D.S. Yang, D. Bhattacharjya, S. Inamdar, J. Park, J.S. Yu, *J. Am. Chem. Soc.*, **2012** 134 16127-16130.
- [6] J. Su, X.L. Wu, C.P. Yang, J.S. Lee, J. Kim, Y.G. Guo, *J. Phys. Chem. C*, **2012** 116 5019-5024.
- [7] D. Mitlin, *Abstr. Pap. Am. Chem. Soc.*, **2014** 248 1.
- [8] J. Ding, H.L. Wang, Z. Li, K. Cui, D. Karpuzov, X.H. Tan, A. Kohandehghan, D. Mitlin, *Energy Environ. Sci.*, **2015** 8 941-955.
- [9] H.C. Gao, L.G. Xue, S. Xin, J.B. Goodenough, *Angew. Chem.-Int. Edit.*, **2018** 57 5449-5453.

APPENDIX

Table A.1 The molar ratio of different configurations in C1s with the sputtering time changing after cycling in two electrolytes in K-ion batteries.

Sputtering time	Species concentration in O1s (at. %)						
	KPF ₆ -based				KFSI-based		
	C-O	C=O	Poly(CO ₃)		C-O	C=O	Poly(CO ₃)
0 min	34.8	43.4	21.8		23.4	31.1	45.5
2 mins	26.9	53.9	19.2		31.3	25.3	43.4
7mins	36.7	45.2	18.1		36.8	33.9	29.3
17 mins	42.1	41.2	16.7		46.9	22.8	30.4
40 mins	20.0	75.2	4.8		49.0	25.5	25.5
100 mins	36.5	54.1	9.4		57.6	28.3	14.4

Table A.2 Surface species concentration of C, O, N elements in N-doped graphene foams.

Samples	Ratio of different elements in NGFs (at. %)		
	C	N	O
NGF-1.03	91.02	1.03	7.95
NGF-2.22	92.19	2.22	5.59
NGF-8.47	85.32	8.47	6.21

*Element, H is not taken into consideration.

Table A.3 Surface species concentration of different bonding types in C1s.

Samples	Ratio of different bonding types in C1s (at. %)				
	C-C/C=C	C-N	C-OH	C=O	COOH
NGF-1.03	54.9	22.7	9.8	5.6	7.0
NGF-2.22	37.4	24.0	21.6	10.8	6.2
NGF-8.47	35.9	30.7	15.3	12.2	5.9

Table A.4 Surface species concentration of different bonding types in N1s.

Samples	Ratio of different bonding types in N1s (at. %)		
	Pyridinic-N	Pyrrolic-N	Graphitic-N
NGF-1.03	45.2	24.8	30.0
NGF-2.22	47.5	35.5	17.0
NGF-8.47	60.7	28.1	11.1

Table A.5 Surface species concentration of different bonding types in O1s.

Samples	Ratio of different bonding types in O1s (at. %)		
	C=O	C-OH/C-O-C	COOH
NGF-1.03	11.6	73.4	15.1
NGF-2.22	16.5	77.4	6.2
NGF-8.47	23.8	67.7	8.5

Table A.6 Influence of nitrogen doping on impedance parameters.

Cells	Impedance parameters			
	$R_s(\text{ESR}) (\Omega)$	$R_1 (R_{\text{SEI}}) (\Omega)$	$R_2 (R_{\text{ct}}) (\Omega)$	W1-P
NGF-1.03	61.3	34.9	826.7	0.57
NGF-2.22	11.1	26.6	466.4	0.62
NGF-8.47	19.6	28.5	393.1	0.73

Figure A.1 SEM images of (a) PANi+CB-10, (b) PANi+CB-50 and (c) PANi+CB-20-SS. The scale bar in FE-SEM figures is 100 nm.

Figure A.2 (a) and (b) N₂ adsorption/desorption isotherms pore size distribution curves of CB. (c) and (d) N₂ adsorption/desorption isotherms and pore size distribution curves of PANi+CB-20-SS.

Figure A.3 (a) CV curves at 2 mV/s of PANi based samples deposited at different scan rates (10, 20, 50 mV/s) on different substrates (GP and SS).

Figure A.4 (a-c) CV curves of $\text{SnS}_2@\text{GF}$, $\text{PANi}@\text{GF}$, $\text{SnS}_2@\text{PANi}@\text{GF}$ at various scan rates, respectively.

Figure A.5 SEM images of (a, d) as-obtained NGF-5.12. And the morphologies after different cycle cycling test in (b, e) KPF_6 -based electrolyte and (c, f) KFSI -based electrolyte.

Figure A.6 Elemental mapping and the EDS spectra of the discharged NGF anodes cycled in (a) KPF₆ and (b) KFSI-based electrolytes.