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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**NANOSTRUCTURED BIMETALLIC SULFIDES AS NA ION
BATTERY ANODES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

NANOSTRUCTURED BIMETALLIC SULFIDES AS NA ION BATTERY ANODES

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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.

12/08/2018

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Date

A rectangular box containing a handwritten signature in black ink. The signature appears to read 'Chen Jingwei' in a cursive script.

.....

Chen Jingwei

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.

17/08/2018

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Date

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Prof. Lee Pooi See

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals where I was the first corresponding author.

Chapter 4 is published as J. Chen, S. Li, K. Qian and P.S. Lee. NiMn layered double hydroxides derived multiphase Mn-doped Ni sulfides with reduced graphene oxide composites as anode materials with superior cycling stability for sodium ion batteries. *Materials Today Energy* 2018, 9, 74-82. DOI: 10.1016/j.mtener.2018.02.008.

The contributions of the co-authors are as follows:

- Prof. Lee Pooi See provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Li Shaohui.
- I co-designed the study with Prof. Lee Pooi See and Dr. Li Shaohui and performed all the laboratory work at the School of Materials Science and Engineering. I also analyzed the data.
- All microscopies, including sample preparation, were conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Qian Kai assisted in the collection of the Raman spectra data.

Chapter 5 is published as J. Chen, S. Li, V. Kumar, and P.S. Lee. Carbon Coated Bimetallic Sulfide Hollow Nanocubes as Advanced Sodium Ion Battery Anode. *Advanced Energy Materials* 2017, 7(19): 1700180. DOI: 10.1002/aenm.201700180.

The contributions of the co-authors are as follows:

- Prof. Lee Pooi See provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Li Shaohui and Dr. Vipin Kumar.

- I co-designed the study with Prof. Lee Pooi See and Dr. Li Shaohui and performed all the laboratory work at the School of Materials Science and Engineering. I also analyzed the data.
- All microscopies, including sample preparation, were conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr. Vipin Kumar assisted in the analysis of the X-ray photoelectron spectroscopy data.

Chapter 6 is published as J. Chen, L. Mohrhusen, G. Ali, S. Li, K. Y. Chung, K. Al-Shamery, and P.S. Lee. Electrochemical Mechanism Investigation of Cu₂MoS₄ Hollow Nanospheres for Fast and Stable Sodium Ion Storage. *Advanced Functional Materials* 2019, 29, 18007753. DOI: 10.1002/adfm.201807753

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- All microscopies, including sample preparation, were conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Mr. Lars Mohrhusen and Prof. Katharina Al-Shamery assisted in the X-ray photoelectron spectroscopy data collection and analysis.
- Dr. Ghulam Ali and Prof. Kyung Yoon Chung assisted in the in-situ X-ray near edge structure data collection and analysis.

12/03/2019

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Date

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Chen Jingwei

Abstract

Sodium ion batteries (SIBs) with major advantage of cost effectiveness has been regarded as promising energy storage alternatives to lithium ion battery (LIB). However, the commercial LIB anode graphite is unable to effectively intercalate Na^+ . Metal sulfides with conversion-based mechanism exhibit higher theoretical capacity than intercalation-based anode materials, and smaller volume change than alloying-based anode materials. Nonetheless, the capacity fading issues caused by volume change of metal sulfides during electrochemical testing are still unsolved problems. This thesis hypothesized that by employing nanostructured bimetallic sulfides with open frameworks and carbon incorporation, the degradation in capacity can be alleviated. In order to achieve this goal, NiMn layered double hydroxides (LDHs) with layered structure and CoFe Prussian blue analogues (PBs) with large interstitial sites are selected as the bimetallic precursors for subsequent sulfidation, resulting in the formation of bimetallic sulfides Mn-doped multiphase Ni sulfides (NMS) and sulfidized PBs (PBS), respectively. In another approach, bimetallic sulfides Cu_2MoS_4 (CMS) with layered structure were directly prepared.

After sulfidation, the open frameworks of bimetallic sulfides NiMn LDHs and CoFe PBs are no longer maintained. However, improved electrochemical performance of bimetallic sulfides over monometallic sulfides have been confirmed. With necessary structure design, size reduction and carbon incorporation, nanostructured bimetallic sulfide-based composites including NMS nanoparticles/reduced graphene oxide (NMGS), carbon coated PBS hollow nanocubes (PBC1-1S) and CMS nanospheres (CMS1)/reduced graphene oxide (CMS1-rGO) can be obtained with improved electrochemical performance. By employing ether electrolyte, bimetallic sulfide-based composites anode further enhanced the rate performance and cycling stability, thus delivering a fast and stable SIB full cell by employing CMS1-rGO anode. In addition, the electrochemical mechanism of NMGS and PBC1-1S have been investigated, confirming the conversion reaction in carbonate-based electrolyte while intercalation is dominant in the ether electrolyte. By combining ex-situ X-ray photoelectron microscopy and in-situ X-ray absorption spectroscopy, the electrochemical mechanism of CMS1 was also studied, revealing the intercalation

dominant electrochemical reaction in ether-electrolyte while conversion occurred in carbonate-based electrolyte. These findings provide insights on the governing factors that explain the structural-electrochemical performance interplay of the bimetallic sulfides.

Lay Summary

Lithium ion batteries (LIBs) have been predominantly used in our daily lives, however, the latent supply risks of Li and Co that are extensively used in LIBs have necessitated the development of alternative batteries. Sodium ion batteries (SIBs) work in the same way as LIBs, yet Na source is much cheaper and evenly distributed.

Nonetheless, the negative electrode used in LIBs, namely graphite, cannot be used in SIBs. Thus new negative electrodes for SIBs need to be developed. Metal sulfides are promising negative electrode materials for SIBs with higher theoretical capacity (often > 500 mAh/g) than graphite (372 mAh/g) in LIBs. However, the stability of metal sulfides is an issue, which can be mitigated by employing bimetallic sulfides. In this research, in order to overcome the stability issue of metal sulfides, utilization of bimetallic sulfides with open frameworks have been proposed to be a solution. With the purpose of further improving the electrochemical performance, several approaches have been incorporated, including size reduction, structure design and incorporation of stable carbon materials.

By carefully designing the structure of bimetallic sulfides, incorporating carbon materials and adjusting the electrolyte, the bimetallic sulfides-based composites materials show improved capacity and stability as SIBs negative electrodes, which allows the fabrication of SIBs battery with excellent cycling stability. The conversion based electrochemical mechanisms of bimetallic sulfides in carbonate-based electrolytes and intercalation-dominant electrochemical mechanism of bimetallic sulfides in ether-electrolyte were confirmed, providing insights in future SIBs development.

Our investigations on nanostructured bimetallic sulfides have shown promising results for SIBs negative electrode applications, which pave the way for further development of metal sulfide based materials for SIBs negative electrode applications as well as accelerating the commercialization of SIBs as alternative cost effective solutions to LIBs.

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The decision made four years ago to start a PhD had changed my life path. With excitement and uncertainty, I started my PhD candidature. With gratitude and pride, I'm coming to the end. It is not an easy decision and it does not always go smooth. There were days when I was flooded by depression and frustration, yet there were also days that I enjoyed the happiness of being a researcher.

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Figure 6.8 First 4 CV curves of (a) CMS, (b) CMS0.5, (c) CMS1 and (d) CMS2. (e) EIS and (f) rate performance of CMS, CMS0.5, CMS1 and CMS2. Reproduced from reference [10] with permission from Wiley online library.

Figure 6.9 (a) XRD patterns and SEM images of (b) CMS1-rGO(4), (c) CMS1-rGO(8) and (d) CMS1-rGO(12). Reproduced from reference [10] with permission from Wiley online library.

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Figure 7.1 Crystal structure of NiS_2 . The figure is reproduced from reference [7] with permission from online Wiley library.

Figure 7.2 Crystal structure Co_9S_8 . (T, tetrahedral; O, octahedral) This figure is reproduced from reference [11] with permission from Royal Society of Chemistry.

Figure 7.3 Rate and cycling Performance comparison of NMGS, PBC1-1S and CMS1-rGO with literatures

Figure. 7.4 Typical ^6Li , ^{23}Na NMR shifts of components in electrochemical cell. The figure is reproduced from reference [28] with permission from American Chemical Society.

Figure. 7.5 Electrochemical mechanism of VS_4 as lithium ion battery anode revealed by in-situ NMR method. The figure is reproduced from reference [29] with permission from American Chemical Society.

Figure. 7.6 Schematics for preparation of (a) flexible electrodes and (b) stretchable electrodes based on nanostructured bimetallic sulfides.

Abbreviations

LIBs	Lithium Ion Batteries
SIBs	Sodium Ion Batteries
LDHs	Layered Double Hydroxides
PBs	Prussian Blue Analogues
CMS	Cu_2MoS_4
CV	Cyclic Voltammetry
GCD	Galvanostatic Charge Discharge
EIS	Electrochemical Impedance Spectra
GITT	Galvanostatic Intermittent Titration Technique
NS	Multiphase Ni Sulfides
NMS	Mn-doped Multiphase Ni Sulfides
GO	Graphene Oxide
NMGS	Mn-doped Multiphase Ni Sulfides/Reduced Graphene Oxide Composites
TEM	Transmission Electron Microscopy
PDA	Poly-dopamine
PBC1-1S	Sulfidized PDA coated PB (weight ratio PB3-1: dopamine = 1: 1)
CMS1	Cu_2MoS_4 Nanospheres
CMS1-rGO	CMS1/reduced GO composites
XPS	X-ray Photoelectron Spectroscopy
XAS	X-ray Absorption Spectroscopy
NVP	$\text{Na}_3\text{V}_2(\text{PO}_4)_3$
HMTA	Hexamethylenetetramine
TAA	Thioacetamide
PVP	Poly(vinyl pyrrolidone)
XRD	X-ray Diffraction
PVDF	Polyvinylidene Fluoride
CMC	Carboxymethyl Cellulose
EC	Ethylene Carbonate
DMC	Dimethyl Carbonate

DEGDME	Diethylene Glycol Dimethyl Ether
EDX	Energy Dispersive X-ray Spectroscopy
NMP	N-Methyl-2-pyrrolidone
BET	Brunauer–Emmett–Teller
TGA	Thermogravimetric Analysis
SEI	Solid Electrolyte Interphase
R_{CT}	Charge Transfer Resistance
SAED	Selected Area Electron Diffraction
CE	Coulombic Efficiency
PBS	Sulfidized Prussian Blue Analogues
HRTEM	High Resolution Transmission Electron Microscopy
FEC	Fluoroethylene carbonate
BE	Binding Energy
XANES	X-ray Absorption near Edge Structure
NMR	Nuclear Magnetic Resonance

Chapter 1

Introduction

Although lithium ion batteries (LIBs) have been dominating the energy storage market due to the high energy density and high voltage output, the latent lithium and cobalt supply risks necessitate the development of alternative energy storage devices. Sodium ion batteries (SIBs) as promising candidates share similar electrochemistry characteristics with LIBs, with advantage of cost effectiveness mainly induced by abundance and even distribution of sodium source. However, the commercial LIB anode graphite is unable to effectively intercalate Na^+ , making it necessary to explore new anode possibilities. Nanostructured bimetallic sulfides are promising solutions due to the relatively high theoretical capacity and good cycling stability. With necessary structure design, treatments and modifications, nanostructured bimetallic sulfides-based SIB anode materials can be directly prepared or derived from different open framework bimetallic precursors, manifesting notably enhanced electrochemical performance.

1.1 Problem statement and Hypothesis

With the depletion of natural sources and alarming rise of carbon dioxide emissions, it has become a necessity to deploy renewable energy including wind and solar energy.^[1, 2] Efforts have been made to develop new materials and devices for large scale energy storage and conservation due to the intermittence of clean energy.^[2, 3] Among those energy storage devices, electrochemical secondary battery has stood out as a promising solution with high energy conversion efficiency and simple maintenance.^[4]

The last few decades have witnessed the research bloom and industry success of lithium ion batteries (LIBs) thanks to its high energy density and high voltage output, enabling its application in various fields including portable electronic devices, electrical vehicles and energy grids, etc.^[3, 5] However, the ever increasing price of Li resources caused by uneven distribution and limited reserve also necessitate the development of “post Li” energy storage devices.^[4, 6, 7]

1.1.1 Problem statement: SIB vs. LIB

Figure 1.1 (a) Price of Lithium carbonates over the past few decades. <http://www.liviakis.com/henk-van-alphen-lithium-price/> Last accessed in May, 2018. (b) Mass fraction of different metals on earth crust. Reproduced from reference [8] with permission from ACS publications.

The limited reserve and uneven distribution of Li resources have been the concern in LIB systems.^[6, 8-10] As can be seen in Fig. 1.1(a), the price of lithium carbonate has been increasing and almost tripled since entering the 21st century.^[11] This can be ascribed to the

limited reserve and uneven distribution of lithium resources that leads to potential Li supply risks.^[12] As shown in Figure 1.1(b), the mass fraction of Li on earth crust is estimated to be only ~ 20 ppm.^[8] In addition, the identified Li reserves are geographically uneven distributed. It can be seen in Figure 1.2, almost 2/3 of world's Li reserves are located in the “lithium triangle” area at South America.^[6, 7]

Besides Li, another important element cobalt is also in latent supply risks.^[10, 13] Large amount of cobalt is extensively used in commercial LIB cathodes LiCoO_2 , which explains why battery industry takes up to 50% share of total cobalt demand.^[6] Similar with the case of Li, Co resource is also unevenly distributed, almost half of the cobalt production and reserves are concentrated in the “Central African Copperbelt” region as indicated in Fig. 1.2.^[6]

Figure 1.2 Geological distribution of Lithium and Cobalt sources. Reproduced from reference [6] with permission from Nature publishing group.

The latent supply risks of Li and Co in LIB battery industry in 2016~2050 were predicted by considering different materials combinations in various reference devices.^[6] It is thus assumed that Li reserves are sufficient to supply the battery industry in a short-to-mid-term without considering other industries. Nonetheless, it should be noted that today's battery industry share of Li demand is already $\sim 46\%$, which will lead to great stress on Li supply in foreseeable future if battery industry's share of Li continues to increase. On the other

hand, in extreme cases of using large size LIB and Ni/Co-rich cathode mixtures, the total Co demand in battery industry during 2016~2050 is predicted to be twice as much as today's identified Co reserves, which will lead to significant Co supply risk in a short term. Even in cases when Ni/Co-poor cathode mixtures are used (e.g. LiFePO_4), the total demand of Co (including battery industry 50% and other industry 50%) will still be higher than the identified reserve. It is thus deduced that the Li supply risk is more on the uneven geographical distribution while the Co supply risk is more severe, which necessitates the use of Co-poor cathodes (eg. LiFePO_4) and alternative energy storage devices, for example sodium ion battery (SIB).^[6, 10]

Sodium as a group I alkaline metal, has much higher concentration of 23600 ppm on earth crust, which is ~ 1000 times higher than that lithium, as shown in Fig. 1.1b. In addition, sodium ions share similar electrochemical behaviors (e.g. similar standard redox potential, Na/Na^+ -2.71 V; Li/Li^+ -3.04 V) with lithium ions, making sodium ion battery promising candidates for beyond-lithium energy storage applications.^[8, 14-16]

Table 1.1 Comparison between SIB system and LIB system. The table is adapted from reference [8] with permission from ACS publications.

Properties	Sodium	Lithium
Molar mass	23	6.94
Ionic radii (Å)	1.02	0.76
E^0 (vs SHE) /V	-2.71	-3.04
Theoretical Capacity of Metal mAh ($\text{g}^{-1}/\text{cm}^{-3}$)	1166/1131	3861/2062
De-solvation energy in PC (kJ/mol)	157.3	218
Abundance in earth crust (ppm)	23600	20
Distribution	Even	Uneven
Price (of carbonates) (€/kg)	0.07-0.37	4.11-4.49

The properties of sodium and lithium are compared in Table 1.1. It can be seen that the cost of sodium carbonate is much lower than that of lithium counterparts, due to the even distribution and much higher abundance of sodium than lithium on earth crust (~ 23600 ppm vs. ~ 20 ppm). However, the ~ 0.3 V higher standard redox potential of Na/Na^+ than Li/Li^+ will lead to compromised voltage output and lower energy density of sodium ion

battery (SIB).^[17] In addition, the higher molar mass of Na (23) than Li (6.94) and larger ionic radii of Na^+ (1.02 Å) than Li^+ (0.76 Å) will hinder the electrochemical kinetics in SIB.^[4, 17] Thus the theoretical capacity (gravimetric /volumetric) of pure Na metal (1166 mAh/g; 1131 mAh/cm³) is inferior to that of Li (3861 mAh/g; 2062 mAh/cm³).^[8]

Although SIB is not as competitive as LIB in terms of energy density, cost effective SIB is still a promising candidate energy storage devices for large scale stationary applications where energy density is not that critical.^[18, 19] In addition to the merit of cost effectiveness, SIB possesses extra advantages compared with LIB.

As shown in table 1.1, the de-solvation energy of Na^+ (157.3 kJ/mol) in polar solvents (e.g. propylene carbonate) is lower than that of Li^+ (218 kJ/mol) due to the relatively lower charge density around Na^+ , which can be deemed as weak Lewis acid.^[8, 13, 14, 20] Additionally, the ionic conductivity of NaClO_4 in propylene carbonate is higher than that of LiClO_4 with relatively lower viscosity, which may originates from the difference in ionic size and solvation energy of Na^+ and Li^+ in aprotic solvents.^[8, 21] The lower de-solvation energy combined with higher ionic conductivity of Na^+ are indicative of possible high power SIB battery development in the future.^[6, 8]

In SIB, lighter and cheaper Al foil can be used as current collector for both the cathode and anode, while only Cu foil can be used as anode current collector in LIB as Al can form LiAl alloy at low potential.^[13, 22] With use of lighter and cheaper Al current collector, the cost of SIB can be further reduced, emphasizing the cost effectiveness of SIB system.^[6, 17] In addition, the use of Al foil as current collector allows bipolar stacking, which may also open up new design strategies.^[6]

The experience accumulated in developing LIBs can often be translated into SIB exploration.^[10, 23] As a result, emerging advanced SIB cathode materials including layered oxides, Prussian blue based materials, and polyanion compounds, etc. have been developed.^[16, 18, 23, 24] One example of advanced SIB cathode is $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, which is able to deliver enhanced capacity at high current density than typical high rate LIB cathode

LiFePO_4 .^[25] On the contrary, the commercial LIB anode, graphite, is unable to intercalate Na^+ alone due to the thermodynamic instability of Na^+ intercalated graphite compounds associated with the increased C-C stretching.^[13, 16, 26] Although co-intercalation phenomena have been observed in ether-based electrolyte for graphite anode in SIB, the capacity realized is often quite limited to $< 200 \text{ mAh/g}$.^[26, 27] Intercalation of Na^+ is enabled in expanded graphite with larger interlayer spacing, however the specific capacity ($< 300 \text{ mAh/g}$) and rate performance are still quite limited.^[28] Hard carbon as another type of carbon materials with disordered structures, is able to deliver increased capacity of $\sim 300 \text{ mAh/g}$. However, safety concern may apply due to the low discharge charge plateaus vs. Na/Na^+ ($< 0.2 \text{ V}$), which may cause Na plating with formation of dendrites.^[10, 16] Thus it is necessary to discover new materials for SIB anodes with improved sodium storage performance.^[18]

1.1.2 Hypothesis

Based on the above discussion, compared with LIBs, SIBs as alternative energy storage systems have major advantage of cost effectiveness. However, efforts need to be made to develop advanced electrode materials, especially anode materials to improve the electrochemical performance of SIBs thus further enhancing their competitiveness.^[18]

Among anode materials applied for SIBs, metal sulfides are deemed as promising candidates, due to the high theoretical capacity (normally $500 \sim 1000 \text{ mAh/g}$ based on conversion mechanism), better reversibility, better thermal and mechanical stability and relatively higher electronic conductivity than metal oxide counterparts.^[29, 30, 31] However, large volume change ($100\% \sim 200\%$) of metal sulfides are accompanied during electrochemical reactions, which will cause limited rate performance and cycling stability.^[13, 30, 32] With the purpose of manifesting the high theoretical capacity of metal sulfides without suffering from fast capacity decay induced by volume change, typical methods including downsizing, structure design, and introducing conductive supports need to be incorporated to facilitate the charge transfer kinetics and alleviate the issues caused by volume change.^[10, 23, 31, 33]

In addition to the above mentioned typical methods, utilization of bimetallic sulfides instead of monometallic sulfides can be another effective strategy. The cycling stability of bimetallic sulfides can be better than monometallic sulfides when applied as anode materials for SIB.^[34] After the first electrochemical conversion reaction, finely distributed nanocomposites composed of respective nanosize metal sulfides will be formed with reduced Na^+ diffusion length and buffering effect, alleviating stress caused by volume changes, thus delivering improved cycling stability.^[35]

The crystal structure of host materials also plays an important role in electrochemical reactions. Considering the large ionic size of Na^+ , host materials with open channels allow fast insertion of Na^+ with relatively small volume change induced, thus improved Na storage capability.^[18, 32, 36] One example is that specific capacity of expanded graphite can be greatly influenced by the inter-layer spacings. Specific capacity of only ~ 13 mAh/g is delivered in pristine graphite with interlayer spacings of 3.4 Å, while capacity of 284 mAh/g is realized when the interlayer spacings are enlarged to 4.3 Å in expanded graphite.^[28] Since the electrochemical reaction of bimetallic sulfides often includes initial intercalation of Na^+ ,^[10, 33] bimetallic sulfides with open framework are believed to be promising SIB anode materials with superior electrochemical performance.

Based on the above discussion, nanostructured bimetallic sulfides with open crystal framework are to be prepared, which is expected to be realized by direct synthesis or sulfidation of open structured bimetallic precursors. It is hypothesized that with necessary structure design/modification and treatments, nanostructured bimetallic sulfides with open crystal frameworks can be obtained with superior charge storage capability as anode materials in SIBs.

1.2 Objectives and Scope

The objective of this thesis is to harvest the high electrochemical performance of nanostructured bimetallic sulfides with open frameworks, for application as anode materials for SIBs. For this purpose, sulfidation of bimetallic precursors with open frameworks, necessary nanostructuring, treatments/modifications, and carbon incorporation processes were conducted. In addition, electrochemical reaction mechanisms of various bimetallic sulfide anode materials in SIB were also investigated using various characterization methods.

As bimetallic precursors with open frameworks and tunable compositions, layered double hydroxides (LDHs) and Prussian blue analogues (PBs) often have hexagonal and cubic crystal structures, with large inter-layer spacings and large interstitial sites respectively.^[36, 37] In addition, various nanostructures, including $\text{NiCo}_2\text{S}_4/\text{Ni}_{0.96}\text{S}$ nanoparticles,^[38] NiCo_2O_4 nanoneedles,^[39] NiS nanoframes,^[40] etc. can be prepared starting from LDHs and PBs precursors.

With hexagonal crystal structure, LDHs have large interlayer spacing and tunable compositions, endowing their extensive applications in electro-catalysts, supercapacitors and sorbents etc.^[37, 41, 42] Among the LDHs, NiMn LDH is claimed to exhibit half-metallic nature enabled by the hybridization among Ni 3d, Mn 3d and O 2p orbitals, with lowered hydrogen de-sorption energy^[41] As a result, electrode materials based on NiMn LDH/Carbon nanotubes composite is able to deliver superior specific capacitance (2960 F/g @ 1.5 A/g) with excellent rate performance (2330 F/g @ 30 A/g) than other LDHs based electrode materials for supercapacitors. Metal sulfides obtained by sulfidation of metal oxides has been shown to be more electronically conductive with reduced bandgap than metal oxide counterparts.^[43] Thus it is expected that after sulfidation of NiMn LDH, nanostructured bimetallic sulfides can be formed with enhanced electronic conductivity and the open framework of NiMn LDH can be preserved, delivering improved electrochemical performance.

Similarly, PBs (normally hexacyanoferrates) with three dimensional cubic crystal structure have tunable compositions with large interstitial sites that allow Na^+ accommodation.^[36, 44] In addition, they can be prepared simply in aqueous solution without thermal stimuli, with formation of monodispersed nanocubes.^[45] With similar crystal structure and lattice parameters, CoS_2 (cubic, $a = 5.5 \text{ \AA}$) can form solid solution with FeS_2 (cubic, $a = 5.4 \text{ \AA}$) at various Co: Fe ratios,^[46] CoS_2 with metallic behavior also have relatively higher electronic conductivity than other metal sulfides.^[47] Thus by applying CoFe PB precursor, it is expected to obtain nanostructured CoFe bimetallic sulfide solid solution maintaining the cubic structure with open framework, realizing improved Na storage capability.

Instead of preparing bimetallic sulfides by sulfidation of bimetallic precursors, efforts were also made to directly prepare bimetallic sulfides with open framework. MoS_2 has a layered structure that allows fast and reversible Na^+ intercalation/de-intercalation.^[32, 48] Similar to MoS_2 , bimetallic sulfides Cu_2MoS_4 (CMS) also has large inter-layer spacings ($5.12 \text{ \AA}$ for tetragonal I-42m symmetry) that allows insertion/extraction of alkaline ions.^[49] However, similar with other metal sulfides, MoS_2 also suffered from limited cycling stability due to the large volume change upon deep discharge,^[50] which is deemed to be resolved by the use of bimetallic sulfides CMS. Thus it is hypothesized that nanostructured and layered CMS is able to deliver excellent Na^+ storage properties with extended cycling life.

In summary, several different materials systems will be investigated in this thesis.

- a) NiMn LDHs were sulfidized by hydrothermal treatment. The resultant multiphase metal sulfides were applied as anode for SIB.
- b) CoFe PBs were sulfidized at elevated temperature in a furnace. Resultant mixture of metal sulfides were applied as anode for SIB application.
- c) Preparation procedure of CMS was modified to obtain nanostructured CMS with hollow interior, which were applied as anode for SIB application.

1.3 Dissertation Overview

The thesis tests the hypothesis that with certain structure design, treatments and

modifications, nanostructured bimetallic sulfide with open frameworks can be obtained, delivering superior electrochemical performance as anode materials for SIBs. The preparation processes of bimetallic sulfides were carefully adjusted to obtain expected products with optimum electrochemical performance. Necessary physical and chemical characterizations of the samples were conducted to understand samples' properties. Electrochemical testing was also conducted for different samples to correlate the electrochemical performance with physical/chemical properties. Electrochemical mechanism in different materials system was studied using various ex-situ or in-situ characterization technologies.

Chapter 1 provides the rationale for the research and outlines the goals and scope of this thesis. In this chapter, SIB is compared with LIB in terms of electrochemical performance and cost effectiveness, etc. The uneven distribution of Li source and latent supply risks of Li and Co elements necessitate the development of alternative energy storage device. With similar electrochemistry and cost effectiveness, SIB are to be tested with development of advanced anode materials. Nanostructured bimetallic sulfides with open frameworks are deemed to be promising solution towards SIB anodes with enhanced electrochemical performance. NiMn LDHs and CoFe PBs are selected as open framework bimetallic precursors to prepare nanostructured bimetallic sulfides. Bimetallic sulfides CMS with large interlayer spacing will also be prepared as SIB anodes.

Chapter 2 reviews the literatures concerning the electrochemical mechanisms, materials categories and the potential challenges in sodium ion battery systems. Electrode materials with intercalation, conversion and alloying-based mechanisms and the accompanied electrochemical behaviors in SIB are also discussed. The advantage/disadvantages of different materials categories used in SIBs are presented. Methods to improve electrochemical performance of anode materials in SIBs are briefly introduced. Nanostructured bimetallic sulfides with open frameworks are deemed as promising SIB anodes. The study on different materials systems NiMn LDHs, CoFe PBs and CMS are rationalized.

Chapter 3 discusses the methods used for sample preparation, including hydrothermal/solvothermal reaction, thermal annealing assisted sulfidation, and room temperature wet chemical synthesis. The detailed preparation process and parameters are elaborated. Characterization methods/conditions and the underlying principles are explained to study physical/chemical properties of different samples. Electrochemical testing including cyclic voltammetry (CV), galvanostatic charge discharge (GCD), electrochemical impedance spectroscopy (EIS), cycling and galvanostatic intermittent titration technique (GITT), etc. are discussed with testing conditions provided. Full cell assembly procedure is also stated in detail.

Chapter 4 presents the NiMn LDH derived multiphase Ni sulfides as SIB anodes with superior cycling stability. The layered structure of NiMn LDHs precursor is no longer preserved after the sulfidation process. Compared to NS (multiphase Ni sulfides), NMS (Mn-doped multiphase Ni sulfides) is more electronically conductive with enlarged crystal d-spacing and higher sodium ion diffusion coefficient, delivering improved rate performance compared to NS. With incorporation of rGO, NMGS (Mn-doped multiphase Ni sulfides/rGO composites) delivers higher capacity, better rate performance and excellent cycling stability. The electrochemical mechanism of NMGS in carbonate-based and ether-based electrolyte was unveiled using ex-situ transmission electron microscopy (TEM).

Chapter 5 elaborates the preparation of carbon coated bimetallic sulfides hollow nanocubes as advanced SIB anode. In this study, CoFe PB with different Co: Fe feeding ratios were sulfidized using thermal annealing assisted sulfidation method. The crystal structure of the dominant phase Co_8FeS_8 (cubic) is the same as the CoFe PBs precursors, while Co_8FeS_8 is closely packed without any large interstitial sites. It was found out that PB3-1S (sulfidized CoFe PB, Co: Fe feeding ratio of 3: 1) delivers optimum rate performance due to the higher sodium ion diffusion coefficient. Subsequently, PB3-1 was coated with varied amount of poly-dopamine (PDA) for sulfidation. It was found out that PBC1-1S (sulfidized PBPDA, weight ratio of PB: dopamine = 1:1) delivers better electrochemical performance than its counterparts due to the smaller charger transfer resistance. The electrochemical mechanism of PBC1-1S was also studied using ex-situ TEM.

Chapter 6 discusses the electrochemical mechanism study in hollow CMS nanospheres with excellent cycling stability in SIB. Glucose was added in the precursor solution to obtain CMS nanospheres with hollow interiors (CMS1). The amount of glucose added was optimized. It is proved that CMS1 has noticeably improved electrochemical performance compared to CMS. With the introduction of reduced graphene oxide (rGO), CMS1-rGO shows extensively improved cycling stability. The electrochemical mechanism of CMS1 was studied using ex-situ X-ray photoelectron spectroscopy (XPS) and in-situ X-ray absorption spectroscopy (XAS). A SIB full cell using CMS1-rGO as anode and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ composites as cathode was assembled with excellent cycling stability.

Chapter 7 summarizes the results presented in this thesis, the future work is also discussed. It is clearly shown that with the tailored syntheses applied for corresponding materials systems, electrochemical performance are improved by utilizing bimetallic sulfide-based materials, although the open framework of bimetallic precursors are not necessarily preserved after sulfidation. Electrochemical mechanism of bimetallic sulfides are also discussed, which is concluded to be intercalation-dominant for bimetallic sulfides in ether-based electrolyte, while conversion reaction occurs in carbonate-based electrolyte. The advantage of bimetallic sulfides over monometallic sulfides have been reiterated and discussed in details. Although the electrochemical performances of the samples are not the best when compared to other materials reported in the literature, the understandings of improved electrochemical performance enabled by incorporating rGO in NMGS and CMS1-rGO, incorporating carbon coating and creating hollow interiors in PBC1-1S nanocubes and CMS1 nanospheres were established. Utilization of bimetallic sulfides NMS and PB3-1S and employing ether-based electrolyte for NMGS, PBC1-1S and CMS1 have been confirmed to further promote the electrochemical performance. Cost, scalable synthesis, electrochemical performance and mechanism of nanostructured bimetallic sulfides are to be considered for development of SIBs for grid applications. The future work of investigating the effect of Mn-doping on the enhanced electrochemical performance of NMS using in-situ nuclear magnetic resonance and fabrication of flexible SIBs are also discussed.

1.4 Findings and Outcomes

This research led to several novel outcomes:

1. Preparing bimetallic sulfides from different open framework bimetallic precursors, or directly preparing bimetallic sulfides with layered structure towards enhanced electrochemical performance as SIB anodes.
2. Incorporating carbon materials in different forms to act as coating layer, scaffold or electron highway to couple with bimetallic sulfides nanostructures, facilitating the charge transfer and enhance the electrochemical performance.
3. Introducing nanostructures and hollow interiors in bimetallic sulfides through structure design, which is conducive for reversible and stable sodium ion storage.
4. Investigating the electrochemical mechanism of bimetallic sulfides in SIB using combined characterization techniques.

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Chapter 2

Literature Review

Sodium ion batteries share similar electrochemical charge storage characteristics with lithium ion batteries. The detailed electrochemical mechanism in electrode materials can be classified into intercalation, alloying and conversion. In order to develop new possibilities for sodium ion battery anodes, metal sulfides based on conversion mechanism are promising candidates with high theoretical capacity, whereby the issues accompanied by the volume change still needs to be resolved. Incorporation of carbon materials, size reduction of metal sulfides and introduction of hollow interiors are the effective approaches to improve the electrochemical kinetics and stability of metal sulfides. In addition, bimetallic sulfides with open frameworks are proposed to exhibit enhanced Na^+ storage capability and stability with facilitated kinetics. Half metallic NiMn layered double hydroxides with large interlayer spacings and CoFe Prussian blue analogues with large interstitial sites are to be sulfidized for preparation of nanostructured bimetallic NiMn sulfides and bimetallic CoFe sulfides solid solutions respectively, maintaining the open frameworks of the precursors. Alternatively, nanostructured Cu_2MoS_4 with large interlayer spacings are also to be obtained for sodium ion battery anode applications.

2.1 Overview: sodium ion battery energy storage mechanism and electrode materials

Figure 2.1 Electrochemical charge/discharge process and schematic of sodium ion battery. Reproduced from reference [1] with permission from American Chemical Society.

As discussed in chapter 1, sodium ion batteries (SIBs) share similar electrochemistry characteristics with lithium ion batteries (LIBs), and the electrochemical mechanisms in SIBs are very essentially the same with LIBs only the charge carrier is replaced from Li^+ to Na^+ .^[1-3] As displayed in Fig. 2.1, SIB is also configured by positive electrode (cathode) and negative electrode (anode), with separator and electrolyte in between. The purpose of separator is to avoid electric contact between the cathode and anode while the electrolyte is an ionic conductor that allows the transportation of charge carriers (Na^+) between two electrodes. During the charging process Na^+ is extracted from the cathode, transferred through electrolyte, and inserted into the anode.^[1, 4] At the same time electrons are driven from cathode to anode through external circuit to remain the charge neutrality of electrodes.^[5] The process is reversed during discharge. Although the electrochemistry of SIBs and LIBs are quite similar, however, the interaction between charge carriers (Li^+ and Na^+) with the host materials can be quite different due to the larger size (Na^+ 1.02Å, Li^+ 0.76Å) of the less polarizing Na^+ .^[3]

The electrode materials applied for SIBs are classified into cathodes and anodes based on their redox potential range. The voltage range for anode materials vs. Na/Na^+ is normally 0.1~2 V, while the voltage range of cathode vs. Na/Na^+ are normally 2.5 ~ 4.0 V.^[5, 6] The redox potential, specific capacity and electrochemical behaviors of electrode materials will greatly affects the energy density, power density, cycling stability and safety issues of a full cell battery.^[1, 5]

Figure 2.2. A brief summary of typical electrode materials applied for SIB with respective specific capacity and voltage range. The figure is reproduced from reference [5] with permission from Wiley online library.

Following the protocols and methodologies for LIB electrodes development, electrode materials for SIBs have been developed.^[6, 7] Cathode materials including layered oxides (e.g. NaCoO_2 and NaMnO_2), Prussian blue based materials (e.g. $\text{Na}_2\text{MnFe}(\text{CN})_6$ and $\text{Na}_{1.92}\text{Fe}[\text{Fe}(\text{CN})_6]$), and poly-anion compounds (e.g. NaFePO_4 , $\text{Na}_3\text{V}_2(\text{PO}_4)_3$), etc. and anode materials including carbon-based materials (e.g. expanded graphite, hard carbon), intermetallic compounds (e.g. Sb, Sn, P, Ge), metal oxides/sulfides (e.g. $\text{Ni}_2\text{Co}_2\text{O}_4$, FeS_2), etc. have been developed.^[2, 4, 5, 7-9] The typical electrode materials for cathode and anode materials applied in SIBs are positioned with respective voltages and capacities, as shown in Fig. 2.2. It can be seen that the potential of anode materials are generally below 2.0 V

with capacity of $\sim$ a few hundred mAh/g, whereby the potential of cathode materials are generally > 2.0 V, with capacity of less than 200 mAh/g.^[5] In order to improve the energy density and output voltage of SIB, the specific capacities of electrode materials need to be improved, while the voltage difference between cathode and anode materials should be expanded.^[3]

The electrochemical behaviors of electrode materials is highly affected by the corresponding electrochemical mechanisms. In a detailed explanation, the electrochemical mechanisms of SIBs electrodes can be categorized mainly into 3 types, namely intercalation, conversion and alloying-based electrode materials, with respective electrochemical behaviors and advantages/disadvantages.^[1, 4, 6, 7, 10]

Figure 2.3. Na⁺ intercalation in expanded graphite. The figure is reproduced from reference [14] with permission from Wiley online library.

In intercalation based electrodes, Na⁺ will be intercalated into the crystal structure of host materials, maintaining structural integrity with substantial limited volume change (normally $< 10\%$).^[6, 11, 12] However, the amount of Na⁺ can be intercalated is quite limited (normally < 2 per formula), thus the specific capacity of intercalation-based materials are often quite low (< 300 mAh/g) due to limited sites for Na⁺ occupation.^[10] For example, Na₂Fe₂(SO₄)₃ with alluaudite-type framework and theoretical capacity of 120 mAh/g has single phase reaction mechanism, with negligible volume change of 1.6% during

intercalation/de-intercalation of Na^+ , realizing outstanding rate performance (102 mAh/g at 1/20C and ~ 60 mAh/g at 20C).^[13] As shown in Fig. 2.3, with large interlayer spacings of 0.43 nm, Na^+ are intercalated into expanded graphite, delivering specific capacity of 284 mAh/g at 20 mA/g with insufficient volume change albeit microstructural distortion and restorations.^[14] Examples of intercalation-based electrode materials include most cathode materials, eg. $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP). It has been confirmed that Na^+ intercalation in NVP is based on the redox of $\text{V}^{3+}/\text{V}^{4+}$ with limited volume change of $\sim 8.26\%$.^[15, 16] The small volume change is similar to that of the high rate LIB cathode LiFePO_4 ($\sim 6.8\%$), thus enabling excellent cycling stability in NVP.^[15, 17] Aside from expanded graphite, some of other anode materials, e.g. carbon based materials (graphene oxide, hard carbon) and Ti oxide based materials (TiO_2 , sodium titanates), etc. also exhibit intercalation based electrochemical mechanism.^[2, 12, 14]

Figure 2.4. Schematics of black phosphorous sodiation. The figure is reproduced from reference [19] with permission from Wiley online library.

For materials with alloying based mechanism, Na will form alloys with the electrode materials through solid solution reaction with phase changes.^[6] In these cases, substantial amount of Na^+ can be accommodated, thus the theoretical capacity of alloy-based electrodes are often very high (e.g. Sn: 847 mAh/g; based on formation of $\text{Na}_{15}\text{Sn}_4$).^[12] In addition, the operating voltage of alloying based materials are normally at ~ 0.5 V vs Na/Na^+ , making them safe anode with high capacity.^[6, 12] Although alloying-based materials have high theoretical capacities, however the cycling stability can be quite limited due to the large volume change ($> 300\%$) induced pulverization and thus loss of electric

contact.^[6] For example, Sn can form $\text{Na}_{15}\text{Sn}_4$ with theoretical capacity of 847 mAh/g at volume change of 420%, Sb can form Na_3Sb with theoretical capacity of 660 mAh/g at volume change of ~ 390%.^[18] Among alloying-based anode materials, P has a very high theoretical capacity of 2596 mAh/g as P can alloy three Na per formula with formation of Na_3P .^[19, 20] As shown in Fig. 2.4, before sodiation, black phosphorous has an orthorhombic crystal structure, which is transformed to Na_3P with hexagonal crystal structure after full sodiation.^[19] The theoretical volume change is calculated to be 499% by considering the molar mass and density of P and Na_3P .^[19] Such a substantial volume change will greatly limit the cycling stability of P.^[19] In addition, Na_3P will react with water to release toxic PH_3 gas and will burn when exposed to oxygen.^[9]

For conversion-based materials (normally MX, M=transition metal, X=O, S, Se), MX will be transformed into pure metal M with formation of Na_2X through multi-electron reactions.^[11, 12] Large amount of Na^+ can also be consumed in conversion reactions, thus the theoretical specific capacity of conversion-based electrodes (400~ 1000 mAh/g) are also much higher than intercalation-based electrode materials.^[11, 21] For example, the theoretical capacity of FeS_2 is 894 mAh/g based on formation of Na_2S and Fe.^[22] Similarly with alloying-based electrode materials, conversion-based materials are also able to deliver high theoretical capacity, while the theoretical volume change is often smaller (100% ~250%),^[11] which will also leads to unsatisfactory electrochemical performances. FeS exhibits theoretical capacity of 610 mAh/g based on electrochemical mechanism expressed as follows:^[23]

Formation of metallic Fe upon deep sodiation can be detected by ex-situ X-ray photoelectron spectroscopy and transmission electron microscopy characterizations, while the volume change based on the above electrochemical reaction is calculated to be ~ 170%.^[23] Thus in order to manifest the high capacity of metal sulfides, methods still needs to be employed to overcome the large volume change issue.

Figure 2.5. Electrochemical mechanism of MoS₂ in SIB. The figure is reproduced from reference [24] with permission from Elsevier.

With the three types of electrochemical mechanisms introduced above, nonetheless it's not necessarily only one type of mechanism in SIB electrodes but very often combination of two or more mechanisms taking place.^[22] As shown in Fig. 2.5, when applied as anode materials for SIB, the electrochemical mechanism of MoS₂ is a combination of intercalation and conversion.^[24] With large interlayer spacings, MoS₂ allows fast and reversible Na⁺ intercalation with high Na⁺ mobility within interlayers.^[21] In the initial discharge stages, Na⁺ ions are intercalated into the interlayers of MoS₂ with transition from 2H phase to 1T phase. With subsequent discharge (at voltage of > 0.4 V vs. Na/Na⁺), more amount of Na⁺ will be intercalated, occupying interlayer octahedral and tetrahedral sites without deteriorating the layered structure. When 1 molar of Na is intercalated (NaMoS₂), all Mo⁴⁺ in pristine MoS₂ will be reduced to Mo³⁺. When being further discharged to < 0.4 V, the layered structure start to collapse, forming Na₂S nanocrystals and isolated Mo metal nanoclusters.^[24] Thus the electrochemical mechanism in layered MoS₂ is voltage dependent, which combines initial intercalation with subsequent conversion upon deep discharge.^[22]

2.2 Challenges in SIBs

As discussed in chapter 1, advanced SIB cathodes have been developed following the experience accumulated in developing LIBs cathodes, ^[6, 7] whereby the commercial LIB anode graphite is unable to effectively intercalate Na^+ alone due to the thermodynamic instability of Na^+ intercalated graphite compounds associated with the increased C-C stretching. ^[2, 3, 25] It has been demonstrated based on theoretical calculations that graphite with interlayer spacings of 0.34 nm is unable to intercalate Na^+ due to the high energy barrier (0.12 eV), which will be reduced to 0.053 eV when the interlayer distance is increased to 0.37 nm. ^[26] Thus the reversible intercalation of Na^+ in graphitic oxide with interlayer spacings of 0.37 nm has been experimentally confirmed, delivering specific capacity of $\sim 200 \text{ mAh/g}$. ^[14] Further improvement in the Na^+ storage capability was realized by further increasing the interlayer spacings to 0.43 nm in expanded graphite as shown in Fig. 2.3, which is able to deliver capacity of 284 mAh/g at 20 mA/g . ^[14] In addition to expanding the interlayer distance, intercalation of Na^+ into graphite has also been enabled by co-intercalation phenomenon. As shown in Fig. 2.6, it is calculated that $\text{Na}^+(\text{diglyme})_2$ complex with radius of $4.1\text{-}4.2 \text{ \AA}$ can be intercalated into graphite, leading to interlayer distance of $11.3 \text{ \AA}$. ^[27] Reversible co-intercalation phenomenon of $\text{Na}^+(\text{diglyme})_2$ complex into graphite through multiple staging steps were also experimentally verified, however, the capacity realized is quite limited to $< 200 \text{ mAh/g}$. ^[25, 28] Thus it's necessary to explore new possibilities for SIB anodes with improved sodium storage performance. ^[4]

Figure 2.6. (a) Calculated structure of $\text{Na}^+(\text{diglyme})_2$ complex. (b) $\text{Na}^+(\text{diglyme})_2$ complex intercalated into graphite. The figure is reproduced from reference [27] with permission from Wiley online library.

Aside from graphite, hard carbon as another type of carbon materials with disordered structures, is able to deliver increased capacity of ~ 300 mAh/g with Na^+ intercalation within the graphene layers and pores filling.^[2] However, safety concern may apply due to the low discharge charge plateaus vs. Na/Na^+ (< 0.2 V), which may cause Na plating with formation of dendrites.^[2, 6] In addition, the limited capacity with low initial coulombic efficiency of hard carbon greatly affects their practical applications.^[2, 8] Thus intercalation-based electrode materials with low specific capacity are still unfavorable as SIB anodes.

As discussed above, alloying-based materials are able to deliver enhanced capacity, however, the substantial volume change will lead to greatly inhibited cycling stability.^[29] For example, capacity of 503 mAh/g for Sb-C composites soon decays to 45 mAh/g after only 40 cycles.^[30] Similarly, the capacity of black phosphorous P was substantially decreased from ~ 650 mAh/g to < 20 mAh/g after only 7 cycles in a voltage range of 0.02~1.5V. Although the cycling stability can be improved by restricting the voltage window to 0.54~1.5V, the specific capacity realized is only ~ 150 mAh/g with formation of $\text{Na}_{0.17}\text{P}$.^[19] Conversion-based materials are also able to deliver high capacity, while the less severe volume change issues still need to be overcome to fully utilize the high theoretical capacity.^[31, 32]

Among conversion-based anode materials for SIBs, metal sulfides are one of the promising candidates due to the better reversibility, better thermal and mechanical stability and relatively higher electronic conductivity than metal oxide counterparts.^[11, 22, 33, 34] However, the accompanied volume change induced by repeated de/sodiation often resulted in unsatisfactory electrochemical performance.^[31, 35, 36] In order to overcome the issues accompanied with volume change of metal sulfides, approaches have been introduced including downsizing, structure design, compositional design and conductive support incorporation, etc.^[37]

Figure 2.7. Schematics of (a) DL-MoS₂; (b) FL-MoS₂ and (c) US-MoS₂ grown on N-doped graphene (NG) sheets. (d) Electrochemical performance comparison of DL-MoS₂@NG, FL-MoS₂@NG and US-MoS₂@NG. The figure is reproduced from reference [40] with permission from Wiley Online library.

It has been reported that for anode materials, downsizing can relieve the stressed caused by volume expansion/shrinkage with facilitated Na⁺ diffusion kinetics, thus enhancing the utilization rate and the rate performance of electrode materials.^[30, 33, 38, 39] Ji. et al. reported that with smaller size of 80 nm anatase TiO₂ can realize superior rate performance (267 mAh/g at 0.1C; 110 mAh/g at 20C) than anatase TiO₂ with average size of 300 nm (212 mAh/g at 0.1C and 39 mAh/g at 20C), due to the enhanced Na⁺ diffusion kinetics and facilitated electron transfer.^[39] As shown in Fig. 2.7, by modifying the synthesis process, dozens layered MoS₂ nanosheets (DL-MoS₂), few layered MoS₂ nanosheets (FL-MoS₂) and ultra-small MoS₂ nanosheet (US-MoS₂) grown on N-doped graphene (NG) sheets can be obtained. US-MoS₂@NG with small MoS₂ nanosheets lateral size of 10~50 nm is able to deliver higher rate performance (416 mAh/g @0.1 A/g; 141 mAh/g at 12.8 A/g) than FL-MoS₂@NG with MoS₂ nanosheets lateral size of 50-100 nm (393 mAh/g @0.1 A/g; 86

mAh/g at 12.8 A/g) and DL-MoS₂@NG with MoS₂ nanosheets lateral size of 100-400 nm (384 mAh/g @0.1 A/g; 38 mAh/g at 12.8 A/g), while US-MoS₂@NG also exhibits improved cycling stability than the other two counterparts due to the faster electrochemical kinetics.^[40]

Figure 2.8. (a) Transmission electron microscope image of yolk-shell FeS@C nanospheres, (b) cycling performance at 100 mA/g for micro-FeS, core-shell FeS/C nanospheres and yolk-shell FeS@C nanospheres. (c) Scanning electron microscope image of Bi_{0.94}Sb_{1.06}S₃ nanorod clusters, (d) cycling stability of Bi_{0.94}Sb_{1.06}S₃-graphite, Sb₂S₃-graphite, and Bi₂S₃-graphite electrodes at 1 A/g. Figure (a-b) is reproduced from reference [23] with permission from Nature publishing group. Figure (c-d) is reproduced from reference [47] with permission from ACS publications.

The other way is to design hierarchical nanostructures with hollow interiors, which can provide internal space for the volume expansion, thus enhancing the cycling stability.^[41] With theoretical volume change of ~ 280% when applied as SIB anode, the cycling stability of FeS₂ itself is quite limited, with capacity retention of ~ 30% after 600 cycles.^[42] Carbon coated FeS₂ with hollow interiors are able to deliver capacity of 560 mAh/g at 100 mA/g and 403 mAh/g at 5 A/g, which is much higher than the carbon coated FeS₂ counterparts

without hollow interiors (~ 510 mAh/g at 100 mA/g and ~ 240 mAh/g at 5 A/g). The cycling stability of carbon coated FeS_2 with hollow interiors are also superior, maintaining capacity of ~ 330 mAh/g at 2 A/g after 800 cycles, while the capacity of carbon coated FeS_2 without hollow interiors decayed to only ~ 120 mAh/g after 800 cycles.^[43] Another example is FeS with theoretical volume expansion of $\sim 170\%$. The nanosize FeS@C with yolk-shell structure has void space of 20 nm as shown in Fig. 2.8a, which is sufficient to sustain $\sim 170\%$ volume change of the FeS core. As a result, yolk-shell FeS@C is able to deliver notably enhanced rate performance (621 mAh/g at 100 mA/g and 452 mAh/g at 2500 mA/g) than the core-shell FeS/C (~ 380 mAh/g at 2500 mA/g) and the micro-sized FeS counterparts (~ 380 mAh/g at 2500 mA/g). The cycling stability of FeS@C ($\sim 67.6\%$ after 300 cycles) is also superior than FeS/C ($\sim 55\%$ after 100 cycles) and micro-FeS ($\sim 37.8\%$ after 300 cycles) as shown in Fig. 2.8b, confirming the importance of structure design and size control of electrode materials to improve the electrochemical kinetics and cycling stability of SIB anode materials.^[23]

Incorporating conductive and stable carbon materials as another strategy could facilitate not just the electron transfer but also buffer the stress caused by volume changes, thus enhancing the rate performance and cycling retention.^[44] By incorporating carbon layers, MoS_2/C composite is able to deliver higher rate performance (227 mAh/g at 200 mA/g and 120 mAh/g at 10 A/g) than the bulk MoS_2 (~ 170 mAh/g at 200 mA/g and ~ 50 mAh/g at 10 A/g) due to more active sites and higher stability.^[45] When interconnected with graphene and carbon nanotubes, the WS_2/C nanocomposites deliver high specific capacity (393 mAh/g at 100 mA/g and 81 mAh/g at 5 A/g) with excellent cycling stability ($> 80\%$ after 300 cycles), which is superior to the specific capacity (~ 330 mAh/g at 100 mA/g) and cycling stability ($\sim 21\%$ after 300 cycles) of pure WS_2 . The enhanced electrochemical performance of WS_2/C nanocomposites is due to the stable structure and accommodated volume change.^[31]

Other than the above mentioned typical methods, utilization of bimetallic sulfides instead of monometallic sulfides can be another effective approach. The cycling stability of bimetallic sulfides can be better than monometallic sulfides when applied as anode

materials for SIB.^[46, 47] Upon first cycle electrochemical conversion reaction, finely distributed nanocomposites composed of respective nanosize metal sulfides will be formed with reduced Na^+ diffusion length and buffering effect, alleviating stress caused by volume changes, thus delivering improved cycling stability.^[48] For example as shown in Fig. 2.8(c-d), $\text{Bi}_{0.94}\text{Sb}_{1.06}\text{S}_3$ solid solution was synthesized with nanorod cluster morphology. When coupled with graphite, the $\text{Bi}_{0.94}\text{Sb}_{1.06}\text{S}_3$ -graphite composite exhibits superior capacity retention of $\sim 79\%$ after 200 cycles as compared to Bi_2S_3 -graphite (58%) and Sb_2S_3 -graphite (10%) due to reduced polarization and improved reversibility.^[47] Also, the yolk shell structured $(\text{Fe}_{0.5}\text{Ni}_{0.5})_9\text{S}_8$ is able to deliver higher capacity (601 mAh/g at 100 mA/g and 465 mAh/g at 5 A/g) and better cycling stability ($\sim 99\%$ after 100 cycles) than the yolk shell structured Fe sulfide (426 mAh/g at 100 mA/g; 82.39% after 80 cycles) and Co sulfide counterparts (563 mAh/g at 100 mA/g; 52% after 80 cycles) due to the multicomponent sulfide composition.^[46]

Figure 2.9. (a) Rate performance comparison of MoS₂ with different interlayer spacings. (b-d) high resolution transmission electron microscope images of MoS₂ with different interlayer spacing values. The figure is reproduced from reference [50] with permission from Elsevier.

Aside from the morphology, structure and composition of the electrode materials that matters, the crystal structure also plays an important role in electrochemical reactions. Host materials with open frameworks allow fast insertion of Na^+ with relatively small volume change, thus improving Na storage capability.^[4, 21, 49] Layered MoS_2 is able to accommodate reversible Na^+ intercalation and de-intercalation within the layers without significant volume change.^[24] As shown in Fig. 2.9c-d, by modifying synthesis process, CG- MoS_2 (well crystalline MoS_2) and FG- MoS_2 (graphene-like MoS_2 nanoflowers) can be prepared with enlarged interlayer spacings than the bulk MoS_2 . The increased rate performance along with the expanded interlayer spacings of MoS_2 based electrode materials ($d_{(002)}$ of 0.62, 0.64 and 0.67 nm) as shown in Fig. 2.9a indicates the faster electrochemical kinetics enabled by larger interlayer distance.^[50] Another example is that by expanding the layer distance of graphite from 3.4 Å to 4.3 Å, specific capacity of expanded graphite can be greatly enhanced from ~ 13 mAh/g to 284 mAh/g.^[14] Since the electrochemical reaction of bimetallic sulfides often includes initial intercalation of Na^+ ,^[6, 51] bimetallic sulfides with open framework are believed to be promising SIB anode materials with superior electrochemical performance.

In a nutshell, in order to obtain SIB anodes with fast and stable Na ion storage capabilities, nanostructured bimetallic sulfides with open crystal framework are to be prepared, which is expected to be realized by direct synthesis or sulfidation of bimetallic precursors with open frameworks so as to allow fast electrochemical kinetics and stable Na^+ storage performance. Necessary treatments/modifications of morphology, and carbon incorporation processes are also to be included to further boost the electrochemical performance.

2.3 Materials systems of interest

2.3.1 NiMn Layered double hydroxides

Figure 2.10. The structure of layered double hydroxides. The figure is reproduced from reference [55] with permission from Royal Society of Chemistry. Here the interlayer anions are predominantly CO_3^{2-} as the hydrolysis of commonly used alkaline source (e.g. urea, hexamethylenetetramine) will release carbonate anions, which have stronger affinity with metal hydroxide slabs than other anions. The presence of carbonate anions maintains the high crystallinity of LDHs yet impedes exfoliation of metal hydroxide layers,^[52] thus the interlayer CO_3^{2-} anions are often exchanged with other anions species, e.g. nitrate, chloride or perchlorate anions before LDHs exfoliation.^[53]

Similar with graphite and MoS_2 , layered double hydroxides (LDHs) as multi-metal clay materials also have layered structures.^[54] As shown in Fig. 2.10, LDHs consist of positively charged metal hydroxide slabs intercalated with charge compensating anions and/or water molecules.^[52, 55] The interlayer spacings of LDHs are normally 0.75-0.8 nm,^[56, 57] which is also tunable by exchanging the intercalated anions.^[58] The composition of LDHs can be generally expressed in a formula as: $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{A}^{n-}]_{x/n} \cdot z\text{H}_2\text{O}$, in which M^{2+} and M^{3+} are metal cations (M^{2+} can be Mg^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} etc. whereas M^{3+} can be Al^{3+} , Fe^{3+} , Mn^{3+} etc.) and A^{n-} is the intercalated charge compensating anions.^[54, 59, 60] In addition to the layered structure, LDHs also have tunable compositions with x (x =molar ratio of

$M^{3+}/M^{2+}+M^{3+}$) generally in the range of 0.2-0.33.^[55] The tunable composition, layered crystal structure with large interlayer spacings and uniform dispersion of cations in host layers have endowed extensive applications of LDHs in electro-catalysts, supercapacitors and sorbents etc.^[36, 54, 57, 60] Several typical LDHs-based composites as supercapacitor electrodes with different electrochemical performance have been listed in Table 2.1.

Table 2.1. Electrochemical performance of electrode materials based on different LDHs.

Materials	Specific C_{sp} (F/g)	Rate	Ref.
NiMn LDH/CNT	2960@ 1.5A/g	2338@30A/g	[57]
NiCo LDH/CNT	2046@ 1A/g	1335@15A/g	[61]
CoMn LDH@CC	1079@2.1	891@42A/g	[56]
CoAl LDH@GO	581.6@2A/g	-	[62]
NiFe LDH@Ni	2708@5A/g	1456@10A/g	[63]
NiAl LDH@G	1255.8@1A/g	755.6@6A/g	[64]
NiZn LDH	1320@1A/g	580@20A/g	[65]
MgAl LDH@rGO	1334@1A/g	~626@10A/g	[66]

CNT: carbon nanotube; CC: carbon cloth; GO: graphene oxide

As can be seen from the table above, different LDHs-based composites deliver varied electrochemical performances. When Ni is incorporated in the LDH, high performance can be expected due to the high electrochemical activity of Ni^{2+} ,^[67] while incorporation of electrochemically inactive Al^{3+} often results in inferior electrochemical performance. Among the LDH-based composites listed in the table, NiMn LDH/CNT is able to deliver superior electrochemical performance with capacitance approaching 3000 F/g and extraordinary rate performance (2338 F/g at 30 A/g),^[57] superior than other LDH-based composites listed in Table 2.1. The superiority of NiMn LDHs over other LDHs is enabled by the half-metallic nature of NiMn LDH with higher carrier mobility and the reduced hydrogen desorption energy (0.439 eV) compared to $Ni(OH)_2$ counterparts (0.539 eV). The half-metallic nature of NiMn LDHs originates from the hybridization of Ni 3d, Mn 3d and O 2p orbitals, resulting in increased spin-up density of states.^[57]

Aside from being applied as supercapacitor electrode materials, LDHs can also be the precursor for preparation of various nanostructured bimetallic compound, e.g. $\text{NiCo}_2\text{S}_4/\text{Ni}_{0.96}\text{S}$ nanoparticles^[68] and NiCo_2O_4 nanoneedles.^[69] In addition, metal sulfides obtained by sulfidation of metal oxides counterparts has been shown to be more electronically conductive with reduced bandgap.^[70]

Table 2.2. Summary of the properties of some typical metal sulfides. The data is from reference [71] with permission from Elsevier.

	Resistance	Crystal structure	Lattice parameter
CoS_2	Metallic $2\text{E-}4 \text{ } \Omega/\text{cm}$	cubic	$5.5 \text{ \AA}$
NiS_2	Semi-conductor $0.6 \text{ } \Omega/\text{cm}$	cubic	$5.7 \text{ \AA}$
FeS_2	Semi-conductor $1.74 \text{ } \Omega/\text{cm}$	cubic	$5.4 \text{ \AA}$
MnS_2	Semi-conductor	cubic	$6.1 \text{ \AA}$
MoS_2/WS_2	Semi-conductor	hexagonal	
TiS_2	Metallic	hexagonal	

The electronic conductivity, crystal structure and lattice parameter of some typical metal sulfides are tabulated as shown in Table 2.2. It can be seen that NiS_2 and MnS_2 share the same cubic crystal structure with similar lattice parameters (NiS_2 $5.7 \text{ \AA}$; MnS_2 $6.1 \text{ \AA}$),^[71] which is indicative of bimetallic NiMn sulfide solid solution formation. Thus it is expected that by sulfidation of NiMn LDHs, nanostructured NiMn bimetallic sulfides can be formed with enhanced electronic conductivity and the open framework of NiMn LDH can be preserved, delivering improved electrochemical performance as SIB anodes.

2.3.2 CoFe Prussian blue analogues

Figure 2.11. Crystal structure of Prussian blue analogues. The figure is reproduced from reference [73] with permission from Royal Society of Chemistry.

Prussian blue with open host framework is in fact ferric ferricyanide ($\text{Fe}^{\text{III}}_4 [\text{Fe}^{\text{II}}(\text{CN})_6]_3$) with Fe^{3+} and Fe^{2+} coordinated to carbon and nitrogen, respectively, while $\text{KFeFe}(\text{CN})_6$ can also be formed at the presence of excess potassium ions.^[72, 73] Prussian blue analogues (PBs) on the other hand, can be formed with various compositions by replacing K^+ , Fe^{2+} or Fe^{3+} with other metal ions, forming MFe PBs ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{etc.}$).^[74, 75] As shown in Fig. 2.11, unlike LDHs with layered structure, PBs (normally hexacyanoferrates) often have three dimensional cubic crystal structure with tunable compositions (the molar ratio between $\text{M}:\text{Fe}$ is normally 0.75~3) and large interstitial sites (size of subcubes of ~ 0.5 nm) that allow fast and reversible alkaline ions accommodation.^[49, 76, 77] For example, pure $\text{Na}_{1.72}\text{MnFe}(\text{CN})_6$ is able to deliver excellent rate performance (~ 118 mAh/g at 0.1C and 45 mAh/g at 40C) albeit poor electronic conductivity.^[74] In addition, PBs can be prepared simply in aqueous solution without thermal input, with formation of monodispersed nanocubes.^[73, 78] Thus they have also been applied as precursor for preparation of various nanostructures including porous Fe_2O_3 microboxes,^[79] $\text{Co}_{0.59}\text{Fe}_{0.41}\text{P}$ nanocubes^[77] and NiS nanoframes^[80].

Figure 2.12. Crystal structure of (a) CoS₂; brown dot: Co, yellow dot: S; (b) FeS₂; blue dot: Fe, yellow dot: S. Figure (a) is reproduced from reference [82c] with permission from IOP publishing group. Figure (b) is reproduced from reference [42] with permission from Royal Society of Chemistry.

As noticed from table 2.2, CoS₂, NiS₂ and MnS₂ both have the same cubic crystal structures with FeS₂, among which CoS₂ has the closest lattice parameters (5.5 Å) to that of FeS₂ (5.4 Å).^[71] The crystal structure of CoS₂ belongs to the cubic phase pyrite type with space group Pa-3.^[81] As shown in Fig. 2.12a, in CoS₂, The Co²⁺ cations are located at the face centered cubic lattice, which are paired with S₂²⁻ anions in the lattice.^[82] Similarly, pyrite FeS₂ are also in a cubic phase with space group of Pa-3 with Fe cations occupying the face centered cubic lattice as shown in Fig. 2.12b.^[42] Thus it has been reported that CoS₂ and FeS₂ can form pyrite Co_xFe_{1-x}S₂ (x < 0.5) solid solution with cubic crystal structure.^[83]

In addition to similar crystal lattice parameter with FeS₂, CoS₂ with metallic behavior also have relatively higher electronic conductivity than other metal sulfides.^[71] Thus it is expected that CoFe PB nanocubes precursor can also be applied as the bimetallic precursor for preparation of nanostructured CoFe bimetallic sulfides solid solutions that maintains the large interstitial sites for Na⁺ accommodations, delivering improved Na⁺ storage capabilities.

2.3.3 Cu₂MoS₄ layered bimetallic sulfide

Figure 2.13. Crystal structure of (a) MoS₂ (2H phase) and (b) Cu₂MoS₄ (I phase). Figure (a) is reproduced from reference [84] with permission from Elsevier. Figure (b) is reproduced from reference [88] with permission from Wiley online library.

Aside from sulfidation of bimetallic precursors with open frameworks, bimetallic sulfides with open framework can also be directly prepared. As shown in Fig. 2.13a, MoS₂ has a layered structure that allows fast and reversible Na⁺ intercalation/de-intercalation within the interlayers.^[21, 84] However, the poor electronic conductivity and large volume change upon deep sodiation often leads to limited electrochemical performance of MoS₂ as anode materials for SIB.^[85] Thus Mo-based layered bimetallic sulfides are envisaged as possible solutions towards improved electrochemical performance.

Bimetallic chevrel phase M_xMo₆S_{8-y} (M=Cu, Ni, Co, Fe, Ag, Cr) have been developed with high electronic conductivity and high Li diffusion coefficient.^[86] Chevrel phase compounds of rhombohedral or hexagonal structure have three dimensional frameworks consisting of nearly cubic Mo₆S₈ clusters with large intercalation sites in between for uptake of guest species.^[87] However, poor cycling stability was observed for Cu₄Mo₆S₈ and AgMo₆S₈ due to the formation of unstable Mo₆S₈, while Ni₂Mo₆S_{7.9}, Fe_{1.25}Mo₆S_{7.8}, Co_{1.6}Mo₆S_{7.7} and Cr_{1.3}Mo₆S_{7.7} often suffers from low capacity (below 100 mAh/g).^[87] In addition, these chevrel phase compounds are often prepared at harsh conditions ($\geq 1000^{\circ}\text{C}$) with long duration of several days.^[87] On the other hand, another type of Mo-based bimetallic sulfide Cu₂MoS₄ have layered structure with two allotropes, the P phase (Pm42 space group) and I phase (Im42 space group), while both phase have tetragonal crystal

structure with large interlayer spacings.^[86, 88] P-phase Cu_2MoS_4 has been applied as anode materials for LIB, however, poor electrochemical performance was observed at large voltage window. Although better stability can be achieved at restricted voltage window of 1.5~2.8V, the realized capacity is quite low ($\sim 100 \text{ mAh/g}$).^[89]

As shown in Fig. 2.13b, similar to MoS_2 , bimetallic sulfides Cu_2MoS_4 (CMS) also have large inter-layer spacings ($5.12 \text{ \AA}$ for tetragonal I-42m symmetry).^[88, 90] This interlayer spacings are already larger than the size of Na^+ ($1.02 \text{ \AA}$) and the interlayer spacings of expanded graphite ($4.3 \text{ \AA}$).^[1, 14] Thus it is hypothesized that nanostructured and layered CMS is able to deliver excellent Na^+ storage properties with extended cycling life.

2.4 Thesis in context of literatures.

Based on the above discussion, nanostructured bimetallic sulfide solid solutions with open frameworks and incorporation of carbon materials are regarded as promising and advanced SIB anodes materials with high capacity, fast electrochemical kinetics and stable cycling stability. Such advanced SIB anodes were to be prepared either by sulfidation of bimetallic precursors with open frameworks or by direct preparation of bimetallic sulfides with open frameworks. During the synthesis, necessary structure design and carbon incorporation were to be incorporated as well.

Considering the large interlayer spacings, tunable compositions and half-metallic nature of NiMn LDHs as well as the similar crystal parameters of NiS_2 and MnS_2 ,^[54, 55, 57, 71] NiMn LDHs are to be sulfidized, forming bimetallic NiMn sulfide solid solutions preserving the layered structure of NiMn LDHs precursors. Negatively charged graphene oxide nanosheets are to be introduced,^[91] which is able to absorb the metal cations and anchor the growth of LDH.^[92]

Following NiMn LDHs with layered structure, CoFe PBs with large interstitial sites and tunable compositions are also materials of interests.^[49, 76, 77] In addition, the crystal parameters of metallic CoS_2 are closer to FeS_2 than other metal sulfides listed in Table

2.2.^[71] Thus CoFe PBs are to be sulfidized toward formation of nanostructured bimetallic CoFe bimetallic sulfide solid solutions, maintaining the open frameworks of bimetallic CoFe PBs. Poly-dopamine as a carbon source can provide amorphous carbon coating layer on nanostructures after thermal annealing.^[93] Since the PBs can easily form nanocubes,^[73, 78] poly-dopamine coating on the nanocubes surface is expected to preserve the CoFe PBs during thermal-assisted sulfidation and provide a conductive layer to facilitate the charge transfer.

Alternatively, instead of starting from bimetallic precursors with open frameworks for subsequent sulfidation, bimetallic CMS with layered structure are to be synthesized. nanostructured Cu_2MoS_4 with layer structure are to be prepared towards fast and stable SIB anode. Since the growth of CMS is a multistep process including formation of nanoscale hollow spheres with subsequent sphere break up and Ostwald ripening towards the final formation of nanoplates,^[88] and glucose also as a carbon source was reported to be able to prevent growth of nanoparticles,^[94] it is thus expected that introduction of glucose is able to prevent the nanoscale hollow spheres from break up, forming nanoscale hollow spheres CMS.

With the above discussions, the detailed preparation process and parameters for respective materials systems will be elaborated in chapter 3 and subsequent result chapters. The physical/chemical properties of experimental products will be studied, and the electrochemical performance of these products as SIB anodes will be systematically investigated.

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Chapter 3

Experimental Methodology

Starting from NiMn Layered double hydroxides and CoFe Prussian Blue analogue bimetallic precursors with open frameworks, bimetallic sulfides were obtained after sulfidation and applied as sodium ion battery anodes. Directly prepared bimetallic sulfide Cu_2MoS_4 -based materials with large interlayer spacings were also studied as sodium ion battery anodes. Selection of these materials were briefly rationalized and the principles of different preparation methods were briefly introduced. The detailed preparation process and parameters for different samples were elaborated, involving necessary optimization process. The principles of different characterization methods including X-ray Diffraction, Scanning Electron Microscopy, Raman spectroscopy, X-ray Photoelectron Spectroscopy, three-electrode/half-cell testing, etc. to study the physical/chemical and electrochemical properties of different samples, were also introduced and discussed. The parameters for different characterization methods were also provided.

3.1 Rationale for selection

In this thesis, several different materials systems were investigated, with the purpose of obtaining nanostructured bimetallic sulfides with open frameworks to be applied as anode materials for sodium ion battery (SIB) application. The detailed rationalization of studying different materials systems can be found in Chapter 2 and is further elaborated in corresponding result chapters.

With open frameworks and tunable compositions, bimetallic precursors layered double hydroxides (LDHs) and Prussian blue analogues (PBs) offer large inter-layer spacings (~ 0.75 nm) and large interstitial sites (~ 0.5 nm) respectively.^[1, 2] NiMn LDHs were firstly selected as the open framework bimetallic precursor for sulfidation due to its half metallic nature together with large interlayer spacing (0.775 nm) and tunable compositions (molar ratio of Ni: Mn = 3~ 7).^[1, 3] It is hypothesized that after sulfidation the layered structure can be preserved while the electronic conductivity can be enhanced, leading to improved electrochemical performance for sodium ion batteries.

PBs with tunable compositions have large interstitial sites that allow Na^+ accommodation (Na^+ 1.02Å). PBs can be prepared simply in aqueous solution without thermal input, and can form monodispersed nanocubes.^[4] Metallic CoS_2 has relatively higher electronic conductivity than other metal sulfides, and shares similar crystal structure and lattice parameters with FeS_2 .^[5] It was also reported that CoS_2 and FeS_2 can form solid solution with various Co: Fe ratios.^[6] Thus CoFe PBs were selected as the open framework bimetallic precursor for the preparation of CoFe bimetallic sulfides. It is hypothesized that sulfidation of CoFe PB allows formation of solid solution CoFe bimetallic sulfides while preserving the large interstitial sites, benefitting the electrochemical performance of SIB anodes.

MoS_2 has a layered structure that allows fast and reversible Na^+ intercalation/de-intercalation within the interlayers.^[7] Similar to MoS_2 , bimetallic sulfides Cu_2MoS_4 (CMS) has large inter-layer spacings (~ 0.5 nm) that allows insertion/extraction of alkaline ions.^[8]

^{9]} It is known that MoS₂ suffered from limited cycling stability due to the large volume change upon deep discharge,^[10] which is calculated to be ~ 194% (based on the molar mass and density of Na₂S, Mo and MoS₂). Bimetallic sulfides, on the contrary, can form distributed nanocomposites with buffer effect after first cycle, delivering improved cycling stability.^[11] Bimetallic chevre phase M_xMo₆S_{8-y} (M=Cu, Ni, Co, Fe, Ag, Cr) have been developed for Li ion storage, however harsh preparation conditions with limited capacity and poor stability were often encountered.^[12] Thus it is hypothesized that CMS is able to deliver excellent Na⁺ storage properties with extended cycling life.

3.1.1 Hydrothermal/solvothermal reactions

Figure 3.1 Schematic of the hydrothermal autoclaves used for material preparation in this thesis. The figure and table are adapted from the user manual (249M 4744-49 Acid Digestion Vessels Operating Instructions) provided by Parr Instrument Company. <https://www.parrinst.com/> Last accessed May, 2018.

In this thesis, hydrothermal autoclaves were intensively used for the preparation/sulfidation of different samples either in aqueous solution (hydrothermal reaction) or in ethylene glycol solution (solvothermal reaction). The schematics of the hydrothermal autoclaves used in this thesis are presented in **Fig. 3.1**. By use of hydrothermal autoclaves, high temperature and high pressure can be established within an enclosed environment, which allows reflux and transfer of various species, leading to the uniform crystallization and growth of nanostructures. The detailed preparation procedure of different samples can be found in Section 3.2.

3.1.2 Room temperature wet chemical synthesis

In wet chemical synthesis process at room temperature, precursor species are homogeneously dissolved in the solution, allowing the uniform precipitation of nanostructures without thermal treatment. Preparation of PB/ polydopamine coated PB (PBPDA) was accomplished by room temperature wet chemical synthesis. PB was accomplished by ageing the solution containing $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; sodium citrate dihydrate and $\text{K}_3\text{Fe}(\text{CN})_6$ for 10 hours. Sodium citrate dihydrate as chelating agent slows down the nucleation process and controls the crystal growth, forming monodisperse nanocubes.^[13]

Coating of PDA on PB precursors was achieved by polymerization of dopamine chloride monomers in buffer solution (pH~8.5). With magnetic stirring, dopamine chloride was uniformly polymerized on the surface of the PB nanocubes, forming PBPDA precursors for subsequent sulfidation in the furnace. The detailed preparation process of PB/PBPDA can be found in Section 3.2.3.

3.1.3 Thermal annealing/sulfidation

Figure 3.2 Schematic of thermal sulfidation using chemical vapor transport method

Sulfidation of PB and PBPDA was accomplished at elevated temperature in a tube furnace. Thiourea as the sulfidation agent was placed at the upstream while the PB/PBPDA to be sulfidized were placed at the downstream of a crucible. As shown in Fig. 3.2, Ar was used as the carrier gas as well as protection gas to isolate the ambient atmosphere. As the temperature slowly increases, thiourea will decompose and release H_2S gas,^[14] which can be carried by Ar to react with the PB/PBPDA samples. As a result, PB/PBPDA will be sulfidized with formation of multiphase metal sulfides.

3.2 Synthesis

3.2.1 Preparation of NS, NMS and NMGS

Chemicals used for preparation of NS (multiphase Ni sulfides), NMS (Mn-doped multiphase Ni sulfides) and NMGS (NMS/ reduced graphene oxide composites) include $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, hexamethylenetetramine (HMTA) and thioacetamide (TAA).

Table 3.1 Sample preparation of NS, NMS and NMGS

Sample preparation	Sample name	Abbreviation
Sulfidation of NiMn LDH	Mn-doped multiphase Ni sulfides	NMS
Sulfidation of Ni hydroxide	Multiphase Ni sulfides	NS
Sulfidation of NiMn LDH/GO composite; (GO 1.0 mg/mL)	Mn-doped multiphase Ni sulfides/rGO composites	NMGS

As can be seen in Table 3.1, NMS were prepared by sulfidation of NiMn layered double hydroxides (LDHs), while NS were prepared in a similar procedure without addition of Mn salts ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) in precursor solution. The preparation flowchart of NMGS can be found in Fig. 3.3. With introduction of graphene oxide (GO), after two steps hydrothermal reactions, NMGS can be obtained.

Figure 3.3. Preparation procedure of NMGS.

With the purpose of optimizing electrochemical performance, the concentration of GO added in the precursor solution were adjusted while the other preparation conditions remained the same. The sample preparation of NMGS1, NMGS2 and NMGS4 can be found in Table 3.2. The detailed preparation steps and preparation parameters of various samples

can be found in chapter 4 experimental section.

Table 3.2 Sample preparation of NMGS1, NMGS2 and NMGS4.

Sample preparation	Abbreviation
Sulfidation of NiMn LDH/GO composite; GO (0.5 mg/mL)	NMGS1
Sulfidation of NiMn LDH/GO composite; GO (1 mg/mL)	NMGS2
Sulfidation of NiMn LDH/GO composite; GO (2 mg/mL)	NMGS4

3.2.2 Preparation of CoFe PB, PBS and PBCS

Chemicals used for preparation of CoFe PB (Prussian blue analogues), PBS (sulfidized PB) and PBCS (carbon coated sulfidized PB) include $K_3Fe(CN)_6$, $CoCl_2 \cdot 6H_2O$, sodium citrate dihydrate, thiourea, dopamine chloride and buffer solution.

Figure 3.4. Preparation procedure of CoFe PB, PBS and PBCS.

As shown in Fig. 3.4a, CoFe PBs were prepared by wet chemical synthesis without thermal input. Afterwards, poly-dopamine (PDA) was coated onto the surface of CoFe PB in buffer solution, forming PBPDA. PB/PBPDA were sulfidized using thermal assisted sulfidation in tube furnace as schemed in Fig. 3.2, obtaining PBS and PBCS as shown in Fig. 3.4b.

The feeding ratio between Co salts ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and Fe salts ($\text{K}_3\text{Fe}(\text{CN})_6$) were adjusted to optimize the electrochemical performance. As shown in Table 3.3, PB4-1, PB3-1, PB3-2, PB3-4 and Fe PB were prepared with different Co: Fe feeding ratio, which were sulfidized into PB4-1S, PB4-1S, PB3-1S, PB3-2S, PB1-2S and Fe PBS, respectively. The amount of dopamine chloride added was also optimized, as shown in Table 3.4, with increased amount of dopamine chloride added, PBPDA2-1, PBPDA1-1, PBPDA2-3 and PBPDA1-2 can be obtained, which were sulfidized into PBC2-1S, PBC1-1S, PBC2-3S and PBC1-2S, respectively. Detailed preparation process can be found in Chapter 5 experimental section.

Table 3.3. Sample preparation of PB and PBS.

Sample preparation	Sample name	Sample preparation	Sample name
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$: $\text{K}_3\text{Fe}(\text{CN})_6$ = 4:1	PB4-1	Sulfidation of PB4-1	PB4-1S
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$: $\text{K}_3\text{Fe}(\text{CN})_6$ = 3:1	PB3-1	Sulfidation of PB3-1	PB3-1S
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$: $\text{K}_3\text{Fe}(\text{CN})_6$ = 3:2	PB3-2	Sulfidation of PB3-2	PB3-2S
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$: $\text{K}_3\text{Fe}(\text{CN})_6$ = 3:4	PB3-4	Sulfidation of PB3-4	PB3-4S
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$: $\text{K}_3\text{Fe}(\text{CN})_6$ = 3:1	Fe PB	Sulfidation of Fe PB	Fe PBS

Table 3.4. Sample preparation of PBCS.

Sample preparation	Sample name	Sample preparation	Sample name
PB3-1 coated with PDA; (PB3-1: dopamine chloride weight ratio= 2:1)	PBPDA2-1	Sulfidation of PBPDA2-1	PBC2-1S
PB3-1 coated with PDA; (PB3-1: dopamine chloride weight ratio= 1:1)	PBPDA1-1	Sulfidation of PBPDA1-1	PBC1-1S
PB3-1 coated with PDA; (PB3-1: dopamine chloride weight ratio= 2:3)	PBPDA2-3	Sulfidation of PBPDA2-3	PBC2-3S
PB3-1 coated with PDA; (PB3-1: dopamine chloride weight ratio= 1:2)	PBPDA1-2	Sulfidation of PBPDA1-2	PBC1-2S

3.2.3 Preparation of CMS, CMS1 and CMS1-rGO and NVP

Chemicals used for preparation of CMS (Cu_2MoS_4 nanoplates), CMS1 (Cu_2MoS_4 nanospheres) and CMS1-rGO (CMS1/reduced graphene oxide composite) include

$\text{CuCl}_2 \cdot \text{H}_2\text{O}$, poly(vinyl pyrrolidone) (PVP), NaOH, ascorbic acid, sodium molybdate (Na_2MoO_4), TAA, glucose and ethylene glycol.

As shown in Fig. 3.5a, Cu_2O nanospheres were firstly prepared as the sacrificial template based on previous reports.^[8] Subsequently, Cu_2O nanospheres were mixed with Na_2MoO_4 , TAA and glucose in ethylene glycol for preparation of CMS1 as shown in Fig. 3.5b. GO was also introduced to mix with CMS1, forming CMS1-rGO after second step solvothermal reactions.

Figure 3.5. Preparation procedure of CMS, CMS1 and CMS1-rGO.

The amount of glucose added was adjusted to improve the electrochemical performance of CMS. As shown in Table 3.5, with increased amount of glucose added, CMS0.5, CMS1 and CMS2 can be obtained.

Table 3.5. Sample preparation of CMS, CMS0.5, CMS1 and CMS2.

Sample preparation	Sample name
$\text{Cu}_2\text{O} + \text{Na}_2\text{MoO}_4 + \text{TAA}$; No glucose added	CMS
$\text{Cu}_2\text{O} + \text{Na}_2\text{MoO}_4 + \text{TAA}$; 60 mg Glucose added	CMS0.5
$\text{Cu}_2\text{O} + \text{Na}_2\text{MoO}_4 + \text{TAA}$; 120 mg Glucose added	CMS1
$\text{Cu}_2\text{O} + \text{Na}_2\text{MoO}_4 + \text{TAA}$; 240 mg Glucose added	CMS2

The duration of second step solvothermal reactions were also optimized. As shown in Table 3.6, with increased duration of second step solvothermal reactions, CMS1-rGO(4), CMS1-rGO(8) and CMS1-rGO(12) were obtained. Na₃V₂(PO₄)₃-based cathode (NVP) was also prepared to couple with the optimized anode materials for sodium ion battery full cell assembly. The detailed preparation procedure and parameters can be found in Chapter 6 experimental section.

Table 3.6. Sample preparation of CMS1-rGO(4), CMS1-rGO(8) and CMS1-rGO(12).

Sample preparation	Sample name
CMS1+ GO; 4 hours	CMS1-rGO(4)
CMS1+ GO; 8 hours	CMS1-rGO(8)
CMS1+ GO; 12 hours	CMS1-rGO(12)

3.3 Characterization

3.3.1 X-ray diffraction

The X-ray diffraction XRD (Cu K α -radiation ($\lambda = 1.5406 \text{ \AA}$); Shimadzu powder diffractometer) technique was applied to detect the crystal structure of the samples. It can be used to reveal the crystalline phases, the crystalline phase composition in the sample, the lattice parameters, etc. Also, it can be used to detect the lattice expansion or shrink through the shift of diffraction peaks.

Figure 3.6 Interaction between incident X-rays with crystal planes. The figure is reproduced from reference [15] with permission from John Wiley & Sons.

Generally, this technique was based on Bragg's law as follows:

$$n \cdot \lambda = 2d \sin \theta$$

As seen in **Fig. 3.6**, the incident parallel X-rays will be reflected by successive crystal planes. When the angle between the incident X-rays and series of crystal planes is θ , the reflected X-rays will have a phase difference ($\Delta_1 + \Delta_2$) of $2d \sin \theta$.^[15] In the case that the phase difference is the whole number of the X-ray wavelength (Bragg's law), the diffracted X-rays will be reinforced, which can be reflected in the X-ray diffraction patterns. The peak intensity ratio and peak width can reflect the crystal plane orientation and crystal size. In this thesis, XRD is used for detection of crystal compositions in different samples.

3.3.2 Scanning Electron Microscope

Scanning electron microscope (SEM, JEOL 7600F) was used to observe the microstructure and morphology of the samples. Energy dispersive X-ray spectroscopy (EDX) mode was also applied to investigate the elemental distribution in the samples.

In SEM, the electron source was focused into a beam by the apertures and the lens as shown in **Fig. 3.7**. When electron beams impinge the samples, aside from absorbed electrons, transmitted electrons and emitted visible light, other kinds of signals will be produced, including secondary electrons, backscattered electrons and characteristic X-rays.^[16] The

secondary electrons intensity can be affected by the angle between the beams and the sample surface, i.e. topography, thus secondary electrons image (SEI) can be used to reveal the surface morphology. The intensity of backscattered electron depends on the atomic weight, thus backscattered electron image (BEI) can be applied to check the elements distribution by contrast. Heavier elements will appear darker in BEI mode. The characteristic X-rays detected are dependent on the atomic structure and the intensity relies on the number of atoms, thus EDX analysis can reflect elements proportion and also distribution in the samples. In this thesis, SEI mode and EDX mode were applied to reveal the morphology, element composition and element distribution in the samples.

Figure 3.7 Configuration of Scanning Electron Microscope instrument. The figure is reproduced from reference [16] with permission from Springer.

3.3.3 Transmission Electron Microscope

Transmission electron microscope (TEM, JEOL 2010 UHR) was applied to reveal the fine structures of the samples at high magnifications.

Figure 3.8 Configuration of Transmission Electron Microscope. The figure is adapted from ammrf (Australian Microscopy and Microanalysis Research Facility). Last Accessed May, 2018. <http://www.ammrf.org.au/myscope/tem/background/concepts/imagegeneration/diffraction/fourier.php>.

In TEM techniques, electron sources are accelerated by high voltage (200 kV) and focused by several electromagnetic lens. Unlike optical microscope or SEM, the light source in TEM is the high energy electron beams with very small wavelength, improving resolution in TEM to less than 1 nanometer. High energy electrons will transmit through ultrathin samples to the fluorescent screen, which can be captured by a CCD camera. In this way, sample preparation should be carefully conducted to allow the transmission of electron beams. Due to the small wavelength of the high energy electron beams, the fine structures of samples can be unveiled, including lattice d-spacings, crystallinity and also morphology

at high magnifications. In this thesis, TEM was applied to reveal the lattice d-spacings and morphology of the samples at high magnifications. SAED mode was also used to analyze the crystallinity, different crystal phases and d-spacings of different crystal planes.

There are two common modes in TEM, the bright field (BF) mode and dark field (DF) mode. In BF mode, an aperture placed at the back focal plane of the objective lens can only allow the direct transmitted electrons to pass through and reach the image screen. As a result, the image captured in BF mode reflects the weakened electron beams caused by the interaction between electron beams and the samples, with thicker areas and heavier atoms appear darker. In DF mode, the aperture is shifted to block the direct beams and allow the diffracted beams to pass through and reach the image screen. Thus in this mode, the image contrast is ascribed to the crystal plane orientation differences. In this case, only those areas that can diffract the electron beams will appear brighter.

3.3.4 Raman Spectroscopy

Raman spectroscopy of the samples were collected to characterize the chemical states. Raman technique can be applied to investigate the vibrational, rotational, and other low-frequency modes in the materials based on inelastic scattering of monochromatic light. The light applied in our study is a monochromatic laser with a wavelength of 633 nm. The laser light will interact with the molecular vibrations, phonons or other excitations in the samples, leading to the shift of laser photons. This energy shift can be reflected in the Raman spectrum, demonstrating the vibrational information in the samples.

3.3.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) of samples were collected by the VG ESCA Lab XPS system with monochromatic Al K α X-ray ($h\nu = 1486.7$ eV), to investigate the elemental composition (quantitatively and qualitatively) and chemical bonds of samples. XPS is a surface technique which can only reflect the information at the top several nanometers of the samples. During the XPS measurements, the sample will be exposed to

a beam of X-rays, the kinetic energy will be measured and amount of electrons escaped will be recorded, reflecting the atomic structure and elemental composition/proportion. Thus XPS can be employed to analyze the element ratio, chemical state and element composition of samples. In this thesis, XPS was used to characterize the elemental composition, chemical binding, valence state of different elements and possible chemical interactions between different phases.

3.3.6 In situ X-ray absorption (XAS) measurement

Figure 3.9 Principle of XAS including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The figure is reproduced from reference [17] with permission from Royal Society of Chemistry.

XAS can be used to detect the chemical and coordination environment of different elements in different samples, regardless of the crystallinity of the samples.^[17] During XAS measurements, incident X-rays with tunable wavelength will be shined on materials of interest. When the energy of the X-rays is high enough to excite an electron into the continuum state, the X-rays absorption will be significantly enhanced, as shown in the XANES region in Fig. 3.9. The energy is dependent on the oxidation state and ligand symmetry of the absorbing atom. On the other hand, the excited photoelectron wave will be backscattered by surrounding atoms, leading to the oscillation in the EXAFS region.

Thus by analyzing XANES and EXAFS results, the chemical and coordination environment of different samples can be revealed.

3.3.7 Electrochemical testing and analysis

The electrochemical performance of different samples were evaluated in a CR2032 half-cell configuration. Na plate was used as both reference and counter electrode. Slurries containing active materials, carbon black and binder (polyvinylidene fluoride PVDF or carboxymethyl cellulose CMC) in weight ratio of 80:10:10 were prepared by overnight magnetic stirring. The working electrode was prepared by drop casting the slurries onto a precut copper foil as current collector, and dried in the oven at 70 °C overnight. The loading mass of the active materials was estimated to be ~ 1.0 mg. The half-cell was assembled in the glove box with both O₂ and H₂O level < 0.1 ppm. Before electrochemical testing, the assembled cells were aged overnight to allow electrolyte penetration as well as cell stabilization. Cyclic voltammetry (CV) measurements were conducted by Autolab with a scan rate of 0.1 mV/s in specified voltage range. The scan rate is quite slow due to the slow kinetics of the de/sodiation of the electrode materials. Electrochemical impedance spectroscopy (EIS) of different samples were also measured with AC voltage (amplitude 10 mV; frequency range 0.01~100 kHz) at open circuit voltage. The galvanostatic charge/discharge testing was conducted by the Neware battery-testing instrument at different current densities, to reveal the rate capability of the electrode materials. Cycling stability of different samples were also revealed by repeated GCD testing for certain number of cycles.

In this thesis, several types of electrolytes were employed, including 1M NaClO₄ in EC (ethylene carbonate): DMC (dimethyl carbonate) (v/v 1:1); 1M NaClO₄ in EC (ethylene carbonate): DMC (dimethyl carbonate) (v/v 1:1) with 5wt % FEC; 1 M NaCF₃SO₃ in diethylene glycol dimethyl ether (DEGDME) and 1M NaPF₆ in DEGDME. The use of different electrolytes were for different purposes, for example FEC additive was incorporated to improve the cycling stability of PB3-1S and PBC1-1S with formation of

stable solid electrolyte interphase. The purpose of using different electrolyte will be discussed in respective result chapters.

Galvanostatic intermittence titration techniques (GITT) were developed based on Fick's law of diffusion,^[18, 19] which can be applied for calculation of ion diffusion coefficient in planar electrodes,^[20] providing that the ion diffusion is one-dimensional without considering the ohmic potential drop, double layer charging or volume change.^[18] In our work, GITT was applied to calculate the Na⁺ diffusion coefficient of different samples. GITT was conducted by Autolab and the calculation was based on the following equation^[21]:

$$D = \frac{4L^2}{\pi\tau} \left(\frac{\Delta E_s}{\Delta E_t} \right)^2$$

in which t is the current pulse duration (s), τ is the relaxation time (s), and ΔE_s is the steady-state potential change induced by the current pulse. ΔE_t is the potential change during the constant current pulse after eliminating the IR drop. L is sodium ion diffusion length (cm), which is considered to be equal to electrode thickness for compact electrode. In our case, constant current pulse of 100 mA/g was applied with duration of 1200s while the relaxation time is 1800s.

For preparation of full cell, the cathode material NVP composites-based slurry was prepared in the same manner, and subsequently casted on aluminum foil, which was then coupled with the anode materials in Argon-filled glove box. The cathode: anode mass ratio in secondary battery cells will greatly affect the coulombic efficiency, rate performance and cycling stability of the full cell.^[22] For example in lithium ion batteries, excess cathode will lead to the deposition of Li on the anode while insufficient amount of cathode will lead to small capacity.^[23] The mass ratio of cathode: anode can be calculated based on full cell reactions. Taking LiNiO₂//graphite full cell as an example, the full cell reaction can be expressed as follows:

Thus the theoretical mass ratio between the cathode and the anode can be calculated to be 1.35.^[23] The theoretical mass ratio between the cathode and anode can also be calculated

based on the capacity of cathode and anode.^[24] Since the amount of charges (in C or mAh) passing through cathode and anode are the same, thus the mass ratio between cathode: anode can be estimated to the capacity ratio between anode (in mAh/g): cathode (in mAh/g). However, in practical cases due to decomposition of electrolyte and formation of secondary electrode interphase, the practical optimized cathode: anode ratio can be deviated from the theoretical value.^[23] In our case, the loading mass between the cathode NVP composites and anode active materials CMS1-rGO are balanced to obtain the optimized full cell performance. The electrolyte used for full cell assembly is 1M NaPF₆ in DEGDME unless otherwise stated.

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Chapter 4* NiMn Layered Double Hydroxide derived Sodium Ion Battery Anodes with Improved Cycling Stability

Bimetallic sulfides as promising sodium ion battery (SIB) anode materials have the advantages of high theoretical capacity and improved cycling stability. Nonetheless, large volume changes still apply upon de/sodiation, thus open framework bimetallic sulfides are proposed to host Na⁺ with limited volume change. NiMn layered double hydroxides (LDHs) with large interlayer spacing, tunable composition and half metallic nature are sulfidized with formation of Mn-doped multiphase Ni sulfides (NMS) nanoparticles. With higher electronic conductivity and larger sodium diffusion coefficient than the multiphase Ni sulfides (NS) nanoparticles, NMS is able to deliver better rate performance. With further incorporation of reduced graphene oxide (rGO), NMS nanoparticles anchored on the surface of rGO (NMGS) were obtained. The optimized NMGS can deliver specific capacity of 460.9 mAh/g at 50 mA/g, while retaining capacity of 169.4 mAh/g at 5000 mA/g, demonstrating good rate performance. In addition, when ether-based electrolyte (1M NaCF₃SO₃ in diethylene glycol dimethyl ether) is used, the rate performance and cycling stability of NMGS are improved, maintaining capacity of 229.2 mAh/g at 5000 mA/g and retaining capacity of 206.1 mAh/g at 500 mA/g after 2000 cycles. The high capacity, great rate performance with excellent cycling stability emphasizes the promising potential of NMGS as advanced SIB anodes.

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4.1 Introduction

Layered double hydroxides (LDHs) could serve as the bimetallic precursors with open frameworks. LDHs have hexagonal crystal structure with large interlayer spacing and tunable compositions.^[1, 2, 3] Among the LDHs, NiMn LDH is claimed to exhibit half-metallic nature enabled by the hybridization among Ni 3d, Mn 3d and O 2p orbitals, with lowered hydrogen de-sorption energy of 0.439 eV compared with 0.539 eV of Ni(OH)₂.^[2] Thus electrode materials based on NiMn LDH/carbon nanotubes composite is able to deliver superior specific electrochemical performance (2960 F/g @ 1.5 A/g; 2330 F/g @ 30 A/g) than other LDHs based electrode materials for supercapacitors as can be seen from Table 2.1 in chapter 2. Sulfidation of metal oxides has been shown to be effective in obtaining more electronically conductive metal sulfides (NiCo₂S₄ 3.41 Ω/cm^2 vs. NiCo₂O₄ 498 Ω/cm^2) with reduced bandgap (NiCo₂S₄ 2.5 eV vs. NiCo₂O₄ 3.6 eV).^[4, 5] Based on the above discussion, it is hypothesized that after sulfidation of NiMn LDH, NiMn bimetallic sulfides can be formed with enhanced electronic conductivity and the open framework of NiMn LDH can be preserved, delivering improved electrochemical performance as SIB anodes.

In this chapter, NiMn LDHs bimetallic precursors were sulfidized to obtain multiphase Mn-doped Ni sulfides (NMS) nanoparticles.^[6] However, the layered crystal structures of NiMn LDHs precursor could not be preserved. It is shown that the NMS possesses higher electronic conductivity, smaller charge transfer resistance and higher diffusion coefficient, leading to improved rate performance compared to pure multiphase Ni sulfides (NS). With the incorporation of rGO, the resultant multiphase Mn-doped Ni sulfides/rGO composites (NMGS) exhibit higher surface area and further reduced charge transfer resistance, resulting in a high capacity 460.9 mAh/g at a current density of 50 mA/g, high rate performance (169.4 mAh/g at 5 A/g), and good cycling stability (240.6 mAh/g after 150 cycles at 500 mA/g). When tested in ether-based electrolyte (1M NaCF₃SO₃ in diethylene glycol dimethyl ether), NMGS delivers further improved rate performance (229.2 mAh/g at 5 A/g) and excellent cycling stability with capacity of 206.1 mAh/g after 2000 cycles at 500 mA/g.

4.2 Experimental

4.2.1 Materials Preparation of NS, NMS and NMGS

Preparation of NS and NMS: Chemicals for sample preparation including $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, hexamethylenetetramine (HMTA) and thioacetamide (TAA) are used as purchased without further purification. NMS (Mn-doped multiphase Ni sulfides) were prepared by two-step hydrothermal reactions. Firstly, NiMn LDHs were prepared by hydrothermal reaction of 20 ml de-ionized water solution containing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (30 mM), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (10 mM) and HMTA (0.56g). The hydrothermal reaction was conducted at 80 °C for 14 hours in a 45 mL Teflon liner, the products NiMn LDHs were collected by centrifuge 10000 rpms for 5 minutes and washed with DI water for three times respectively. After freeze-drying overnight, NiMn LDHs were obtained. In the second step, the NiMn LDHs were re-dispersed into 20 mL DI water and 25 mM TAA was added. Subsequently, NiMn LDHs were sulfidized through hydrothermal reaction at 160 °C for 8 hours in a 45 mL Teflon liner. The black products were collected by centrifugation at 10000 rpms for 5 minutes, then washed three times using DI water and ethanol respectively. After being freeze-dried overnight, the final product powders NMS were collected. In the same process, 40 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added instead in the first step without providing Mn salt, the final products were denoted as NS (multiphase Ni sulfides) after the two step hydrothermal reactions.

Preparation of NMGS: Graphite oxide (GO) was prepared by modified Hummer's method using graphite powders.^[3] In order to prepare NMGS (NMS/reduced GO composite), GO was introduced into the starting solution. Similarly, 30 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 10 mM $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 0.56 g HMTA were added into GO (1.0 mg/mL) aqueous solution. NiMn LDH/rGO composite was obtained after the first step hydrothermal treatment at 80 °C for 14 hours. Subsequently, the NiMn LDH/rGO composite was re-dispersed in 20 mL DI water followed by adding 50 mM TAA. NiMn LDH/rGO composite was then sulfidized by hydrothermal treatment at 160 °C for 8 hours, the black product was washed and freeze dried, obtaining the final NMGS composite. The amount of GO was also varied to optimize the electrochemical performance of NMGS, NMGS with GO

feeding concentration of 0.5, 1.0 and 2.0 mg/mL are labeled as NMGS1, NMGS2 and NMGS4. Similarly, pure GO was also selected as the starting material without addition of metal salts or HMTA, and the final product is denoted as rGO after the two step hydrothermal reactions.

4.2.2 Materials Characterization

Physical/chemical characterization: The X-ray diffraction (XRD) (Shimadzu powder diffractometer; Cu K α -radiation ($\lambda = 1.5406 \text{ \AA}$)) technique was applied to investigate the crystal structure of the samples. Scanning electron microscopy (SEM, JEOL 7600F) and Transmission electron microscope (TEM, JEOL 2010 UHR) were applied to reveal the structure and morphology of the samples. Energy dispersive X-ray (EDX) spectroscopy attached to SEM was also applied to analyze the element composition of different samples. Raman spectroscopy was employed to characterize the chemical states of the samples with a monochromatic laser with a wavelength of 633 nm. X-ray photoelectron spectroscopy (XPS) analysis was performed using the VG ESCA Lab XPS system equipped with monochromatic Al K α X-ray source ($h\nu = 1486.7 \text{ eV}$), to investigate the chemical bonds of samples. N₂ adsorption/desorption experiments were implemented applying the Tristar II 3020 analyzer, the specific surface area and total pore volume of the samples were calculated using the Brunauer-Emmett-Teller (BET) method. Thermal gravimetric analysis (TGA, TA Instruments 2950) was also applied to estimate the carbon content in the samples, with a heating rate of 10 °C/min from room temperature to 700 °C in air atmosphere.

Electrochemical characterization: The electrochemical performance of electrode were evaluated in a CR2032 half-cell configuration, see detailed assembly process in Chapter 3, section 3.3.7. The CV, EIS GCD and GITT measurements were conducted according to the parameters discussed in chapter 3, section 3.3.7. The electrolyte employed is 1M NaClO₄ in EC (ethylene carbonate): DMC (dimethyl carbonate) (v/v 1:1), with 5wt % FEC if not specified. Ether-based electrolyte 1 M NaCF₃SO₃ in diethylene glycol dimethyl ether (DEGDME) was also applied to extend the cycling stability of NMGS, with narrowed voltage window of 0.5~ 3.0 V.

4.3 Results and discussion

4.3.1 Physical/chemical characterization of NS, NMS and NMGS

Figure 4.1. (a) XRD and (b) SEM of NiMn LDH. Reproduced from reference [6] with permission from Elsevier.

Bimetallic NiMn LDH precursor was firstly prepared before the subsequent sulfidation. The XRD and SEM of NiMn LDHs can be seen from Fig. 4.1. The diffraction pattern can be ascribed to the hexagonal LDH structure,^[13] demonstrating the successful preparation of NiMn LDH. It can be seen from Fig. 4.1b that NiMn LDH has a flower-like morphology, composed of nanosheet “petals”. The NiMn LDH precursors were subjected to subsequent sulfidation.

Figure 4.2 (a) XRD of NS, NMS and NMGS; SEM images of (b) NS; (c) NMS; and (d) NMGS. Reproduced from reference [6] with permission from Elsevier.

NMS had been prepared by sulfidation of NiMn LDH, while NS and NMGS were prepared by slightly modified procedure as presented in experimental section. The crystal structure and composition of the NS, NMS and NMGS were characterized by XRD as shown in Fig. 4.2a. It can be seen that for NS is composed of multiphase Ni sulfides, including NiS (# 00-002-1280 hexagonal), NiS₂ (# 04-002-2589 cubic) and Ni₃S₄ (# 04-003-2272, cubic). With the introduction of Mn and GO into the sulfidation reaction, the final composition of the products NMS and NMGS are similar to that of NS. The hexagonal crystal structure of NiMn LDH precursors are clearly not preserved. However, the 2-theta value of (200) crystal plane of NiS₂ for NS and NMS is slightly different, as can be seen from Fig. 4.3a. Compared with NS, the 2-theta value of NMS is downshifted by $\sim 0.2^\circ$, indicating a slightly expanded lattice parameter. Based on the diffraction angles of NiS₂ (200) in NS and NMS and Bragg equation ($2d \cdot \sin\theta = \lambda$), the crystal parameter of NiS₂ in NS, and NMS can be calculated. The a values of NiS₂ in NS and NMS are 0.573 nm and 0.5694 nm, indicating a 0.6% increase in the lattice parameters, which can be ascribed to the doping of Mn with larger ionic radii.^[7] The morphology of the samples were revealed by SEM under the same

magnification as seen in Fig. 4.2(b-d). It is noticed that both NS and NMS consist of nanoparticles, while the NMS nanoparticles size is slightly larger than that of NS. The morphology of NMGS can be seen from Fig. 4.2d, the crumpled large sheets indicate the presence of rGO, and the nanoparticles were randomly distributed on the rGO surface, demonstrating successful introduction of rGO and the well attachment of the NMS nanoparticles on the rGO surface.

Figure 4.3 (a) The enlarged XRD pattern of NS and NMS; (b) SEM images of NMGS at low magnification; (c) SEM image and (d) EDX spectrum of NMS. Reproduced from reference [16] with permission from Elsevier.

The low magnification SEM image of NMGS has been provided as in Fig. 4.3b, which resembles that of crumpled graphene oxide. The presence of Mn in NMS is also confirmed by SEM EDX, as can be seen in Fig. 4.3(c-d).

Figure 4.4 (a) TEM images of NMGS at high magnification, (b) High resolution TEM image of NMGS; (c) N₂-isotherms of NS, NMS and NMGS, inset is the table summarizing the surface area and pore volume; (d) pore size distribution of NS, NMS and NMGS. Reproduced from reference [16] with permission from Elsevier.

The fine nanostructures of NMGS were further revealed by TEM. As shown in Fig. 4.4a, nanoparticles are randomly distributed on the surface of large rGO sheets, consistent with the SEM observations. The size of the nanoparticles is estimated to be around tens of nanometers. The lattice fringes of the nanoparticles can be distinguished under higher magnification. As shown in Fig. 4.4b, lattice fringes of the nanoparticles can be clearly distinguished with measured d-spacing of 0.54 nm, in consistence of the (111) crystal plan of Ni₃S₄ (cubic). The surface area and pore size distribution of the samples were revealed by Brunauer-Emmett-Teller (BET) measurements. The N₂ adsorption-desorption isotherms of the three samples can be seen in Fig. 4.4c. The isotherm shape of NS and NMS are quite similar, indicating similar amount of surface areas and pore volumes. For the NMGS, the isotherm shape exhibits a typical IV type curves, indicating mesoporous structure and larger surface area.^[2] The pore size distribution for the three samples are plotted in Fig. 4.4d. The pores in NMGS have a distributed size of less than 100 nm,

creating more surface area, while no obvious pores are present in NS and NMS. The surface area and pore volume of NS, NMS and NMGS are summarized in the inset table in Fig. 4.4c for comparison. With the incorporation of rGO, NMGS exhibits larger surface area and higher pore volume, which is conducive to electrolyte uptake and beneficial to enhancing the electrochemical performance.^[3, 8]

Figure 4.5 (a) Raman spectrum of NMGS; XPS spectra of NMGS (b) C 1s spectra; and (c) Ni 2p spectra; (d) S 2p spectra. Reproduced from reference [6] with permission from Elsevier.

The Raman spectrum of NMGS was obtained as shown in Fig. 4.5a. Two peaks with wavenumbers of 1350 and 1581 cm^{-1} are observed, corresponding to the D (disorder) band and G (graphitic) band of graphitic structured carbon materials, which can be ascribed to the A_{1g} breathing vibration and the E_{2g} in-plane vibrational mode of sp^2 -bonded carbon respectively.^[9] Compared with the Raman spectrum of GO as shown in Fig. 4.6a, downshift of the G band of NMGS is ascribed to the recovered hexagonal carbon networks, indicating formation of reduced GO in NMGS.^[10, 11] The high intensity ratio between D band to G band is indicative of plenty defects, which can also be extracted from the XPS C 1s spectra

in Fig. 4.5b. The Ni 2p and S 2p spectra of NMGS were also obtained as shown in Figure 4.5c-d. It can be seen from Fig. 4.5c that two doublets located at 853.7 and 871.0 eV; 856.3 and 874.2 eV with two satellite peaks can be deconvoluted. The peaks located at binding energy of 853.7 and 871.0 eV suggests the Ni 2p_{3/2} and Ni 2p_{1/2} of Ni²⁺ (typical of Ni-S bonds), while the peaks located at 856.3 and 874.2 eV are indicative of the Ni 2p_{3/2} and Ni 2p_{1/2} of Ni³⁺,^[5, 12] demonstrating the coexistence of divalent and trivalent Ni ions. The S 2p spectrum of NMGS can be seen in Fig. 4.5d, the peak located at 168.7 eV can be ascribed to S-O or SO₄²⁻ species, which is probably caused by surface oxidation.^[13] Additionally, a peak located at the binding energy of 163.7 eV and a pair of spin-orbit doublets can be deconvoluted. The peaks located at 163.7 eV is indicative of C-S bond, in association with the S doping into the graphitic structure,^[14] while the peaks located at 161.9 and 162.9 eV can be ascribed to the S 2p_{3/2} and S 2p_{1/2}, typical of S²⁻ in sulfides.^[12]

Figure 4.6 (a) Raman spectra and (b) XRD patterns of GO and rGO; (c) FESEM and the EDX mapping of rGO. (d) EDX elemental spectrum and the correspondingly derived atomic ratio. Reproduced from reference [6] with permission from Elsevier.

The Raman spectra of GO powder without any treatment and GO sample after the two steps hydrothermal reaction for sulfidation were also collected as shown in Fig. 4.6a, the characteristic D band and G band are clearly observed for both samples. The intensity ratio of D band to G band I_D/I_G for sulfidized GO (~ 0.99) is higher than that of GO (~ 0.89), indicative of the increased size of sp^2 carbon domains and increased amount of defects.^[15] It is also noticed that the wavenumber of G band for sulfidized GO is blue shifted to 1579.6 cm^{-1} compared to $\sim 1587.1\text{ cm}^{-1}$ of GO, which is caused by the “self-healing” effects that recover the hexagonal carbon networks.^[10, 11] The characteristic 2D band of graphene is also restored for the sulfidized GO sample, confirming the reduction of GO after sulfidation, hereby identified as rGO.^[3, 10, 11] From the XRD patterns of GO and rGO as in Fig. 4.6b, it can be seen that rGO exhibits a broadened peak located at 2θ of 24.6° compared to 2θ of 10.8° for GO, indicating reduced interlayer distance of 0.36 nm for rGO compared to 0.82 nm of GO, due to the reduction of GO and the rGO restacking.^[15] The SEM EDX mapping of rGO can be found in Figure 4.6c, indicating the presence of O and S elements in rGO. Presence of O and S in rGO are also verified from the XPS C 1s spectra of NMGS, with C-O and C-S bonds deconvoluted as shown in Fig. 4.5b. It can be seen that the dominating peak located at 284.6 eV corresponds C=C sp^2 hybridized bonds, while C-C and C-O bonds are still present, due to the presence of defects.^[11, 16] The peak located at 287.9 eV can be assigned to C-S bond, indicating the S doping into the graphitic structure.^[11, 14]

Figure 4.7 XPS spectra (a) Ni 2p spectrum of NMS; (b) Mn 2p spectra of NMS and NMGS; (c) S 2p spectrum of NMS; (d) slow scan XRD pattern of NMGS (scan speed: 0.5°/min). Reproduced from reference [6] with permission from Elsevier.

The Ni 2p XPS spectrum of NMS was shown in Fig. 4.7a. Similar with NMGS, the Ni 2p spectra of NMS can also be deconvoluted into two pairs of spin-orbit doublets with two satellite peaks. The peaks located at 854.3 and 871.7 eV suggests the Ni 2p_{3/2} and Ni 2p_{1/2} of Ni²⁺ (typical of Ni-S bonds), while the peaks located at 856.7 and 875.0 correspond to the Ni 2p_{3/2} and Ni 2p_{1/2} of Ni³⁺. The Mn 3p spectrum of NMS and NMGS can be found in Fig. 4.7b. The peak located at 641.4 eV is in association of the Mn 2p_{3/2}, typical of Mn-S bond in MnS, while the possibility of Mn-O bond in MnO or Mn₃O₄ could not be eliminated due to the similar binding energy.^[12] From a detailed slow scan XRD analyses of NMGS as shown in Fig. 4.7d, there are no MnS_x or MnO_x species detected. Therefore, the XPS peak of the Mn 2p_{3/2} located at 641.4 eV is assigned to Mn-S bonds in NMS. The Mn doping ratio was extracted using XPS technique, based on the peak intensities and relative sensitivity factors. As can be seen in the inset of Fig. 4.7b, the atomic ratio of Mn

in NMS at the surface is 1.7%. The atomic ratio between S to Ni is ~ 1.96 , correlating with the dominant phase of NiS_2 in NMS.

Figure 4.8 The thermal gravimetric analysis of NMS and NMGS in temperature range from room temperature to 700 °C. Reproduced from reference [6] with permission from Elsevier.

The weight content of rGO in NMGS was estimated using thermal gravimetric analysis (TGA). As shown in Fig. 4.8, NMS can retain a weight percentage of 78.9 % after being heated to 700 °C, while NMGS can only retain a weight percentage of 59.8 % due to the extra combustion from rGO, thus the rGO content is estimated to be ~ 24 wt.% ($1 - 59.8/78.9$).

4.3.2 Electrochemical characterization of NS, NMS and NMGS

Before comparing the electrochemical performance of NS, NMS and NMGS, the GO feeding ratio in NMGS was first optimized. GO with concentration of 0.5, 1.0 and 2.0 mg/mL were added prior to the first step hydrothermal reaction, and the final products were labeled as NMGS1, NMGS2 and NMGS4, in which the number stands for the increased GO concentration added in the sequence of 0.5, 1.0 and 2.0 mg/mL, respectively.

Figure 4.9. GO content optimization. (a) XRD patterns and SEM images of (b) NMGS0.5; (c) NMGS1.0, inset is the high magnification SEM image; (d) NMGS2.0 inset is the high magnification SEM image. Reproduced from reference [6] with permission from Elsevier.

From Fig. 4.9a it is shown that with various amount of GO added, the final composition of NMGS remains similar, consisting of a mixture of multiphase Ni sulfides. The SEM images of the three samples were shown in Fig. 4.9(b-d), it can be seen that with a low GO concentration large amount of nanoparticles were observed in NMGS1, some of which are not anchored on the surface of GO. With increased GO concentration, nanoparticles randomly anchored on the surface of GO can be observed both in NMGS2 and NMGS4, while the nanoparticles are more sparsely distributed in NMGS4 due to the higher amount of GO, as can be seen in the inset in Fig. 4.9c-d.

Figure 4.10. (a) The rate performance of NMGS1, NMGS2 and NMGS4; (b) cycling stability of NMGS1, NMGS2 and NMGS4 at a current density of 500 mA/g for 150 cycles and the coulombic efficiency of NMGS2 during the cycles. Reproduced from reference [6] with permission from Elsevier.

GO feeding concentration was optimized based on electrochemical performance, thus the specific capacity, rate performance and cycling stability of NMGS1, NMGS2 and NMGS4 were evaluated. As shown in Fig. 4.10a, at low current density, the specific capacity of NMGS2 is slightly higher than that of NMGS1 and NMGS4, while at higher current densities, NMGS is still able to deliver higher specific capacities than NMGS1 and NMGS4, maintaining a capacity of 169.4 mAh/g at 5 A/g. The cycling stability of the three samples were also evaluated at 500 mA/g for 150 cycles as shown in Fig. 4.10b. It can be seen that the specific capacity of the three samples are decreased after 150 cycles. However, NMGS2 can maintain higher capacity than NMGS1 and NMGS4 during the cycling process with coulombic efficiency (CE) approaching 100%, retaining capacity of 240.6 mAh/g after 150 cycles. With low amount of GO added, the nanoparticles are not well attached to the rGO surface in NMGS1, resulting in poor electron conduction. On the other hand, with excess amount of GO added in NMGS4 the specific capacity can be compromised, due to the low capacity of carbon materials. The electrochemical performance of rGO was also evaluated as will be discussed later in Fig. 4.15. Based on the above analysis, the GO concentration is optimized to be 1.0 mg/ml.

Figure 4.11. The first 4 Cyclic voltammograms (CV) of (a) NS; (b) NMS and (c) NMGS measured in a potential range of 0.01V ~3.0 vs. Na/Na⁺ at a scan rate of 0.1 mV/s; (d) the EIS spectrum of NS, NMS and NMGS obtained after the 4 CV scans. Reproduced from reference [6] with permission from Elsevier.

Upon optimization of GO feeding content, electrochemical performance of the samples NS, NMS and NMGS are compared. CV curves of the three samples can be seen from Fig. 4.11a-c, obtained under scan rates of 0.1 mV/s in potential range of 0.01~3.0 V for 4 cycles. It can be seen that for NS, during the first sodiation process, two cathodic peaks were noticed at ~ 1.1 V and 0.8 V, which is possibly related to the conversion-based mechanism forming Ni metal and Na₂S, and the formation of solid electrolyte interface (SEI).^[17-19] After sodiation, the peak at ~2.2 V is indicative of the reversed oxidation process. However, for the NS sample, both the cathodic and anodic current densities decreased dramatically upon cycling, hardly retaining the redox peaks after 4 cycles, indicating poor performance retention. NMS samples have similar electrochemical behaviors with smaller polarization between the cathodic and anodic peaks. In addition, the current density is retained with distinguished redox peaks after the cycling, demonstrating increased retention capability of NMS compared with NS. With the addition of GO, NMGS exhibits another cathodic

peak at ~ 2.0 V during the first sodiation process, which is possibly related with the reduction of doped S present in rGO.^[20] In the subsequent cycles, the current densities of both cathodic and anodic scans are well preserved and almost overlapped with each other, representing further improved electrochemical stability compared with NMS. The EIS spectra of samples were collected as shown in Fig. 4.11d, in which the semi-circle at the high-medium frequency region represents the charge transfer resistance (R_{ct}). It is noticed that compared with NS, with the incorporation of Mn, the R_{ct} of NMS is decreased, indicating faster electrochemical reaction kinetics. The better retention and faster charge transfer kinetics of NMS can be ascribed to its enhanced electronic conductivity with higher sodium ion diffusion coefficient than NS, as shown in Fig. 4.12c-d and Fig. 4.13. With the addition of rGO, the R_{ct} of NMGS is further reduced compared with NMS, indicating the further facilitated charge transfer, in agreement with the CV analysis.

Figure 4.12 (a) Photographs of copper foil current collectors before (left) and after electrode materials loading (right); (b) Pellets of NS (left) and NMS (right) powders prepared by hydraulic pressing at load of 5000N, the pellets are ~ 1.3 cm in diameter. The electrical conductivity measurement of pellets (c) NS; (d) NMS using portable four point probe tester (M-3 Mini type). Reproduced from reference [6] with permission from Elsevier.

The photographs of round-shaped copper foil current collector before and after electrode materials loading are provided as in Fig. 4.12a, it can be seen that the diameter of the electrode is ~ 1.1 cm, thus the area of the electrode is ~ 0.95 cm². In order to demonstrate the difference in electronic conductivity of NS and NMS, NS and NMS powders are pressed into pellets for four point probe measurements by a portable tester. The photographs are taken after the reading is stabilized. It can be seen from Fig. 4.12c-d that NMS delivers a sheet resistance of 1.049 Ω /sq, which is much lower than that of NS pellet (2.868 Ω /sq). Given the pellet thickness of 52 and 79 μ m for NS and NMS (measured by micrometer), the conductivity of NS and NMS pellets are calculated to be 67.05 and 120.67 S/cm, demonstrating the higher electronic conductivity of NMS than NS.

Figure 4.13 The sodium diffusion coefficient of NS and NMS at different sodiation degree measured by GITT methods. Details can be found in experimental section. Reproduced from reference [6] with permission from Elsevier.

The sodium diffusion coefficients of NS and NMS at different sodiation degree were measured using GITT technique, as plotted in Fig. 4.13. It can be seen that with Mn doping, NMS is able to realize higher sodium diffusion coefficient than NS, explaining the higher charge transfer kinetics of NMS over NS.

Figure 4.14 The first 5 charge discharge curves of (a) NS, (b) NMS and (c) NMGS at a current density of 50 mA/g. Reproduced from reference [6] with permission from Elsevier.

The galvanostatic charge discharge (GCD) curves of NS, NMS and NMGS measured at 50 mA/g in voltage range of 0.01~3.0V were plotted in Fig. 4.14. It can be seen that both samples deliver a pair of plateaus in subsequent GCD cycles, corresponding to the redox peaks in CV curves shown in Fig. 4.11. Compared with the decreasing capacity of NS, the discharge/charge capacities of NMS are well retained in the subsequent GCD cycles, showing good capacity retention. In contrast, for NMGS the GCD curves in the subsequent cycles are almost overlapped, with higher capacity values than NS and NMS. However, NMGS exhibits a very high first discharge capacity of 1141.2 mAh/g, indicating a low first cycle coulombic efficiency (CE), which is in association with electrolyte decomposition, SEI formation and the larger surface area of NMGS with incorporation of rGO.^[18, 21]

Figure 4.15. (a) The first 5 GCD curves of rGO under current density of 50 mA/g; (b) the specific capacity of rGO under various current densities. Reproduced from reference [6] with permission from Elsevier.

The GCD curves of rGO itself is also presented as shown in Fig. 4.15a, rGO shows a much higher discharge capacity than charge capacity in the first cycle, indicating poor initial coulombic efficiency, which is often caused by the formation of SEI and the plating of alkaline metal within the micro-pores.^[18, 21, 22] The low CE of rGO contributes to the limited CE of NMGS. The specific capacity of rGO under various current densities are shown in Fig. 4.15b. It can be seen that under low current density, the specific capacity of rGO is around 200 mAh/g, which further degrades to less than 50 mAh/g at increased current densities.

Figure 4.16 TEM image of NMGS discharged to 0.01V (a) low magnification, (b) high magnification; (c) TEM image of NMGS after 2000 cycles. Reproduced from reference [6] with permission from Elsevier.

The TEM image of NMGS discharged to 0.01V was captured as shown in Fig. 4.16a-b. It can be seen that compared with the original NMGS, the size of the nanoparticles was obviously reduced after being fully discharged, in association with the nanoparticles breakage caused by volume change upon sodiation, leading to the discharge capacity fade after the first cycle. Thus the higher capacity decay of NMGS in the first cycle than NS and NMS can be ascribed to the higher contribution of electrolyte decomposition to the overall capacity, due to the presence of rGO and the higher surface area of NMGS.^[23] The contribution of rGO towards sodium capacity is to enhance surface area/porosity to create more active sites. Inclusion of rGO also provides the conductive pathways for fast electron transfer and also acts as a stable scaffolds that buffers stress caused by volume change during testing, leading to improved capacity, rate capability and cycling stability of the electrode materials. In the meantime, the conductivity/porosity of composites can be

controlled by varying the experimental conditions.^[24] This issue of low initial CE of NMGS is tackled by replacing the electrolyte as shown in Fig. 4.18, which will be discussed later.

Figure 4.17 (a) GCD curves of NMGS at various current densities; (b) the specific capacity of NS, NMS and NMGS under different current densities, solid symbol is for discharge capacities while the hollow symbol is for the charge capacities; (c) the specific capacity of NS, NMS and NMGS upon 150 cycles at current density of 500 mA/g and (d) the high resolution TEM images of NMGS discharged to 0.01V, inset is the selected area electron diffraction (SAED) pattern. Reproduced from reference [6] with permission from Elsevier.

The GCD curves of NMGS at different current densities were plotted as in Fig. 4.17a. It can be seen that with increased current densities, the specific capacity was reduced, however the shape of the GCD curves were well retained with a pair of oxidation/reduction plateaus, showing good capacity retention. Obvious voltage hysteresis of NMGS can be observed from the GCD curves upon increasing current density, due to the limited kinetics of the electrode materials which is in association with electrode polarization and the limited electronic/ionic conductivity.^[25] This phenomenon is commonly observed in conversion-based sulfide materials. The specific capacities of the samples under different current densities were compared as shown in Fig. 4.17b. NS exhibits high specific capacities

approaching 400 mAh/g at 50 mA/g, which decreases to 8 mAh/g at increased current density of 5000 mA/g. In comparison, NMS delivers better capacity retention capabilities than NS with higher specific capacities at increased current densities. The increased rate performance of NMS over NS can be attributed to the reduced R_{ct} , increased electronic conductivity, and also the slightly increased sodium diffusion coefficient derived by GITT measurements, as discussed previously. With the formation of rGO, NMGS exhibits improved discharge capacity of 460.9 mAh/g at 50 mA/g. Upon increasing current densities, NMGS delivers notably higher capacities than NMS, retaining discharge capacity of 169.4 mAh/g as the current density is increased 100 times (to 5000 mA/g), which is much higher than that of NS and NMS. When the current density is decreased back to 50 mA/g, the specific capacity of NMGS can be restored to 395 mAh/g, showing excellent rate performance. The cycling stability of the samples were also evaluated, the samples were cycled at current density of 500 mA/g for 150 times. It is seen from Fig. 4.17c that NS suffers from a sharp capacity decay in the first tens of cycles and exhibits capacity of only ~ 30 mAh/g afterwards. NMS delivers improved capacity retention properties in the initial tens of cycles, but the capacity is also gradually decreased upon further cycling. On the other hand, NMGS exhibits much higher capacity retention, retaining capacity of 240.6 mAh/g after 150 cycles, demonstrating good cycling stability of $\sim 70\%$.

The electrochemical reaction mechanism of NMGS upon discharging was investigated using TEM. As can be seen in Fig. 4.17d, in the high resolution TEM image of NMGS discharged to 0.01V, three sets of lattice fringes are observed with d-spacings measured to be $d_1=0.255$ nm, $d_2=0.380$ nm and $d_3=0.176$ nm, corresponding to the remnant NiS_2 (210), the discharge products Na_2S (111) and pure Ni metal (200). The SAED pattern in the inset also confirms the presence of discharge products, namely Na_2S and pure Ni, proving the effect of conversion-based mechanism, in agreement with the earlier works on FeS_2 and Ni_3S_2 ^[26, 27]

Figure 4.18. (a) The specific capacity of NMGS at different current densities and (b) the cycling stability of NMGS in different electrolyte systems. Solid symbol is for discharge capacities while the hollow symbol is for the charge capacities. Reproduced from reference [6] with permission from Elsevier.

Electrolyte can greatly affect the electrochemical performance of electrode materials. It is reported that for conversion-based anode materials, the cycling stability can be extended to thousands of cycles by applying ether-based electrolyte, which is due to the smaller apparent activation energy, reduced voltage polarization and suppressed reaction between electrolyte and poly-sulfides.^[28-30] In order to extend the cycling performance of NMGS, ether-based electrolyte (1 M NaCF₃SO₃ in diethylene glycol dimethyl ether (DEGDME)) was also employed in our work. The voltage window is narrowed to 0.5~3.0 V to avoid deep discharge with enhanced cycling stability.^[28, 30] As seen in Fig. 4.18a, the initial CE of NMGS in ether-based electrolyte is much improved compared to that in the carbonate-based electrolyte. At low current density, the specific capacity of NMGS in ether-based electrolyte is 388.4 mAh/g (loading mass of ~ 0.75 mg, excluding the mass of binder and carbon black), lower than that in carbonate-based electrolyte due to the smaller voltage window applied that suppresses the solid electrolyte interface formation and polysulfide-electrolyte interactions.^[29, 30] However, the capacity retention of NMGS is improved in ether-based electrolyte, delivering capacity of 229.2 mAh/g at 5000 mA/g. When the current density is brought back to 50 mA/g, the capacity of NMGS in ether-based electrolyte can be restored to 338.6 mAh/g. In addition, as shown in Fig. 4.18b, the cycling stability of NMGS in ether-based electrolytes is also significantly improved, delivering specific capacity of 269.2 mAh/g after being cycled for 150 times. When the cycle number

is extended to 2000 cycles, specific capacity of 206.1 mAh/g can still be retained, showing superior cycling stability than that of NMGS in carbonate-based electrolyte. The TEM image of NMGS after the 2000 electrochemical cycles is also captured, as shown in Fig. 4.16c. It can be seen that even after 2000 cycles, the morphology of nanoparticles dispersed on the surface of rGO are still maintained, explaining the good cycling stability of NMGS in ether-based electrolyte.

Figure 4.19. Electrochemical reaction mechanism of NMGS in ether-based electrolyte. (a) low magnification SEM image of NMGS discharged to 0.5V, the corresponding EDX mapping of C; Ni; O; Na; S, and the corresponding EDX spectrum; (b) high magnification SEM image; (c) TEM image and (d) high resolution TEM image of NMGS discharged to 0.5V, the inset in (d) is the corresponding SAED pattern. Reproduced from reference [6] with permission from Elsevier.

The electrochemical reaction mechanism of NMGS in ether-based electrolyte is also studied as shown in Fig. 5.19. As can be seen from the EDX mapping and spectrum in Fig. 4.19a, after being discharged to 0.5 V, Na element is detected and uniformly dispersed in

the discharge product. From the high magnification SEM image in Fig. 4.19b, small nanoparticles are observed with some agglomeration noticed. Similarly, small nanoparticles with size of less than 10 nm are also observed from TEM images in Fig. 4.19c-d, which is probably caused by nanoparticle breakage associated with Na^+ insertion. From the SAED pattern in the inset of Fig. 4.19d, 5 sets of diffraction rings are observed, with d-spacings calculated to be $d_1 = 0.393 \text{ nm}$; $d_2 = 0.291 \text{ nm}$; $d_3 = 0.203 \text{ nm}$; $d_4 = 0.183 \text{ nm}$; $d_5 = 0.169 \text{ nm}$. D-spacings of d_1 and d_3 can be ascribed to (111) crystal planes of Na_2S and (111) crystal planes of Ni, respectively. The other d-spacing values of $d_2 = 0.291 \text{ nm}$, $d_4 = 0.183 \text{ nm}$ and $d_5 = 0.169 \text{ nm}$ are related with the NiS_2 ($d_{(200)} = 0.283 \text{ nm}$) and Ni_3S_4 ($d_{(511)} = 0.182 \text{ nm}$; $d_{(440)} = 0.167 \text{ nm}$) respectively. The slightly larger d-spacing values in the discharge product than the standard NiS_2 and Ni_3S_4 can be ascribed to Na^+ intercalation, leading to expanded crystal structures. Based on the above discussions, it is concluded that in ether-based electrolyte, it is intercalation reaction for NMGS while conversion reaction also takes place.

The electrochemical performance of NMGS is compared with other conversion-based sulfide materials as sodium ion battery anode, as shown in Table 4.1. With the introduction of heteroatom Mn-doping, NMS has expanded crystal structures, higher sodium diffusion coefficient and smaller charge transfer resistance, leading to enhanced rate performance. In addition, the formation of rGO helps to anchor the NMS nanoparticles, providing high surface area and electron conduction highways. As a result, compared to some Ni sulfide based materials reported in literatures,^[17-19, 31-36] our NMGS exhibits competitive specific capacity (388.4 mAh/g at 50 mA/g) and excellent rate performance as shown in Fig. 4.20a. NMGS is able to retain ~ 60 % specific capacity even when the current density is increased by 100 times from 50 mA/g to 5000 mA/g, as shown in Fig. 4.20b. On the other hand, when compared with other conversion-based sulfide materials,^[27, 38-43] although NMGS does not exhibit the highest capacity, it delivers excellent rate performance with retained specific capacity of 229.2 mAh/g at high current density of 5000 mA/g. In addition, the specific capacity of NMGS can reach 606.4 mAh/g [$460.9/(1-24\%)$] in carbonate-based electrolyte excluding the weight of rGO, which is also quite competitive.

Table 4.1 Performance comparison of metal sulfide-based materials as sodium ion battery anode. Reproduced from reference [6] with permission from Elsevier.

	Capacity (mAh/g @mA/g)	Rate (mAh/g @mA/g)	Cycling stability (% @ cycle No.)	Current collector	Ref.
NiS/rGO	496 @ 50	181@200	88.4% @10	Ni foam	[31]
NiS ₂ /rGO	382 @ 80.7	168@1614	77% @200	Stainless	[18]
Ni ₃ S ₂ -Ni ₇ S ₆ /rGO	450@50	300@1000	76.4@ 50	Cu foil	[32]
Ni ₃ S ₂ /Ni	373.4@50	220@800	90.6@100	Ni foam	[17]
Ni ₃ S ₂ /G@Ni	791@50	284@600	70.4@110	Ni foam	[33]
NiS hollow sphere	683.8@100	337.4@5000	73% @50	Cu foil	[19]
NiS ₂ nanosphere	681@300	253@5000	~44% @1000	Ti foil	[34]
Ni ₃ S ₂	395.5@150	188.5@3000	70.6@200	Ni foam	[35]
NiS _x -NSC [#]	327@100	201@2000	99% @200	Cu foil	[36]
NiS _x -rGOS	516@200	414@4000	96.8@100	Cu foil	[37]
FeS/Fe ₃ C/GC	750@100	292@5000	~50% @200	Cu foil	[38]
FeS@C	621@100	452@2500	67.6% @300	Cu foil	[39]
FeS ₂ @C	560@100	403@5000	~66@800	Cu foil	[27]
Fe _{1-x} S	492.7@200	365.3@5000	97.4% 200	Cu foil	[40]
MoS ₂ /rGO	240@25	173@200	68.5% @20	Freestanding	[41]
MoS ₂ /G	491.7@50	247.2@2000	81% @200	Cu foil	[42]
1T MoS ₂	330@50	175@2000	71.1% @200	Freestanding	[43]
NMGS	388.4@50	229.2@5000	80% @315 <u>70.1% @1187</u>	Cu foil	*

[#]NSC: N/S co-doped carbon, *This work.

Figure 4.20. (a) Specific capacity and (b) rate capability comparison of NMGS (Black line: NMGS in DEGDM electrolyte; Red line: NMGS in EC/DMC FEC electrolyte) with other metal sulfide based materials.

Aside from excellent rate capability, in ether-based electrolyte system NMGS also exhibits superior cycling stability, with capacity retention of 70.2% after 1100 cycles and 63.5% even after 2000 cycles as shown in Fig. 4.21, while other conversion-based sulfide materials hardly go beyond 1000 cycles with limited capacity retention. Therefore, our

NMGS can be regarded as a promising SIB anode materials with excellent electrochemical performance. From TEM and SAED analyses, we also revealed that the electrochemical discharge of the NMGS electrode in carbonate-based electrolyte is based on electrochemical conversion mechanism that correlates with the high specific capacity of NMGS in carbonate-based electrolytes.

Figure 4.21. Cycling stability comparison of NMGS in DEGDME (labeled in red) with other metal sulfides.

4.4 Conclusion

In summary, using NiMn layered double hydroxide/graphene oxide as the precursor, multiphase Mn-doped Ni sulfide nanoparticles anchored on the surface of rGO (NMGS) can be obtained. Nonetheless, the hexagonal crystal structure and large interlayer spacings of NiMn LDH precursors are not preserved. Smaller charge transfer resistance, higher electronic conductivity and higher sodium ion diffusion coefficient of NMS are resulted from Mn-doping. Enhanced surface area and further reduced charge transfer resistance upon formation of rGO enables NMGS to deliver a specific capacity of 460.9 mAh/g at 50 mA/g with good rate performance (169.4 mAh/g at 5000 mA/g). In addition, NMGS can

maintain capacity of 240.6 mAh/g after being cycled at 500 mA/g 150 times. By employing ether-based electrolyte, NMGS delivers further improved rate performance and cycling stability, retaining capacity of 229.2 mAh/g at 5000 mA/g with improved capacity of 269.2 after 150 cycles. Furthermore, capacity of 206.1 mAh/g can still be maintained even after 2000 cycles at 500 mA/g, showing excellent rate cycling stability. The high capacity, high rate performance and outstanding cycling stability of NMGS emphasizes the potential of bimetallic sulfide as SIB anode materials, paving the way for future studies and applications of bimetallic sulfide based materials for SIB.

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Chapter 5* Sulfidation of CoFe Prussian Blue Analogues towards Advanced Sodium Ion Battery Anodes

Bimetallic sulfides materials have the merits of high theoretical capacity and improved cycling stability, making them attractive for promising sodium ion battery (SIB) anode. Nevertheless, large volume changes still posed as a daunting challenge upon de/sodiation. It is proposed that 3D open framework bimetallic sulfides which host Na^+ with limited volume change can alleviate issues caused by large volume change. Bimetallic CoFe Prussian blue analogues (PBs) with 3D framework and large interstitial sites were sulfidized into CoFe bimetallic sulfides. In addition, poly-dopamine coated PBs (PBPDA) derived carbon coated bimetallic sulfide hollow nanocubes (PBCS) were prepared. By careful composition and structure design, PBCS exhibits higher surface area, smaller charge transfer resistance, and higher sodium diffusion coefficient than the uncoated bimetallic sulfides. An optimum PBCS anode (PBC1-1S) delivers specific capacity of $\approx 500 \text{ mA h/g}$ at 50 mA/g in carbonate-based electrolyte, and capacity of 122.3 mAh/g at 5000 mA/g , showing good rate performance. In addition PBC1-1S can maintain capacity of 255.4 mAh/g after being cycled for 500 times at 500 mA/g in ether-based electrolyte, indicating its good cycling stability. The structure integrity, high specific capacity, good rate performance, and cycling stability of PBCS render it a promising anode material for advanced SIB.

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5.1 Introduction

As another type of bimetallic precursor, Prussian blue analogues (PBs, normally hexacyanoferrates) have a three dimensional open framework with large interstitial sites (~ 0.5 nm) as shown in Fig. 2.11 in chapter 2, providing pathways for Na^+ conduction.^[1-3] In addition, they can be prepared simply in aqueous solution without thermal heating, with formation of monodispersed nanocubes.^[3, 4] With similar crystal structure and lattice parameters, CoS_2 (cubic, $a = 5.5$ Å) can form solid solution with FeS_2 (cubic, $a = 5.4$ Å) at various Co: Fe ratios.^[5] CoS_2 with metallic behavior also has relatively higher electronic conductivity than other metal sulfides (NiS_2 , MnS_2 , MoS_2 , WS_2 , TiS_2) as shown in Table 2.2 in chapter 2.^[6] Thus it is expected that sulfidation of CoFe PB precursor can lead to the formation of CoFe bimetallic sulfide solid solution maintaining the cubic structure with open framework, thus delivering improved Na storage capability.

Based on the above discussions, CoFe PBs were sulfidized into CoFe bimetallic sulfides. In addition, a layer of poly-dopamine (PDA) was coated onto CoFe PBs before sulfidation to realize a carbon coating layer.^[7] As a result, after sulfidation, hollow nanocubes can be obtained, providing a rigid structure with internal space for the de/sodiation induced volume change and high surface area for electrolyte uptake, which is beneficial to realizing improved electrochemical performance.^[8]

Compared to the non-carbon coated bimetallic sulfides (PBS), the carbon coated bimetallic sulfide hollow nanocubes (PBCS) possess higher surface area, smaller charge transfer resistance and higher Na^+ diffusion coefficient, allowing it to endure the volume change and facilitate charge transfer/storage process during the electrochemical testing. As a result, the optimum carbon coated bimetallic sulfide hollow nanocubes (weight ratio between PB3-1:dopamine chloride= 1: 1) delivers a high capacity of ~ 500 mAh/g at a current density of 50 mA/g, capacity of more than 100 mAh/g can be retained even at a high current density of 5 A/g. In addition PBC1-1S can maintain capacity of 255.4 mAh/g after being cycled for 500 times at 500 mA/g in ether-based electrolyte, indicating its good cycling stability.

5.2 Experimental

5.2.1 Materials Preparation of PB, PBS and PBCS

Preparation of CoFe PB: Chemicals for sample preparation including $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, sodium citrate dihydrate and thiourea are used as purchased without further purification. CoFe Prussian blue analogues (PBs) were prepared by wet chemical bath method. Firstly, 100 mL aqueous solution A was obtained by dissolving 30 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 4.5 mM sodium citrate dihydrate. Secondly, 100 mL aqueous solution B was obtained by dissolving 20 mM $\text{K}_3\text{Fe}(\text{CN})_6$. Subsequently, solution A was slowly added into solution B under magnetic stirring, then the mixed solution was aged for 10 hours at room temperature. After centrifugation at 10000 rpms for 5 minutes and washed with DI water and ethanol for 3 times, the precipitates were dried in oven at 60 °C overnight and collected. The product was denoted as PB3-2. The feeding ratio between $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{K}_3\text{Fe}(\text{CN})_6$ was also adjusted to 4:1, 3:1 and 3:4, and PB4-1, PB3-1, and PB3-4 were obtained after the same preparation procedure. In separate experiments, Fe PB was also prepared by replacing $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The PBs with different Co : Fe ratio were subjected to subsequent sulfidation by thiourea at elevated temperature.

Preparation of PBS: PBs were sulfidized by thiourea at elevated temperature in a furnace with argon as the flow gas, the weight ratio between PBs and thiourea is maintained at 1: 2. PBs and thiourea were put into the downstream and upstream of a ceramic crucible in a furnace respectively. The temperature of the furnace was slowly increased to 500 °C at a rate of 1 °C/min and maintained for 3 hours. After that the furnace was cooled down to room temperature, and the sulfidized product as PBS. The sulfidation product of PBs with different Co: Fe feeding ratio was labeled accordingly. Sulfidized PB4-1, PB3-1, PB3-2, PB1-2 and Fe PB were labeled as PB4-1S, PB3-1S, PB3-2S, PB1-2S and Fe PBS respectively.

Preparation of PBCS: After optimizing the electrochemical performance, PB3-1 was selected for carbon coating. 80 mg PB3-1 was dispersed in 100 mL alkaline buffer solution (pH ~8.5) by ultra-sonication. The pH of the buffer solution was carefully adjusted using

dilute HCl and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solutions. 80 mg dopamine chloride was dissolved in 10 mL DI water by magnetic stirring for 10 minutes, which was then added into the PB3-1 dispersed buffer solution dropwise under magnetic stirring. After 4 hours stirring, poly-dopamine coated PB3-1 (PBPDA) was collected by centrifuged at 10000 rpms for 5 minutes and washed by DI water for 3 times, with subsequent drying in oven at 60 °C overnight. The products were denoted as PBPDA1-1 (the ratio 1-1 indicates the weight ratio of PB3-1 and dopamine chloride). Products of PBPDA2-1, PBPDA2-3 and PBPDA1-2 were also obtained by adjusting the weight of dopamine chloride to 40, 120 and 160 mg, respectively. Lastly, PBPDA was sulfidized by a similar procedure as mentioned above. The sulfidized products of PBPDA1-1 were collected and denoted as PBC1-1S, whereby the sulfidized products of PBPDA2-1, PBPDA2-3 and PBPDA1-2 were labeled as PBC2-1S, PBC2-3S and PBC1-2S respectively.

5.2.2 Materials Characterization

The X-ray diffraction (XRD) (Shimadzu powder diffractometer; Cu $K\alpha$ -radiation ($\lambda = 1.5406 \text{ \AA}$)) technique was applied to detect the crystal structure of the samples. Scanning electron microscopy (SEM, JEOL 7600F) was used to observe the structure and morphology of the samples. Transmission electron microscope (TEM, JEOL 2010) was applied to reveal the fine structure at high magnification of the samples. Raman spectroscopy was employed to characterize the chemical states of the samples with a monochromatic laser with a wavelength of 633 nm. X-ray photoelectron spectroscopy (XPS) analysis was performed using the VG ESCA Lab XPS system with monochromatic Al $K\alpha$ X-ray ($h\nu = 1486.7 \text{ eV}$), to investigate the chemical bonds of samples. Thermal gravimetric analysis (TGA, TA Instruments 2950) was also applied to estimate the carbon content in the samples, with a heating rate of 10 °C/min from room temperature to 600 °C in air atmosphere.

5.2.3 Electrochemical testing and analysis

The electrochemical performance of different samples were evaluated in a CR2032 half-cell configuration, see detailed assembly process in Chapter 3, section 3.3.7. The CV, EIS

GCD and GITT measurements were conducted according to the parameters discussed in chapter 3, section 3.3.7. The electrolyte employed is 1M NaClO₄ in EC (ethylene carbonate): DMC (dimethyl carbonate) (v/v 1:1). 5wt % FEC was added to prevent electrolyte decomposition. 1M NaCF₃SO₃ in diethyl glycol dimethyl ether was also employed as the electrolyte to further improve the rate performance and cycling stability.

5.3 Results and discussion

5.3.1 Structural characterization of PB, PBS and PBCS

Figure 5.1 (a) XRD diffraction patterns of Prussian blue precursors with different Co: Fe feeding ratios; SEM images of (b) Fe PB; (c) PB4-1; (d) PB3-1; (e) PB3-2; (f) PB3-4. Reproduced from reference [7] with permission from Wiley online library.

PB precursors with different Co: Fe feeding ratios were prepared and characterized by XRD and SEM. As can be seen from Fig. 5.1a, PB precursors with different Co: Fe feeding ratios show similar diffraction peaks, which can be indexed to a series of crystal planes of cubic Prussian blue analogues (JCPDS # 73-0687), in accordance with literatures.^[1, 4, 9] The morphology of PB precursors with different Co: Fe feeding ratios were revealed by SEM as seen from Fig. 5.1b-e. All PB analogues show nanocube structures, forming isolate

nanocubes with size of ~ 100 nm. Fe PB exhibits an overlapping nanocube morphology, with nanocubes interconnecting with each other, while the size of nanocubes is tens of nanometers.

Figure 5.2 (a) XRD diffraction patterns of sulfidized Prussian blue precursors; SEM images of (b) Fe PBS; (c) PB4-1S; (d) PB3-1S; (e) PB3-2S; (f) PB3-4S. Reproduced from reference [7] with permission from Wiley online library.

The PB precursors were subjected to subsequent sulfidation process by thiourea at elevated temperature and the products were characterized by XRD and SEM. As seen in Fig. 5.2a, after sulfidation the Prussian blue analogues were transformed into a mixture of sulfides. Monometallic sulfides can be obtained by applying monometallic Fe PB as precursor. It is noted that with high Co: Fe ratio in PB precursor (PB4-1), no bimetallic sulfides can be obtained after sulfidation (PB4-1S). By further reducing the Co: Fe ratio in the PB precursor, bimetallic sulfide Co₈FeS₈ (cubic; JCPDF #029-0484) can be obtained, with the presence of monometallic sulfides Co₄S₃ (hexagonal; JCPDF #002-1458) and Fe₇S₈ (hexagonal; JCPDF #024-0220). By increasing the amount of Fe from PB3-1S to PB3-2S, we can see that the diffraction peaks of Fe₉S₁₀ are restrained while Fe₇S₈ was formed instead with increased amount of Co₄S₃. If the amount of Fe is further increased, both

Fe_9S_{10} and Fe_7S_8 will be obtained with lessened amount of Co_4S_3 . Thus it is shown that in the sulfidation process, there is a competition between the formation of Co_4S_3 and Fe sulfides (Fe_9S_{10} and Fe_7S_8), resulting in the difference in the diffraction patterns for PB3-1S, PB3-2S and PB3-4S. As seen from Fig. 5.2b-f, after the sulfidation process, the PB precursor nanocubes were transformed into random particles, with different degree of agglomeration. It is noted that Fe PBS and PB4-1S are less agglomerated than the other 3 sulfide products, which might be associated with the components in the solid solution to form bimetallic sulfides (PB3-1S, PB3-2S, PB3-4S). The electrochemical performance of these samples were studied and compared, which will be discussed later.

Figure 5.3 (a) XRD patterns of PBC2-1S, PBC1-1S, PBC2-3S, PBC1-2S; and SEM images of (b) PBC2-1S; (c) PBC1-1S; (d) PBC2-3S; (e) PBC1-2S. Reproduced from reference [7] with permission from Wiley online library.

PB3-1 was selected as the precursor and coated by different amount of PDA for further sulfidation. Selection of PB3-1 was based on the optimized electrochemical performance of PB3-1S compared to the other PB derived metal sulfides, which will be discussed later. The amount of dopamine chloride to be added are 40, 80, 120 and 160 mg for the preparation of PBC2-1S, PBC1-1S, PBC2-3S, and PBC1-2S. The carbon coated sulfide nanocubes were characterized by XRD and SEM as displayed in Fig. 5.3. After the sulfidation process, the PDA coated PB3-1 was transformed into a mixture of sulfides

including bimetallic sulfide Co_8FeS_8 (cubic; JCPDF #029-0484), and monometallic sulfides Co_4S_3 (hexagonal; JCPDF #002-1458), Co_3S_4 (hexagonal; JCPDF #042-1448) and Co_{1-x}S (hexagonal JCPDA # 042-0826). The morphology of the carbon coated bimetallic sulfide nanocubes were revealed by SEM as shown in Fig. 6.3b-e. With different amount of carbon coating, the nanocube morphology of PB3-1 can be well retained after the sulfidation process, forming carbon coated bimetallic sulfide nanocubes. The electrochemical performance of these samples were studied and compared and PBC1-1S possess the optimum electrochemical performance, which will be discussed later.

Figure 5.4 (a) XRD patterns of the sulfidized products PB3-1S and PBC1-1S; SEM images of (b) PB3-1S; (c) PBC1-1S; and (d) TEM images of PBC1-1S, inset is the HRTEM image. Reproduced from reference [7] with permission from Wiley online library.

The structural characterization of optimized samples PB3-1S and PBC1-1S were compared. As shown in Fig. 5.4a, the XRD patterns of PB3-1S can be ascribed to a mixture of sulfides including bimetallic sulfides Co_8FeS_8 (cubic #029-0484) and monometallic sulfides Co_4S_3 (hexagonal, #002-1458); Co_3S_4 (cubic, #042-1448) and Fe_9S_{10} (hexagonal, #035-1043).

Based on the relative intensity of the diffraction peaks, it is evident that the bimetallic sulfide Co_8FeS_8 is the dominant component in PB3-1S. By introducing PDA coating layer, the PDA coated PB3-1 precursor was transformed into PBC1-1S after the same sulfidation process. The XRD patterns of PBC1-1S resemble that of PB3-1S, indicating that carbon coating does not affect the composition of the sulfidized products. The morphology of PB3-1S and PBC1-1S was revealed by SEM, as seen in Fig. 5.4b-c, the PB3-1 nanocubes without PDA coating decomposed into randomly distributed particles. On the other hand, with a layer of PDA coating the nanocube morphology was retained after the sulfidation process. PBC1-1S was further characterized by TEM, as shown in Fig. 5.4d. It is clearly seen that the nanocube morphology can be retained with size of ~ 100 nm in line with SEM observations. The higher transmittance at the interior of the nanocubes is indicative of the porous and hollow nature, which is expected to exhibit higher porosity. From the high resolution TEM image, the lattice d-spacings were measured to be ~ 0.57 nm, which is in association with the preferred orientation of (111) crystal planes of cubic Co_8FeS_8 . This observation of predominantly Co_8FeS_8 crystals also reflect the majority phase is Co_8FeS_8 in the product. The amorphous carbon coatings in PBC1-1S can also be confirmed from the HRTEM image, the thickness of the coating layer is more than 4 nm.

Figure 5.5 TEM images of PBC1-1S (a) high resolution images; (b) low magnification observation of two nanocubes, inset is the high resolution TEM images of the dashed circle area; (c) low magnification observation of the hollow interior of a nanocube, inset is the high resolution TEM images of the dashed circle area. Reproduced from reference [7] with permission from Wiley online library.

The hollow nature of the nanocubes and the random distribution of the sulfides can be further confirmed from Fig. 5.5. The high resolution TEM image of PBC1-1S can be found in Fig. 5.5a, lattice fringes with different d-spacings can be observed, which were measured to be 0.24, 0.29, 0.26, 0.24 and 0.59 nm. D-spacing values of 0.29 and 0.59 nm corresponds to the (311) and (111) crystal planes of Co_8FeS_8 , 0.24 nm corresponds to (400) crystal plane of Co_3S_4 , while 0.26 nm corresponds to (101) crystal plane of Co_4S_3 , which confirms the presence of multiphase metal sulfides and the random distribution of these sulfides. In Fig. 6.5b, two nanocubes were clearly observed, while the high resolution (the dashed circle area) analysis evidently shows the hollow interior of the nanocubes. Also, the hollow interior of the nanocubes can be seen from Fig. 6.5c (from the dashed circle area), it is found that no lattice fringes can be observed in the “void” area, confirming the hollow nature of the PBC1-1S nanocubes.

Figure 5.6 (a) N₂-sorption isotherms of PB3-1S and PBC1-1S, inset is the pore size distribution; (b) Raman spectrum of PBC1-1S; (c-d) Co 2p and Fe 2p spectrum of PB3-1S. Reproduced from reference [7] with permission from Wiley online library.

N₂-sorption isotherms of PB3-1S and PBC1-1S were measured to quantify the specific surface area and porosity of the samples. As seen in Fig. 5.6a, only limited amount of N₂ can be ad/desorbed by PB3-1S even at high pressure, while for PBC1-1S the quantity of N₂ ad/desorbed is larger, exhibiting a typical IV type isotherms.^[10] The surface area and total pore volume of PBC1-1S calculated by Brunauer–Emmett–Teller (BET) method were 25.45 m²/g and 0.0665 cm³/g respectively, which is much higher than those of PB3-1S (1.79 m²/g and 0.0023 cm³/g). The pore size distribution of PB3-1S and PBC1-1S can be seen from the inset in Fig. 6.6a, it is found that PB3-1S hardly exhibits any porous structure, in line with the SEM observation of random isolated particles as in Fig. 5.4b. With introduction of a carbon coating layer, large amount of meso-pores with size of less than 50 nm are present in PBC1-1S, corresponding to the hollow interior of the carbon coated nanocubes. The higher surface area and pore volume of PBC1-1S is beneficial for electrolyte penetration, which is expected to deliver better electrochemical performance.^[11] The Raman spectrum of PBC1-1S was also measured and collected as in Fig. 5.6b. It can be seen that two main peaks located at wavenumber of around 1360 cm⁻¹ and 1572 cm⁻¹ respectively, corresponding to the D (disorder) band and G (graphitic) band, confirming the presence of carbon coating on the bimetallic sulfide hollow nanocubes.^[12, 13] The intensity ratio between the D band and G band is indicative of defect ratio. The higher intensity of D band indicates large amount of defects in the carbon coating layer, in line with the C-N bond detected as seen in Fig. 5.7c. X-ray photoelectron spectroscopy (XPS) technique was applied to reveal the chemical bonds in PB3-1S, as displayed in Fig. 5.6c-d. In the Co 2p spectrum, the extensive broadening is caused by multiple splitting and the two doublets can be deconvoluted with shakeup satellites. The peaks located at 780.5 eV, 797 eV are characteristic of Co 2p_{3/2} and Co 2p_{1/2} of Co²⁺ (typical of Co-S bond),^[14, 15] while peaks located at 778.5 eV, 794 eV are associated with the Co 2p_{3/2} and Co 2p_{1/2} of Co³⁺. The peak separation is 14.5 eV between Co 2p_{3/2} and Co 2p_{1/2}, presence of a pair of satellite peaks in the high binding energy side (marked as sat. in figure) indicates that few Co²⁺ cations occupy octahedral coordination and majority are likely Co³⁺ in the octahedral sites.^[16] Similarly, the Fe 2p spectrum can also be deconvoluted into two doublets with shakeup satellite peaks. The peaks located at 708.8 eV and 722.5 eV suggest the Fe 2p_{3/2} and Fe 2p_{1/2} of Fe²⁺ (typical of Fe-S bond), the other two peaks located at 710.5 eV, 724.2

eV correlate with the Fe 2p_{3/2} and Fe 2p_{1/2} of Fe³⁺.^[17] The intense satellite structure (marked as sat in figure) is assumed to be a direct consequence of the band structure associated with octahedral Fe²⁺ in the sulfide lattice, which allows for admixture of sulfur 2p character.^[16]

Figure 5.7 X-ray photoelectron analysis of (a) Co 2p, (b) Fe 2p and (c) C 1s spectrum in PBC1-1S. (d) S 2p spectrum in both PB3-1S and PBC1-1S. Reproduced from reference [7] with permission from Wiley online library.

The XPS spectra of PBC1-1S were also collected as shown in Fig. 5.7. The Co 2p and Fe 2p spectra of PBC1-1S resembles those of PB3-1S, indicating the presence of Co²⁺, Co³⁺, Fe²⁺ and Fe³⁺ in PBC1-1S. The C 1s spectrum of PBC1-1S can be deconvoluted into two peaks located at 284.6 eV and 285.9 eV respectively, representing the graphitic carbon and the C=N bonds derived from the pyrolysis of PDA.^[18] The S 2p spectrum of PB3-1S can be found in Fig. 5.7d, which can be splitted into two peaks located at 162.6 and 163.5 eV, corresponding to S 2p_{1/2} and S 2p_{3/2}.^[13, 15] The exact identification of the chemical environment of S in the bimetallic sulfide is extremely difficult due to the close electronegativity of Co (1.88 eV) and Fe (1.83 eV). In comparison to other bimetallic sulfide (Co_xMo_yS),^[19] in which splitting in the XPS spectrum of S2p can be seen due to the

large electronegativity difference (Mo-S and Co-S), there is no peak splitting of S2p in the sample PB3-1S due to the negligible electronegativity differences between Co-S and Fe-S, possibly forming polar covalent bond. The Co 2p, Fe 2p and S 2p spectra of PBC1-1S resemble those of PB3-1S, indicating similar chemical environment for the elements.

Figure 5.8 Thermal gravimetric analysis of PB3-1S and PBC1-1S. Reproduced from reference [7] with permission from Wiley online library.

The thermal gravimetric analyses (TGA) of PB3-1S and PBC1-1S were measured to estimate the carbon content in PBC1-1S as shown in Fig. 5.8. As can be seen from the TGA curves of PB3-1S, from room temperature to ~ 250 °C gradual weight loss can be observed, which can be ascribed to the evaporation of water molecules absorbed at the surface of particles.^[20] The gradual weight increase upon temperature increase can be ascribed to the oxidation of the sulfides into sulfates and also oxidation state change of the metal ions.^[12, 20] On the other hand, the weight increase caused by the sulfide oxidation was compromised by the decomposition of carbon coating layer in PBC1-1S, leading to a total weight decrease at high temperature. Based on these analysis, the carbon content in PBC1-1S was estimated to be 24 wt% ($1 - 63.1\%/82.9\%$).

5.3.2 Electrochemical characterization of PB, PBS and PBCS

Figure 5.9 (a) Specific capacities of different sulfide products at various current densities; (b) the diffusion coefficient of sulfide products at different sodiation degree. The measurement of diffusion coefficient was realized by applying GITT (galvanostatic intermittent titration technique), details can be found in experimental section. Reproduced from reference [7] with permission from Wiley online library.

In order to measure the specific capacity of the PB precursor sulfidized products, galvanostatic charge discharge (GCD) method was applied under different current densities, as shown in Fig. 5.9a. In the first several cycles, degradation of capacities can be observed from all samples, which is related to the SEI formation and side reactions, commonly observed in conversion mechanism based anode materials.^[18, 21] After the first 4 charge/discharge cycles, the discharge capacity of PB3-1s can retain 530.78 mA/g, while that of Fe PBS, PB4-1S, PB3-2s and PB3-4s are 520.69, 468.18, 439.24 and 315.14 mAh/g respectively, indicating the higher capacity of PB3-1s at 50 mA/g. Upon increasing the current densities, PB3-1s can still retain higher capacity than the other 4 samples, demonstrating the better rate performance of PB3-1S. In addition, the discharge capacity of PB3-1s can be restored to ~470 mAh/g when the current density is decreased to 50 mA/g. The better rate performance of PB3-1S can be ascribed to the higher diffusion coefficient than that of other sulfide products at different sodiation degree as shown in Fig. 5.9b, the values can be found in Table 5.1. The variation of diffusion coefficient at different sodiation degree can be ascribed to the multi-step mechanism during the discharge process, in accordance to what has been reported for Ge-based and MoS₂-based anode materials.^[22]

Table 5.1 Diffusion coefficient values (cm^2/s) of different samples. Reproduced from reference [7] with permission from Wiley online library.

Sodiation level	Fe PBS	PB4-1S	PB3-1S	PB3-2S	PB3-4S	PBC1-1S
25%	1.89E-11	6.82E-12	5.00E-11	3.01E-12	1.17E-11	8.28E-11
50%	1.32E-11	5.78E-12	8.35E-12	1.56E-12	5.25E-12	3.58E-11
75%	1.85E-11	1.28E-11	3.04E-11	3.67E-12	9.14E-12	1.33E-10
100%	2.58E-11	2.13E-11	8.74E-11	5.94E-12	1.61E-11	1.44E-10

Figure 5.10 (a) Specific capacity at different current densities and (b) EIS spectrum of carbon coated bimetallic sulfide hollow nanocubes with different amount of PDA coating before sulfidation. Reproduced from reference [7] with permission from Wiley online library.

As shown above, PB3-1S shows better electrochemical performance than the other PB derived sulfide products, thus PB3-1 was selected as the precursor to optimize the amount of PDA coating. The rate performance of the bimetallic sulfide nanocubes coated with different amount of carbon was also investigated as revealed in Fig. 5.10a. It can be seen that PBC1-1S exhibits best capacity retention upon increasing current density, and capacity approaching 400 mAh/g can be restored after decreasing the current density to 50 mA/g. Carbon coating can mitigate the stress caused by volume change during de/sodiation process, with small amount of carbon coating this buffer effect is not obvious while the capacity will be compromised if excess amount of carbon coating, as carbon species are considered to have limited contribution to the total capacity of the electrode.^[23] As a result, with appropriate amount of carbon coating PBC1-1S exhibits the best rate performance,

which is also in association with the smallest charge transfer resistance of PBC1-1S than the other carbon coated sulfides as shown in Fig. 5.10b.

The selection of samples was based on the optimization of electrochemical performance as discussed above, which are PB3-1S and PBC1-1S, respectively. The electrochemical performance optimization have been shown and discussed in Fig. 5.9 and Fig. 5.10. Due to the higher diffusion coefficient, PB3-1S delivers the best rate performance than the other bimetallic sulfides with different Co: Fe feeding ratios. After carbon coating, PBC1-1S shows the better rate performance with the smallest charge transfer resistance. It should be noted that the electrochemical performance evaluation of PBC1-1S was based on the total weight of active materials including the carbon layer, which is ~ 24 wt. % according to the TGA in Fig. 5.8.

Figure 5.11. CV curves of (a) PB3-1S; (b) PBC1-1S measured in a potential range of 0.01~3.0V vs. Na/Na^+ at a scan rate of 0.1 mV/s; (c) the first 4 galvanostatic charge discharge cycles of PB3-1S and PBC1-1S at a current density of 50 mA/g; (d) the high resolution TEM images of PBC1-1S discharged to 0.01 V, inset is the selected area electron diffraction pattern. Reproduced from reference [7] with permission from Wiley online library.

CV curves were tested to investigate the electrochemical behavior of the sulfidized products PB3-1S and PBC1-1S as anodes for SIB, as shown in Fig. 5.11a-b. These two samples show similar electrochemical behaviors. In the first cycle, the two cathodic peaks at ~ 0.5 and ~ 0.8 V can be ascribed to the multistep sodiation mechanism, including the sodium insertion that forms sodiated metal sulfides and the conversion mechanism forming metal and Na_2S .^[17, 24] The anodic peaks at ~ 1.7 V can be ascribed to the reverse oxidation process of the metal into metal sulfides. In the subsequent cycles, the cathodic peaks overlapped and shifted to a higher potential at ~ 0.9 V, due to the structure and volume change during the first conversion reactions. The current density of the cathodic and anodic peaks of PB3-1S was significantly decreased along with cycles, indicating a poor capacity retention. The first 4 GCD profiles of PB3-1S and PBC1-1S were also presented in Fig. 5.11c. The first discharge/charge capacity of PB3-1S and PBC1-1S were 744.53/522.41 mAh/g and 867.12/539.53 mAh/g. Here the capacity of PBC1-1S is not obviously improved by carbon coating, however it should be noted that the capacity is calculated based on the total weight of electrode materials, including the low capacity amorphous carbon coating layers (~ 24 wt.%). Thus actually an increase in capacity can be induced by carbon coating after subtracting the weight of carbon (due to negligible contribution in sodium ion storage), giving a value of 1140.9/709.9 mAh/g for PBC1-1S. The low efficiency in the first cycle can be ascribed to the formation of solid electrolyte interface (SEI).^[25] The discharge and charge plateaus are in correspondence with the cathodic and anodic peaks in CV curves as shown in Fig. 5.11a-b. In addition, the electrochemical mechanism was analyzed based on the ex-situ TEM analysis as shown in Fig. 5.11d. From the high resolution TEM images d-spacings of 0.22, 0.28 and 0.43 nm can be observed, corresponding to the diffraction rings in the selected area electron diffraction patterns as shown in the inset. D-spacings of 0.22 nm can be ascribed to (100) planes of pure Co (JCPDF # 005-0727) or Fe (JCPDF # 034-0529) metal. However, d-spacings of 0.28 and 0.43 nm indicated the presence of remnant Co_3S_4 (JCPDF # 047-1738) and Co_4S_3 (JCPDF # 019-0363). Based on these findings, it is indicated that the electrochemical mechanism of PBC1-1S in carbonate-based electrolyte was a conversion-based mechanism.

Figure 5.12. (a) Specific capacity of PB3-1S and PBC1-1S at different current densities; (b) EIS measurements of PB3-1S and PBC1-1S measured at open circuit potential after four cycles of CV test; and (c) the diffusion coefficient of PB3-1S and PBC1-1S at different sodiation degree. Reproduced from reference [7] with permission from Wiley online library.

GCD tests under different current densities were also conducted to reveal the rate capability of PB3-1S and PBC1-1S, as shown in Fig. 5.12a. At low current density of $< 200 \text{ mA/g}$, PB3-1S and PBC1-1S shows similar capacity and rate performance. By subtracting the contribution of low capacity amorphous carbon coating ($\sim 24 \text{ wt.}\%$), increased capacity of PBC1-1S at low current densities is realized. As the current density was increased, the capacity of PBC1-1S was notably higher than that of PB3-1S. After the current density was brought back to 50 mA/g , PB1-1S can restore a capacity of 350 mAh/g , similar to that of PB3-1S (470 mAh/g) after subtracting the carbon content (460 mAh/g). The EIS spectra of PB3-1S and PBC1-1S were plotted in Fig. 5.12b. It can be seen that PBC1-1S delivers a smaller charge transfer resistance, demonstrating the good electrical contact between the carbon layer shell and inner bimetallic sulfides, facilitating the charge transfer process. The diffusion coefficients of Na^+ in PB3-1S and PBC1-1S were also evaluated using GITT techniques (see details from experimental section) and plotted in Fig. 5.12c. The variation of diffusion coefficient at different sodiation degree can be ascribed to the multi-step sodiation process including intercalation and conversion, which is consistent with literature.^[22] It can be seen that with a carbon layer coating, the Na^+ diffusion coefficient in PBC1-1S is much higher than that in PB3-1S at different sodiation degree, as listed in Table 5.1. The better rate performance of PBC1-1S than PB3-1S can be ascribed to the smaller charge transfer resistance and faster Na^+ diffusion in PBC1-1S.

Figure 5.13 (a) the specific capacity of PBC1-1S with and without the presence of FEC at various current densities and (b) the cycling stability of PB3-1s and PBC1-1s with the presence of FEC. Reproduced from reference [7] with permission from Wiley online library.

Electrolyte as ionic conductor can greatly affect the performance of electrode materials. It has been found that with addition of fluoroethylene carbonate (FEC) in the electrolyte, the specific capacity and cycling stability of anode materials can be notably enhanced, which can be ascribed to the thinner and more stable passivation layer on metal counter/reference electrode, mitigated electrolyte decomposition and a faster charge transfer process.^[23, 26] In our work, FEC was added in the electrolyte to further improve the performance of PBC1-1S as shown in Fig. 5.13. It can be seen from Fig. 6.13a that with presence of FEC in electrolyte, the specific capacity of PBC1-1S can reach 122.3 mAh/g at 5000 mA/g, which is almost 6 times than that of PBC1-1S without FEC (20.84 mAh/g at 5000 mA/g). With current density decreased to 50 mA/g, capacity of ~ 380 mAh/g can be restored, higher than that of PBC1-1S in absence of FEC additives. The cycling stability of PB3-1S and PBC1-1S were evaluated in the electrolyte with FEC additives, it is found that after 150 cycles at 500 mA/g, the specific capacity of PB3-1S was significantly decayed from 201 to 25 mAh/g, demonstrating poor cycling performance even with presence of FEC additives. On the contrary, PBC1-1S can still maintain a capacity of 87 mAh/g out of 361.3 mAh/g after 150 cycles at 500 mA/g, revealing the better cycling stability.

Figure 5.14 SEM images of (a) PB3-1S and (b) PBC1-1S after 150 cycling tests. Reproduced from reference [7] with permission from Wiley online library.

The SEM images of cycled PB3-1S and PBC1-1S can be found in Fig. 5.14. As shown in the images, after 150 cycles for PB3-1S the random particles agglomerated and merged together due to the repeated de/sodiation. On the other hand, the nanocube morphology of PBC1-1S remains distinguishable after 150 cycles, albeit noticeable agglomeration that also explains the capacity decay upon cycling.

Table 5.2 Performance comparison of PBC1-1S with other PB-based materials. Reproduced from reference [7] with permission from Wiley online library.

Material System	Specific capacity (mAh/g @ mA/g)	Rate (mAh/g @ A/g)	Cycling (% @ cycle No.)	Ref.
$\text{Na}_{1.72}\text{MnFe}(\text{CN})_6$	~120 @ 12	45 @ 4.8	93% @ 30	[40]
$\text{Na}_{0.61}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.94}$	~ 165 @ 25	80 @ 0.6	100% @ 150	[19]
$\text{Na}_{1.70}\text{FeFe}(\text{CN})_6$	120 @ 200	73.6 @ 1.2	~ 80% @ 100	[18]
$\text{Na}_{1.68}\text{Ni}_{0.14}\text{Co}_{0.86}[\text{Fe}(\text{CN})_6]_{0.84}$	145 @ 30	~ 87 @ 1.5	~ 90% @ 600	[41]
$\text{K}_{0.88}\text{Fe}_{2.04}(\text{CN})_6 \cdot y\text{H}_2\text{O}$	400 @ 8.75	150 @ 1.75	~ 60% @ 100	[42]
$\text{Mn}[\text{Fe}(\text{CN})_6]_{0.6667} \cdot n\text{H}_2\text{O}$	565.6 @ 100	132 @ 1	~ 54% @ 100	[43]
$\text{Co}_3[\text{Co}(\text{CN})_6]_2$	299.1 @ 20	132.5 @ 2	N.A.	[44]
$\text{KMn}[\text{Fe}(\text{CN})_6] \cdot y\text{H}_2\text{O}$	500 @ 50	83 @ 1	97.2% @ 30	[45]
PBC1-1S	497 @ 50	122 @ 5	30% @ 150	This work

The electrochemical performance of PBC1-1S was compared with other PB-based materials applied as battery electrodes, as shown in Table 5.2. Normally PB-based materials are applied as cathode materials, with capacity less than 200 mAh/g at low current density and less than 100 mAh/g at high current density, while delivering good cycling

performance.^[1, 2, 27] When applied as anode materials, PB-based materials can deliver high capacity at low current densities, while suffering from fast capacity decay upon increasing current densities with limited cycling performance.^[29-31] By applying PB as precursor, our PBC1-1S is able to deliver high capacity with high rate performance among PB-based electrode materials, while the cycling stability still needs to be enhanced.

Figure 5.15. Performance comparison of PBC1-1S with PB based materials and other metal sulfide based materials.

Aside from PB-based anode materials,^[29-31] the electrochemical performance of PBC1-1S was also compared with other metal sulfide based anode materials.^[33] As shown in Fig. 5.15, PBC1-1S delivers enhanced specific capacity and rate performance than the other PB-based electrode materials. However, the specific capacity and rate performance of PBC1-1S are not very competitive when compared with other metal sulfide-based electrode materials. It is suspected that in PBC1-1S the carbon coating layer alone is unable to bridge the electron transfer between separate nanocubes, thus it is believed that with further incorporation of effective electron conduction highways and/or scaffolds, for example

large area graphene or high aspect ratio carbon nanotubes, the electrochemical performance of PBC1-1S can be further enhanced.

Figure 5.16. (a) Rate performance and coulombic efficiency and (b) cycling stability of PBC1-1S in different electrolyte.

With the purpose of further increasing the cycling stability of PBC1-1S, ether-based electrolyte was also employed, which has been shown to be effective in improving rate performance and cycling stability of NMGS as discussed in Chapter 4. Here it can be seen in Fig. 5.16a that in ether-based electrolyte, PBC1-1S also exhibits improved rate performance with much higher coulombic efficiency at different current densities. The cycling stability of PBC1-1S in ether-based electrolyte is also greatly enhanced, delivering capacity of 255.4 mAh/g after 500 cycles, demonstrating better cycling retention of PBC1-1S in ether-based electrolyte than in carbonate-based electrolyte, due to the suppressed polysulfide dissolution, smaller apparent activation energy and reduced voltage polarization in ether-based electrolyte.^[34]

5.4 Conclusion

In summary, by coating poly-dopamine on Prussian blue precursors prior to sulfidation process, carbon coated bimetallic sulfide hollow nanocubes PBC1-1S were prepared. Although the three dimensional framework with large interstitial sites of the PB precursors are not preserved, the nanocube morphology of Prussian blue precursors were well-retained in PBC1-1S, with higher surface area, smaller charge transfer resistance and higher

diffusion coefficient. As a result with fluoroethylene carbonate additives in the electrolyte, PBC1-1S anodes can deliver a specific capacity of ~ 500 mAh/g at 50 mA/g while maintaining capacity of 122.3 mAh/g at 5000 mA/g, showing good rate performance. In addition PBC1-1S can maintain capacity of 255.4 mAh/g after being subjected to 500 cycles at 500 mA/g in ether-based electrolyte. The overall good electrochemical performance of PBC1-1S represents the merits of composition tuning and structural design, which serves to inspire advances in sodium ion battery anodes based on bimetallic sulfides.

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Chapter 6* Bimetallic Sulfide Cu_2MoS_4 Hollow Nanospheres as Sodium Ion Battery Anodes

Bimetallic sulfide Cu_2MoS_4 with tetragonal crystal structure has large interlayer spacings. By introduction of glucose, Cu_2MoS_4 nanoplates were transformed into hollow Cu_2MoS_4 nanospheres (CMS1) with enhanced electrochemical performance. By employing ether-based electrolyte, the electrochemical mechanism of CMS1 was changed from conversion-based in carbonate electrolyte to intercalation-based, allowing fast and reversible Na^+ storage. With further introduction of reduced graphene oxide (rGO), CMS1-rGO composites were obtained maintaining the hollow nanospheres structure of CMS1. CMS1-rGO is able to deliver excellent rate performance (258 mAh/g at 50 mA/g and 131.9 mAh/g at 5000 mA/g) and notably enhanced cycling stability, with capacity retention of 95.6% after 2000 cycles. Full cell SIB was assembled by coupling CMS1-rGO anode with stable $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ -based cathode. As a result, the full cell SIB is able to deliver excellent cycling stability with capacity retention of 75.5% even after 500 cycles due to the well matched electrochemical kinetics between the optimized cathode and anode materials.

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6.1 Introduction

As discussed in chapter 4 and chapter 5, it has been confirmed that the formation of bimetallic sulfides is able to deliver improved electrochemical performance than monometallic sulfides. However, the open frameworks of bimetallic precursors (NiMn layered double hydroxides and CoFe Prussian blue analogues) were no longer preserved after sulfidation.^[1, 2] Instead of deriving bimetallic sulfides from bimetallic precursors with open frameworks, bimetallic sulfides with open frameworks are to be directly prepared.

In this chapter, incorporation of hetero-atom into MoS₂ and simultaneously resembling the layered structure is envisaged as a possible solution towards MoS₂ based bimetallic sulfide SIB anodes with improved cycling stability. Bimetallic chevreton phases M_xMo₆S_{8-y} (M=Cu, Ni, Co, Fe, Ag, Cr) have been developed with high electronic conductivity (10²-10³ S/cm) and high Li diffusion coefficient.^[3] Although chevreton phases have three dimensional frameworks (rhombohedral or triclinic) for uptake of Li⁺, poor cycling stability was observed for Cu_xMo₆S_{8-y} and Ag_xMo₆S_{8-y} due to the deposition of Cu and Ag with the formation of unstable Mo₆S₈, while Ni_xMo₆S_{8-y}, Fe_xMo₆S_{8-y}, Co_xMo₆S_{8-y} and Cr_xMo₆S_{8-y} often suffers from low capacity (below 100 mAh/g).^[4] In addition, these chevreton phase compounds are often prepared at harsh conditions (≥ 1000°C) with long duration of several days.^[4]

Unlike chevreton phase, another type of Mo-based bimetallic sulfide Cu₂MoS₄ (CMS) has layered structure with two allotropes, the P phase (Pm42 space group) and I phase (Im42 space group), while both phases have tetragonal crystal structure with large interlayer spacings (I-phase 5.12 Å, P-phase 5.23 Å) as described in Chapter 2.^[3, 5, 6] The I-phase CMS has been applied as photocatalysts with promising performance due to the suitable bandgap (1.71 eV) for visible light absorption.^[6, 7] P-phase CMS has been applied as anode materials for LIB, however, poor electrochemical performance was observed at large voltage window. Although better stability can be achieved at restricted voltage window of 1.5~2.8V, the realized capacity is quite limited (~ 100 mAh/g).^[8] In P-phase CMS, Mo atoms are located directly above each other in adjacent layers while in I-phase CMS the

Mo atoms are offset by a vector of $(1/2, 1/2, 0)$, minimizing the electrostatic repulsion of S atoms between adjacent layers thus higher energy is required to exfoliate a monolayer in I-phase than in P-phase CMS.^[9] P-phase CMS are often prepared at low temperatures ($< 180\text{ }^{\circ}\text{C}$ and as low as $135\text{ }^{\circ}\text{C}$), while high temperature and high pressure solvothermal conditions favor the allotropic change from P-phase to low volume and stable I-phase CMS.^[5] Considering the limited electrochemical performance of P-phase CMS as LIB anodes and the better structural stability of I-phase, thus I-phase CMS is targeted as the bimetallic sulfide anode materials, which is expected to deliver fast Na^+ diffusion with improved stability.

In order to improve the cycling stability, glucose and reduced graphene oxide (rGO) were incorporated to further enhance the electrochemical performance of CMS.^[10] Glucose as one of the common carbon source that can be transformed into amorphous carbon, while large area reduced graphene oxide is able to facilitate the charge transfer between isolate nanostructures.^[1, 11, 12] With addition of glucose, CMS hollow nanospheres with enhanced rate performance and cycling stability were attained. Further introduction of rGO leads to formation of CMS1-rGO composites with boosted cycling stability.

6.2 Experimental

6.2.1 Materials Preparation of CMS, CMS1 and CMS1-rGO

Preparation of Cu_2O nanoparticles: Preparation of CMS based materials was based on the sacrificial template of Cu_2O nanoparticles, which were obtained based on previous reports.^[5] In a typical process, 0.171 g of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ and 3.333 g of poly(vinyl pyrrolidone) (PVP) were dissolved in 100 mL of de-ionized (DI) water under intense magnetic stirring for 30 minutes to form a transparent light blue solution. Subsequently, NaOH (2.0 M, 10.0 mL) was added into the solution under magnetic stirring for 10 minutes. Afterwards aqueous ascorbic acid solution (0.6 M, 10.0 mL) were added dropwise. After stirring for another 1 hour, the color of the liquid was turned to yellow. The products were collected by centrifugation at 10000 rpm for 5 minutes and washed using DI water and ethanol for

three times respectively. After further drying in vacuum oven at 60 °C overnight, Cu₂O nanoparticles are obtained.

Preparation of CMS and CMS1: To prepare Cu₂MoS₄ nanospheres, 40 mg Cu₂O powder and 120 mg glucose were dispersed in 20 mL of ethylene glycol by sonication. Afterwards, 60 mg sodium molybdate (Na₂MoO₄) and 120 mg thioacetamide (TAA) was added into the solution and sonicated for another 15 minutes. The solution was subsequently transferred into a 45-mL Teflon lined stainless-steel autoclave and maintained at 200 °C for 24 hours. The black precipitates were collected by centrifugation at 10000 rpm for 5 minutes and washed three times using ethanol and DI water respectively. After drying in vacuum oven at 60 °C overnight, Cu₂MoS₄ nanospheres were obtained, which was denoted as CMS1. In a similar preparation procedure, pure CMS nanoplates can be obtained without the addition of glucose. The amount of glucose was also varied to 60 and 240 mg, the final products were labeled as CMS0.5 and CMS2, respectively.

Preparation of CMS1-rGO: In order to prepare CMS1-reduced graphene oxide (rGO) composites, 20 mg of graphene oxide (GO) powders were first dispersed in 20 mL ethylene glycol solution by sonication for 1 hour. The CMS1 precipitates were added into the GO solution and re-dispersed by sonication for another 30 minutes. The black solution was subsequently added into 45-mL Teflon lined stainless-steel autoclave and maintained at 200 °C for 8 hours. The final products were also collected by centrifugation, after drying in vacuum oven at 60 °C overnight, the final product was obtained and denoted as CMS1-rGO. The duration for this hydrothermal reaction was also varied to 4 and 12 hours. The final products were labeled as CMS1-rGO(4) and CMS1-rGO(12), respectively.

Preparation of Na₃V₂(PO₄)₃ cathode: In a typical preparation procedure of Na₃V₂(PO₄)₃ based composite (NVP), 0.327g vanadium pentoxide (V₂O₅) and 0.680g oxalic acid dehydrate (H₂C₂O₄•2H₂O) were added into 20 ml DI water and stirred at 70 °C for 30 min to obtained blue solution. Afterwards, 0.648g sodium dihydrogen phosphate (Na₂H₂PO₄), 0.33g glucose and 0.210g citric acid were added into the blue solution and stirred for 30 min. Subsequently, the solution was dried at 70 °C to obtain the precursor powders. Lastly,

the precursor was preheated at 400 °C for 4h followed by annealing at 750 °C for 8h in Ar atmosphere in a tube furnace.

6.2.2 Materials Characterization

The crystal structure of samples were revealed by X-ray diffraction (XRD) (Shimadzu powder diffractometer; Cu K α -radiation ($\lambda = 1.5406 \text{ \AA}$)). The sample structure and morphology was captured using scanning electron microscopy (SEM, JEOL 7600F) and transmission electron microscope (TEM, JEOL 2010 UHR). The chemical states of GO and rGO were characterized by Raman spectroscopy (monochromatic laser; wavelength of 633 nm). X-ray photoelectron spectroscopy (XPS) analyses were performed using the VG ESCA Lab XPS system equipped with Al K α X-ray source (monochromatic, $h\nu = 1486.7 \text{ eV}$), to investigate the chemical bonds of samples. Ex-situ XPS was conducted to investigate the electrochemical mechanism of CMS1 in carbonate-based electrolyte. In situ X-ray absorption spectroscopy (XAS) was used to detect the chemical and coordination environment of Cu and Mo in CMS1, revealing the electrochemical mechanism of CMS1 in ether-based electrolyte. N₂ adsorption/desorption experiments were conducted on Tristar II 3020 analyzer, the specific surface area of the samples were calculated using the Brunauer-Emmett-Teller (BET) method. Thermal gravimetric analyses (TGA, TA Instruments 2950) were also applied to estimate the carbon content in the samples, the samples were heated from room temperature to 900 °C in air at a heating rate of 10 °C/min.

6.2.3 Electrochemical Characterization

The electrochemical performance of different samples were evaluated in a CR2032 half-cell configuration, see detailed assembly process in Chapter 3, section 3.3.7. The CV, EIS GCD and GITT measurements were conducted according to the parameters discussed in chapter 3, section 3.3.7. In this chapter, carbonate based electrolyte of 1M NaClO₄ in EC (ethylene carbonate): DMC (dimethyl carbonate) (v/v 1:1) with 5wt % FEC (fluoroethylene carbonate) and ether based electrolyte of 1 M NaCF₃SO₃ in diethylene glycol dimethyl

ether (DEGDME; diglyme) were used for evaluating the electrochemical performance of electrode materials.

For preparation of full cell, the cathode material $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ composites (NVP) -based slurry was prepared in the same process, and subsequently casted on aluminum foil, which was then coupled with the anode materials in Argon-filled glove box. The loading mass between the cathode NVP composites and anode active materials CMS1-rGO are balanced to obtain the optimized full cell performance. The electrolyte used for full cell assembly is 1M NaPF_6 in DEGDME unless otherwise stated. The calculation of capacity of full cell is based on the total mass of active materials in both cathode and anode.

6.3 Result and discussion

6.3.1 Optimization of glucose amount, solvothermal duration and electrolyte

Figure 6.1. (a) XRD pattern of Cu_2O , (b) SEM image of Cu_2O nanospheres. Reproduced from reference [10] with permission from Wiley online library.

In order to prepare CMS, Cu_2O nanospheres as the Cu source and sacrificial template were firstly synthesized. As can be seen from Fig. 6.1, Cu_2O was successfully prepared with diffraction peaks indexed to cubic Cu_2O phase (PDF# 005-0667), which is composed of nanospheres with size of < 100 nm.

Figure 6.2. (a) XRD patterns and SEM images of (b) CMS, (c) CMS0.5, (d) CMS1 and (e) CMS2, (f) thermogravimetric analysis (TGA) of CMS, CMS0.5, CMS1 and CMS2. Reproduced from reference [10] with permission from Wiley online library.

Starting from Cu_2O precursors, samples with different amount of added glucose were prepared. As can be seen from Fig. 6.2a-b, without incorporation of glucose, pure CMS (I-phase) with nanoplatform morphology can be obtained. The size of the nanoplates are 1~3 microns with thickness of ~ 100 nm. With increased amount of glucose, the diffraction patterns of CMS0.5 and CMS1 resemble that of pure CMS, both of which can be indexed to I- Cu_2MoS_4 , while the nanoplates morphology is no longer preserved with formation of nanoparticles. With further amount of glucose added (240 mg), the crystal structure of CMS2 is transformed to P-phase, which is also composed of nanoparticles with smaller

sizes. The altered morphology induced by glucose incorporation can be ascribed to the retarded nanoparticle growth caused by glucose.^[5, 11] The different phase of CMS2 can be possibly ascribed to the limited diffusion of species within the solvothermal suspension caused by excess glucose. The carbon content in these samples were analyzed using thermal gravimetric analysis as shown in Fig. 6.2d, it is calculated that the carbon content in CMS0.5, CMS1 and CMS2 are 6%, 6.6% and 15.4% ($=1-68.9/81.4$) respectively. The weight increase at temperature higher than 400 °C can be ascribed to the oxidation of sulfides into sulfates and also oxidation state change of metal ions.^[13]

Figure 6.3. The first 4 cyclic voltammetry (CV) curves of (a) CMS and (b) CMS1 in 1M NaClO₄ in EC/DMC FEC at a scan rate of 0.1 mV/s. The highlighted six states (in the first cycle) in (b) are the potential states at which ex-situ X-ray photoelectron spectroscopy were conducted. A (discharged to 1.7V), B (discharged to 1.0V), C (discharged to 0.2 V), D (discharge-charged to 1.4V), E (discharge-charged to 2.2 V), F (discharge-charged to 2.7V). (c) Rate performance and (d) electrochemical impedance spectroscopy (EIS) of CMS and CMS1. Reproduced from reference [10] with permission from Wiley online library.

The electrochemical performances of CMS and CMS1 were firstly evaluated in carbonate-based electrolyte to validate the positive effects of glucose incorporation. As shown in Fig. 6.3a-b, both the CV curves of CMS and CMS1 have two pairs of dominant redox peaks at first cycle. However, the redox peaks in CMS decayed quickly and no distinguishable peaks can be observed after 4 cycles. On the contrary, the CV curves of CMS1 are somehow overlapped in subsequent cycles, indicating improved capacity retention of CMS1, in line with the improved rate performance of CMS1 as shown in Fig. 6.3 c. The improved rate performance of CMS1 can be ascribed to the reduced charge transfer resistance as shown in Fig. 6.3d. The distinguished redox peaks after 4 cycles, better rate performance and reduced charge transfer resistance of CMS1 can be ascribed to the carbon incorporation with formation of nanospheres, which is favorable for more reaction sites, mitigated stress caused by volume change during testing and expedited charge transfer.

The Cu and Mo spectra at different cut-off voltages (at various potential vs Na/Na⁺) in the first cycle CV curves were collected by ex-situ X-ray photoelectron spectroscopy (XPS). Thus electrochemical mechanism of CMS1 in carbonate-based electrolyte was tentatively analyzed. The six points A, B, C, D, E, and F for XPS measurements were highlighted as shown in Fig. 6.3b, the two dominant redox peaks are labeled as C1, C2, A1 and A2, respectively.

As can be seen in Fig. 6.4a, the XPS spectra of Cu at all stages are deconvoluted into doublets of Cu 2p_{3/2} and Cu 2p_{1/2}. The Cu 2p_{3/2} binding energies (BEs) of the raw CMS are located at 932.6 and 933.5 eV, which are indicative of the presence of Cu⁺ (typically of Cu-O or Cu-S, BE value of 932.2~ 932.7 eV) and Cu²⁺ (typically Cu-O, BE value of 933.4~ 934 eV), respectively.^[14] The presence of Cu²⁺ can be ascribed to the possible oxidation of CMS1 at the surface. The Cu 2p_{3/2} binding energy of samples at different states are located at BE close to ~ 932.5 eV, indicating the dominance of Cu⁺. However, when CMS1 is discharged to 0.2V (state C), aside from the Cu 2p_{3/2} peak located at 932.5 eV, another Cu 2p_{3/2} peak located at 931.9 eV can be also deconvoluted, which is related with the presence of pure Cu.^[14] Upon reversal charging to 2.7 V (state F), the binding energy value is restored back to ~ 932.6 eV, demonstrating the reversible valence change

of Cu. The brief analysis of Cu 2p spectra indicates that the Cu^+ in pristine CMS1 was not reduced until being discharged to 0.2V (state C), indicating that second cathodic peak (C2) peak is related with the Cu^+ reduction.

Similarly, the Mo 3d spectra of the samples at all stages are deconvoluted into doublets of Mo 3d_{3/2} and Mo 3d_{5/2} as can be seen in Fig. 6.4b. For the raw CMS1, the Mo 3d_{5/2} binding energies are located at 232.4, 230.4 and 228.7 eV. The peaks located at 232.4 and is indicative of the presence of Mo^{6+} (typically of Mo-O, BE value of 232.3-232.8 eV).^[14] While the Mo 3d_{5/2} peaks located at 230.4 eV and 228.7 eV (typically Mo^{4+} of Mo-S, BE value of 228.3-229.0 eV) are possibly related with the surface reduction of Mo^{6+} caused by Cu^+ oxidation, the reducing nature of glucose or possible charge transfer from the carbon layer at surface.^[15, 16] For samples discharged/charged to different stages, the dominant Mo 3d_{5/2} peak is located at 232.2~232.3 eV, correlating to the dominance of Mo^{6+} . For CMS1 discharged to 1.0 V (state B), a new Mo 3d_{5/2} peak located at 228.6 eV is deconvoluted, indicative of the presence of Mo^{4+} due to electrochemical reduction of the pristine Mo^{6+} . For CMS1 further discharged to 0.2 V (state C), the minor Mo 3d_{5/2} peak is further down shifted to 228.1 eV, indicative of the presence of trace pure Mo metal,^[14] which is caused by the electrochemical reduction at low voltage. Upon further charging, the oxidation state of Mo has been restored with improved BE values, which indicate dominance of Mo^{6+} in CMS1 after being discharge-charged to 2.7V (state F). The detailed BE values of deconvoluted Cu 2p_{3/2} and Mo 3d_{5/2} peaks have been tabulated as shown in Table 6.1

Table 6.1. Binding Energy values of deconvoluted Cu 2p_{3/2} and Mo 3d_{5/2} peaks. Reproduced from reference [10] with permission from Wiley online library.

State	Cu 2p _{3/2}			Mo3d _{5/2}		
Pristine	933.45	932.26		232.41	230.36	228.68
A		932.61		232.14		
B		932.7		232.27		228.59
C		932.55	931.93	232.12		228.12
D	932.77	932.42		232.17		228.67
E		932.47		232.28		228.72
F		932.63		232.27

Figure 6.4. (a) Cu 2p and (b) Mo 3d ex-situ XPS spectra in CMS1 at different electrochemical states. Reproduced from reference [10] with permission from Wiley online library.

Based on the above discussions, it is briefly concluded that redox peak C2/A2 is corresponding to the Cu^+/Cu , while C1/A1 is corresponding to $\text{Mo}^{4+}/\text{Mo}^{6+}$ and further reduction of Mo at low voltage is also detected, confirming the conversion-based electrochemical mechanism of CMS1 in carbonate-based electrolyte.

As shown in Fig. 6.3, glucose incorporation is effective in improving the electrochemical performance of CMS, although it is still far from satisfactory. In addition, the initial coulombic efficiency of CMS1 is very limited ($< 40\%$), which is possibly related with electrolyte decomposition at low voltage with formation of solid electrolyte interphase (SEI).^[17] In this case, in order to boost the electrochemical performance of the samples and to improve the initial CE, ether-based electrolyte (1M NaCF_3SO_3 in DEGDME) is employed instead. The cycling stability of metal sulfide-based materials in ether-based electrolyte can be enhanced, which is ascribed to the smaller apparent activation energy, reduced voltage polarization and suppressed poly-sulfides dissolution in ether-based electrolyte.^[18, 19]

Figure 6.5. The first 4 CV curves of CMS1 (a) in 1M NaClO₄ in EC/DMC FEC and (b) in 1M NaCF₃SO₃ in DEGDME at a scan rate of 0.1 mV/s. (c) rate performance; (d) EIS after 4 CV cycles (inset) and cycling stability of CMS1 in different electrolytes. Reproduced from reference [10] with permission from Wiley online library.

As evidenced from Fig. 6.5(a-c), in ether-based electrolyte, the CV curves of CMS1 are almost overlapping in subsequent cycles with significantly enhanced rate performance, maintaining specific capacity of 133.3 mAh/g at 5000 mA/g, which is related with the smaller charge transfer resistance of CMS1 in DEGDME as evidenced in the inset of Fig. 6.5d. The coulombic efficiency of CMS1 in ether-electrolyte at various current densities are stable and approaching 100%. The cycling stability of CMS1 is also extended, with capacity of 90.6 mAh/g retained after 2000 cycles at 500 mA/g.

Figure 6.6. The X-ray absorption near edge structure (XANES) spectra of (a) Cu K-edge and (b) Mo K-edge at pristine, discharged and recharged state. The spectra of Cu and Mo foil were also included for reference. Inset in (a) is the first derivative of XANES spectra. (c) The corresponding first cycle galvanostatic discharge-charge curve of CMS1 and the 10 states subjected to in-situ XANES characterization. Point 1 stands for “pristine” state prior to application of bias, point 6 and point 10 stands for “discharged” and “recharged” state, where CMS1 was discharged to ~ 0.55 V and charged back to ~ 2.4 V, respectively. In situ XANES spectra of Mo during (d) discharge and (e) charge process. Reproduced from reference [10] with permission from Wiley online library.

In order to investigate the effect of electrolyte on the electrochemical performance, electrochemical mechanism of CMS1 in ether-electrolyte was studied using in-situ X-ray absorption near edge structure (XANES). The corresponding GCD curves during in-situ

XANES measurements of CMS1 can be found in Fig. 6.6b. As shown in Fig. 6.6a, the Cu K-edge of CMS1 is down-shifted to lower energy when discharged, which is restored to higher energy when recharged. The Cu K-edge position of recharged CMS1 is close to that of the pristine sample, demonstrating the reversible valence change of Cu during the discharge-charge process. The edge position of Cu at different states were quantified from the first derivative of the spectra as in Fig. 6.7a inset. The absorption edge for Cu foil is located at 8979 eV, corresponding to the existence of Cu⁰ valence state in pure Cu foil.^[20, 21] The absorption edge of the pristine CMS1 is located at 8980.5 eV, which is higher than that of Cu foil, indicating a higher valence state of Cu⁺ in the pristine CMS1.^[20, 22] The absorption edge of the discharged sample is located at 8979.7 eV, indicating the partial reduction of Cu from Cu⁺ to Cu⁰. However, the edge and the post-edge absorption features of the discharged sample is different from that of pure Cu foil, due to different geometry of the first coordination sphere of Cu and the complexation of Cu elements in the discharged sample.^[20] After being recharged, the Cu absorption edge is restored back to 8980.5 eV, indicating the oxidation state restoration during the charging process. Although the pre-edge absorption of the recharged sample is identical with the pristine CMS1, the higher post-edge absorption is related with the more intense multiple scattering with the surrounding atoms, indicative of the restructuring of local Cu environment in CMS1 after being discharged-charged.^[20]

Figure 6.7. Enlarged in-situ XANES spectra of Mo during (a) discharge and (b) charge process. First derivative of the in-situ XANES spectra to detect edge position of Mo during (c) discharge and (d) charge process. Estimated average Mo valence state during (e) discharge and (f) charge process. Reproduced from reference [10] with permission from Wiley online library

The Mo K-edge spectra at selected points can be seen in Fig. 6.6b, obvious variations in the XANES features between the pristine, discharged and charged samples are observed. These variations of Mo spectra during the discharge-charge process indicate the remarkable differences in the Mo local coordination environment.^[23, 24] As for the pristine sample, a pre-edge located at ~ 20002 eV is observed, which is related with the local symmetry around the Mo atoms and the $1s \rightarrow 4d$ transition.^[25] Additionally, a higher energy of the absorption edge compared with the Mo foil are indicative of the higher oxidation state of Mo^{6+} ,^[5, 16, 26] which are dominant in the pristine CMS1. The Mo k-edge spectra during the

discharge and charge can be seen in Fig. 6.7(a-b). The absorption edges of Mo during discharging are generally decreasing to lower photon energy, while the absorption edges of Mo during charging are generally increasing to higher photon energy, indicating the reversible Mo valence state changing.^[24, 27] The first derivatives of Mo XANES spectra during discharge and charge process were plotted in Fig. 6.7(c-d). It can be seen that the edge position of Mo foil is located at 19999.7 eV, corresponding to the Mo⁰ valence state. A pre-edge feature is also present in the pristine sample, and the Mo edge position of pristine sample is located at 20007.8 eV, thus the valence state in the pristine sample is estimated to be 6⁺.^[16] As the Mo valence state is correlated with the K-edge position, the average valence state of Mo atoms at different points can be estimated.^[16, 27, 28] Taking the valence state of 0 in Mo foil and 6⁺ in the pristine sample, the average valence states at different points can be estimated providing their respective k-edge positions as in Fig. 6.7(e-f). It can be seen that during the discharge process, the estimated average Mo valence state at point 3 is obviously decreased to ~ 4.29, indicating the significant reduction of Mo⁶⁺ to Mo⁴⁺ during the plateau at point 2, which corresponds to C1 peak in Fig. 6.3b. In the charging process, the estimated average Mo valence state at point 10 is significantly reversed to 6.15, indicating the fully oxidation of Mo⁴⁺ to Mo⁶⁺ at the charging plateau at ~ 2.1V, corresponding to the A1 peak in Fig. 6.3b. The Mo average valence state at various points are generally maintained at > 4, excluding the occurrence of further reduction of Mo⁴⁺ to Mo. The fluctuation of the average valence state at other states can be ascribed to the varying local coordination and charge transfer between Mo and surrounding atoms during the discharge-charge process.

In a nut shell, in ether-electrolyte Cu and Mo can be reversibly reduced and oxidized during the galvanostatic discharge-charge process through $\text{Cu}^+ \leftrightarrow \text{Cu}^0$ and $\text{Mo}^{6+} \leftrightarrow \text{Mo}^{4+}$. Variation of local coordination environment and surrounding atoms are also observed, indicating the accompanied phase evolution process along with the galvanostatic reduction/oxidation of Cu and Mo atoms in CMS1. The electrochemical mechanism of CMS1 in ether-electrolyte is not conversion-based as no Mo metal is detected at discharged state, while Cu⁺ is only partially reduced. The results indicate the intercalation reaction dominant electrochemical

mechanism of CMS1 in ether-electrolyte, facilitating electrochemical kinetics and cycling stability of CMS1.

Figure 6.8. First 4 CV curves of (a) CMS, (b) CMS0.5, (c) CMS1 and (d) CMS2. (e) EIS and (f) rate performance of CMS, CMS0.5, CMS1 and CMS2. Reproduced from reference [10] with permission from Wiley online library.

With the purpose of optimizing carbon content, the electrochemical performance of CMS, CMS0.5, CMS1 and CMS2 in ether-based electrolyte were studied and compared as in Fig.

6.8. It can be seen from the CV curves that with proper amount of carbon coating, the redox peak after 4 CV cycles are well maintained for CMS0.5 and CMS1. With excess amount of carbon coating, the redox peaks are diminished after four cycles, which can be explained by the higher weight ratio of less electrochemical active carbon coating and the more hindered charge transfer process evidenced from Fig. 6.8e. Based on the rate performance of the four samples as in Fig. 6.8f, it is concluded that CMS1 is the optimized sample with carbon content weight ratio of 6.6%.

Figure 6.9. (a) XRD patterns and SEM images of (b) CMS1-rGO(4), (c) CMS1-rGO(8) and (d) CMS1-rGO(12). Reproduced from reference [10] with permission from Wiley online library.

In order to bridge the electron transfer between separate CMS1 nanospheres and further improve the cycling stability, graphene oxide was mixed with CMS1 for subsequent solvothermal reaction, leading to the formation of CMS1-rGO composite. The duration of second step solvothermal reaction was adjusted. As can be seen from Fig. 6.9, the crystal structure of CMS1 is maintained with varied solvothermal reaction duration, as a result thin and large area rGO nanosheets with CMS1 nanoparticles can be obtained. In addition,

graphene oxide is successfully reduced to rGO in CMS1-rGO (8) as this can be confirmed from the Raman spectra in Fig. 6.10.

Figure 6.10. Raman spectra of GO and rGO. rGO is prepared by 8 hours solvothermal reactions in ethylene glycol. Reproduced from reference [10] with permission from Wiley online library.

The Raman spectra of GO and rGO were collected as shown in Fig. 6.10, the characteristic D band and G band of GO and rGO can be clearly observed. The lower D band to G band intensity ratio of rGO ($I_D/I_G = 0.7$) than that of GO (~ 0.9) is indicative of the reduced amount of defects.^[29] In addition the G band wavenumber of rGO is 1574.1 cm^{-1} , indicating a blue shift compared to $\sim 1581.7 \text{ cm}^{-1}$ of GO, which is ascribed to the “self-healing” effects recovering the hexagonal carbon networks.^[30] The restoration of the characteristic graphene 2D band in rGO sample also confirms the reduction of GO to rGO.^[30, 31]

Figure 6.11. Transmission electron microscopy (TEM) images of (a) CMS1-rGO(8) and (b) CMS1-rGO(12). (c) Rate performance and (d) cycling stability of CMS1, CMS1-rGO(4), CMS1-rGO(8) and CMS1-rGO(12). Reproduced from reference [10] with permission from Wiley online library.

The high resolution TEM images of CMS1-rGO(8) and CMS1-rGO(12) can be seen in Fig. 6.11a-b. It can be seen that even with a difference in the second step solvothermal durations, the hollow nanospheres morphology of CMS1 can be still preserved, while the surface of the nanospheres are smoothed by lengthened reaction time. The rate performance and cycling stability of the samples were evaluated as shown in Fig. 6.11c-d. It can be seen that the rate performance of CMS1-rGO(4) is inferior to that of CMS1, possibly because the GO is not fully reduced. With prolonged elongated solvothermal time, CMS1-rGO(8) and CMS1-rGO(12) are able to deliver slightly improved rate performance compared to that of CMS1. The cycling stability of the samples were also evaluated for 2000 cycles as shown in Fig. 6.11d. It can be seen that with incorporation of rGO, the cycling stability of CMS1 is greatly enhanced. For CMS1-rGO(8), specific capacity of 205.7 mAh/g is maintained even after 2000 cycles.

Figure. 6.12. TGA analysis of CMS, CMS1 and CMS1-rGO. Reproduced from reference [10] with permission from Wiley online library.

The content of rGO in CMS1-rGO is also analyzed based on TGA as shown in Fig. 6.12. The final weight ratio of CMS1-rGO is greatly reduced compared to CMS1 due to the decomposition of rGO in air. The carbon content in CMS1-rGO(8) can be calculated to be 19.0 wt. % ($1 - 65.9/81.4$), thus the content of rGO can be calculated to be 12.4 wt. % by subtracting the content of glucose derived amorphous carbon.

Based on the above discussion, the amount of glucose added and the second step solvothermal reaction time were both optimized to realize bimetallic sulfide electrodes with optimum electrochemical performance in ether electrolyte. Thus CMS, CMS1 and CMS1-rGO(8) were selected for subsequent comparisons and discussions in DEGDME electrolyte. CMS1-rGO(8) is hereafter abbreviated as CMS1-rGO.

6.3.2 Performance comparison of CMS, CMS1 and CMS1-rGO

CMS, CMS1 and CMS1-rGO were successfully prepared starting from Cu_2O nanospheres. As can be seen in Fig. 6.13a. The XRD patterns of the three samples resemble with each other, indicating similar crystalline compositions with incorporation of carbon materials. The diffraction peaks can be ascribed to several different crystal planes of Cu_2MoS_4 (tetragonal cell, space group: I-42m).^[5] The absence of rGO peak in CMS1-rGO is possibly

related with the low content of rGO in the composite (12.4 wt. %). As revealed in Fig. 6.13(b-d), unlike the pure CMS that has square-shaped nanoplates with size of 1~2 μm and thickness of < 100 nm, CMS1 are composed of nanoparticles of $\sim 100\text{nm}$. Similarly, nanoparticles are also observed in CMS1-rGO composite, co-existing with the large area rGO nanosheets.

Figure 6.13. (a) XRD patterns of CMS, CMS1 and CMS1-rGO and SEM images of (b) CMS, (c) CMS1 and (d) CMS1-rGO. Reproduced from reference [10] with permission from Wiley online library.

Figure 6.14. Transmission electron microscopy (TEM) images of (a) CMS, (b) CMS1 and (c) CMS1-rGO. (d) High resolution TEM images of CMS, CMS1 and CMS1-rGO. (e) N₂-isotherms of the three samples, inset is the corresponding pore size distribution. (f) The surface area and pore volume of the three samples. Reproduced from reference [10] with permission from Wiley online library.

The nanostructures of the samples were further investigated using transmission electron microscopy (TEM). The TEM images of CMS, CMS1 and CMS1-rGO are displayed in Fig. 6.14(a-c). The square-shaped nanoplates with size of $\sim 1 \mu\text{m}$ of CMS is in good agreement with the SEM observations. It is noted that the nanoplates are composed of multilayers, due to the oriented growth along the (002) direction.^[5] Different from CMS, CMS1 and CMS1-rGO are composed of hollow nanospheres with size of $\sim 100 \text{ nm}$ and shell thickness of $\sim 20 \text{ nm}$. It is noted that the surface of the nanospheres in CMS1-rGO is smoother than in CMS1, which can be tentatively explained by the prolonged reaction time allowing further Ostwald ripening at the surface.^[5] From the HRTEM images in Fig. 6.14d, lattice spacings of CMS, CMS1 and CMS1-rGO are measured to be 0.51 nm, 0.51 nm and 0.31 nm, corresponding to the (002), (002) and (112) crystal planes of Cu₂MoS₄ (I-42m) respectively. The N₂-isotherms of the three samples were also recorded using Brunauer–

Emmett–Teller (BET) method, as presented in Fig. 6.14e, it can be seen that the N_2 -isotherms of CMS1 and CMS1-rGO show typical type IV curve, indicating the presence of mesoporous structure.^[32] From the inset pore size distribution it is seen that numerous pores with size of < 100 nm are present in both CMS1 and CMS1-rGO, due to the hollow interior of CMS nanospheres and introduction of rGO. The surface area and pore volume of the three samples are summarized as in Fig. 6.14f. It is expected that the higher surface area and pore volume of CMS1 and CMS1-rGO are conducive to creating more reaction sites and increasing electrolyte uptake, leading to improved electrochemical performance.^[31, 33]

Figure 6.15. The first 4 cyclic voltammetry (CV) curves of (a) CMS, (b) CMS1 and (c) CMS1-rGO at a scan rate of 0.1 mV/s, voltage range 0.5~3.0 V. (d) Electrochemical impedance spectra of CMS, CMS1 and CMS1-rGO. Reproduced from reference [10] with permission from Wiley online library.

The electrochemical performance of CMS, CMS1 and CMS1-rGO were studied in ether-based electrolyte. As shown in Fig. 6.15(a-c), the CV curves of all three samples are almost overlapping after the first cycle, indicating good reversibility in DEGDME. While the redox peaks of CMS are weak and indistinguishable in the CV curves, two pairs of strong

and intense redox peaks of CMS1 and CMS1-rGO are noticed, demonstrating better charge storage capability resulted from formation of hollow nanospheres and introduction of carbon materials. The semi-circle in the EIS plots are indicative of the charge transfer resistance (R_{CT}) of electrode materials. It is seen that CMS1 has a slightly larger R_{CT} value than CMS, which can be related with the glucose-derived carbon coating layer on the nanospheres. With further incorporation of rGO, the R_{CT} is again reduced, allowing faster electrochemical kinetics in CMS1-rGO.

Figure 6.16. (a) Galvanostatic charge discharge (GCD) curves of CMS1-rGO at a current density of 50 mA/g. (b) rate performance of CMS, CMS1 and CMS1-rGO. (c) Cycling stability test of CMS, CMS1 and CMS1-rGO for 2000 cycles at 500 mA/g. (d) GCD curves of CMS1-rGO at different cycles during the cycling test. Reproduced from reference [10] with permission from Wiley online library.

In order to quantify the electrochemical charge storage properties, galvanostatic charge-discharge (GCD) tests were conducted for three samples. As can be seen from Fig. 6.16a, CMS1-rGO is able to deliver specific capacity of 258 mAh/g after 5 GCD cycles at 50 mA/g. The two discharge plateaus at ~1.8 V and ~0.8 V and two charge plateaus at ~1.5 V and ~2.2 V are corresponding to the two pairs of dominant redox peaks as in the CV

curves in Fig. 6.15c. The rate performance of the three samples were also compared as displayed in Fig. 6.16b. It can be seen that for CMS, capacity of 259.2 mAh/g can be achieved at 50 mA/g, which is greatly reduced to 40.3 mAh/g when the current density is improved to 5000 mA/g. On the other hand, specific capacity of 133.3 and 131.9 mAh/g can be maintained for CMS1 and CMS1-rGO at 5000 mA/g, demonstrating better rate performance of CMS1 and CMS1-rGO compared with pure CMS, corroborating the CV curves analysis. Cycling stability of the three samples are also evaluated at current density of 500 mA/g as in Fig. 6.16c. It can be seen that, starting from 109.0 mAh/g, the capacity of CMS gradually decreased to 73.1 mAh/g only after 700 cycles. Nevertheless, for CMS1 the capacity can still maintain 120.7 mAh/g after 1000 cycles and retains 90.6 mAh/g even after 2000 cycles, demonstrating the improved cycling stability resulted from glucose incorporation. With further introduction of rGO, starting from 215.2 mAh/g, the specific capacity of CMS1-rGO can still maintain 205.7 mAh/g after 2000 cycles, indicating capacity retention of 95.6 %, with coulombic efficiency of $\sim 100\%$ during 2000 cycles. It is noticed that during the cycling process the capacity of CMS1 and CMS1-rGO was reduced during the first ~ 500 cycles. While capacity of CMS1 is further decreasing in subsequent cycles, the capacity of CMS1-rGO is slowly restored and finally stabilized after ~ 1300 cycles, which is also reflected in the GCD curves of CMS1-rGO at different cycle numbers as plotted in Fig. 6.16d.

Figure 6.17. (a) TEM image of CMS1-rGO after 2000 cycles. (b) HRTEM image of CMS discharged to 0.5V. Reproduced from reference [10] with permission from Wiley online library.

The structure of CMS1-rGO after the cycling test was examined using TEM. As shown in Fig. 6.17a, after 2000 cycles the hollow CMS1 nanospheres structure is no longer maintained, which is transformed into smaller nanoparticles dispersed on rGO, allowing more active sites for electrochemical reactions. Thus the initial capacity decay and subsequent restoration of CMS1-rGO during cycling is tentatively explained by the cycling induced structure collapse of CMS1 that leads to the initial capacity decay, and the exposure of new reactive sites that lead to capacity restoration. The HRTEM image of CMS discharged to 0.5V was also captured as shown in Fig. 6.17b. Unlike the pristine single crystalline nanoplates as in Fig. 6.14d, after being discharged, large amount of small fragments were observed with d-spacings of 0.54 nm in CMS, indicating an expansion of the $d_{(002)}$ interlayer spacings due to Na^+ intercalation. The phenomenon is also observed during sodiation of MoS_2 .^[34] The creation of small fragments with obvious grain boundaries can be ascribed to the large in-plane misfit stressed caused by Na^+ sodiation, which will accelerate the transition from intercalation reaction to conversion reaction with more amount of Na^+ uptake.^[34] As the voltage window is limited to 0.5V, no further conversion reactions were observed, in line with the in-situ XAS analysis from Fig. 6.6-6.7.

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Table 6.2. Electrochemical performance comparison of CMS1-rGO with literatures. Reproduced from reference [10] with permission from Wiley online library.

	Specific Capacity (mAh/g @mA/g)	Rate capability (mAh/g @mA/g)	Cycling stability (% @ cycle No.)	Voltage window (V)	Ref.
MoS ₂ /rGO	240@25	173@200	68.5% @20	0.1~2.2	[35]
MoS ₂ /G	491.7@50	247.2@2000	81% @200	0.1~2.5	[36]
1T MoS ₂	330@50	175@2000	71.1% @200	0.01~3.0	[37]
MoS ₂ /N-rGO	254@200	215@5000	94.65% @1300	0.4~3.0	[38]
MoS ₂	227@200	148@5000	88.6% @1200	0.4~3.0	[39]
MoS ₂ /S-G	~175@100	~80@5000	90.9% @800	0.4~3.0	[40]
MoS ₂ /C	400.6@50	89@5000	74.8% @600	0.01~3.0	[41]
MoS ₂ -G foam	449@50	172@200	~54% @50	0.01~3.0	[42]
CuV ₂ S ₄	473@100	232@2000	>100% @300	0.01-3.0	[43]
CuS	180@50	90@1600	95.8@200	0.6-3.0	[44]
CuS-rGO	509.1@100	359.5@1000	96.2@450	0.4-2.6	[19]
CMS1-rGO	258@50	131.9@5000	95.6% @2000	0.5~3.0	*

Figure 6.18. Electrochemical performance comparison of CMS1-rGO with metal sulfides reported in literatures. (a) Rate capability. (b) Cycling number (in column) and corresponding retention of Cu/Mo based sulfide materials. Reproduced from reference [10] with permission from Wiley online library.

The electrochemical performance of CMS1-rGO was compared with other Cu or Mo based sulfide materials reported in literatures as shown in Table 6.2 and Fig. 6.18. It can be seen that at a similar voltage range, CMS1-rGO delivers higher capacity than MoS₂-based electrodes at low current density.^[38-40] The smaller capacity of CMS1-rGO than other MoS₂ based electrode materials can be ascribed to the limited Na⁺ uptake due to the intercalation dominant electrochemical mechanism.^[34, 45] The capacity of CMS1-rGO at high current density is also superior to some of the MoS₂-based and CuS-based electrodes.^[40, 41, 44] As shown in Fig. 6.18a, the rate performance of CMS1-rGO is among the best, maintaining ~60% of the capacity when the current density is increased by 100 times from 50 to 5000 mA/g. The cycling stability of CMS1-rGO is also superior to other Cu or Mo based sulfide materials, maintaining 95.6 % of the initial capacity even after 2000 cycles, while other Cu/Mo sulfide based materials hardly sustain such cycling numbers with comparable cycling retention.

Figure 6.19. (a) XRD and (b) SEM of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ -based composite (NVP) cathode materials. Reproduced from reference [10] with permission from Wiley online library.

In order to demonstrate practical applications, a full cell sodium ion battery was to be assembled using CMS1-rGO as anode and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ -based composite (NVP) as the cathode material. As can be seen in Fig. 6.19, the diffraction peaks of NVP can be well indexed to $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (JCPDF #53-0018).^[46, 47] The NVP electrode is composed of random particles as revealed from Fig. 6.19b.

Figure 6.20. First 4 CV cycles of NVP cathode in different voltage ranges (a) 2.5~3.8 V, (b) 2.5~4.0 v. (c) Rate performance and coulombic efficiency (hollow squares); (d) cycling stability (at 500 mA/g) and EIS (inset) of NVP in different voltage ranges. Reproduced from reference [10] with permission from Wiley online library.

The electrochemical performance of NVP is also evaluated in ether-based electrolyte. However, NaPF_6 salt is used instead of NaCF_3SO_3 due to the better stability of PF_6 ions.^[48] The effect of testing voltage range of NVP on the electrochemical performance is investigated. As can be seen in Fig. 6.20(a-b), NVP delivers overlapping CV curves with one pair of redox peaks, corresponding to the redox behavior of $\text{V}^{3+}/\text{V}^{4+}$.^[47, 49] The splitting of the cathode peak is related with the rearrangement of local redox environment caused by Na^+ transfer.^[50] However, it is noticed that the voltage polarization values are different after four CV cycles, which are 152 mV and 168 mV in 2.5-3.8 V and 2.5- 4.0 V testing voltage range respectively, indicating faster electrochemical kinetics in narrowed voltage range.^[51] The rate performance and coulombic efficiency (CE) of NVP in different voltage range were also evaluated as in Fig. 6.20c. It can be seen that when tested under narrowed voltage range NVP can deliver capacity of ~57 mAh/g at 5000 mA/g with coulombic efficiency approaching 100%, while the capacity realized at 5000 mA/g is only 34.7 mAh/g at large voltage range with more scattered CE values, indicating inferior rate performance and enhanced irreversibility at expanded voltage window. The EIS spectra after 4 CV cycles and the cycling stability of NVP are also presented as inset in Fig. 6.20d, the smaller charge transfer resistance enabled by narrowed voltage window is correlating with the reduced polarization, improved rate performance and mitigated irreversibility. As at higher voltage, oxidative decomposition of the ether-based electrolyte may occur on the surface of NVP.^[52] As a result, NVP is able to sustain capacity of 79.6 mAh/g after 2000 cycles at 500 mA/g in narrowed voltage range, while in voltage range of 2.5-4.0V the capacity already drops to 73 mAh/g after 1200 cycles. The CE of NVP in narrowed voltage window over 2000 cycles are stable and approaching 100%. Based on the above discussion, NVP in 2.5~3.8 V was selected as the cathode condition to couple with CMS1-rGO anode for SIB full cell fabrication.

Figure 6.21. (a) The first 5 galvanostatic charge discharge (GCD) curves of the full cell (cathode: anode weight ratio= 2.5: 1) at a current density of 25 mA/g, voltage range (0~2.8 V). (b) GCD curves of the full cell (cathode: anode weight ratio= 2.5: 1) at different current density. (c) Rate performance and (d) cycling stability test (500 cycles at 100 mA/g) of full cell assembled with different cathode: anode weight ratio. Reproduced from reference [10] with permission from Wiley online library.

SIB full cells employing NVP as cathode and CMS1-rGO as anode were assembled with different cathode: anode weight ratios in voltage range of 0~2.8V. The GCD curves of a SIB full cell assembled with cathode: anode weight ratio of 2.5: 1 was displayed in Fig. 6.21a. The multiple discharge/charge plateaus are related with the various redox reactions in the full cell. It can be seen that, under current density of 25 mA/g, the full cell is able to deliver reversible capacity of ~ 60 mAh/g after 5 cycles. The GCD curves of full cell at different current densities were also measured as shown in Fig. 6.21b. It can be seen that when current density is increased to 200 mA/g, specific capacity of 38 mAh/g can still be retained. The rate performance and CE of full cells with different cathode: anode weight ratios were also investigated as shown in Fig. 6.21c. With optimized weight ratio of 2.5: 1,

the full cell is able to deliver improved rate performance and stable CE approaching 100%, indicating the well matched electrochemical kinetics between the cathode and anode. As a consequence, as shown in Figure 6.21d the optimized full cell SIB is able to deliver capacity of 34 mAh/g even after 500 cycles at 100 mA/g, corresponding to 75.5% of the initial capacity of 45.03 mAh/g, demonstrating superior cycling stability as a SIB full cell.

Table 6.3 Performance comparison of SIB full cells. Reproduced from reference [10] with permission from Wiley online library.

Full cell configuration	Capacity (mAh/g @mA/g)	Rate (mAh/g @mA/g)	Cycling (% @ cycle No.)	Capacity calculation	Voltage window (V)	Ref
NVP//MoS ₂ /N-rGO	~250@50	N.A.	74.9% @ 50	N.A.	0.6~3.0	[38]
NVP-CBN//NVP-CBN [#]	109@110	104@1100	84% @100	Active materials	0.8-2.3	[53]
NaNi _{0.5} Ti _{0.5} O ₂ //Hard carbon	93@10	~82@30	72% @100	Cathode mass	1.5-4.0	[54]
Na ₂ Ti ₃ O ₇ //VOPO ₄	114@10	74@200	92.4@100	Cathode mass	1.8-3.8	[55]
Na ₃ (VO) ₂ (PO ₄) ₂ F//VO ₂	90@130	48@1560	80@220	Active materials	1-4	[56]
NVP//P-TiO ₂ [#]	107@67	~60@1675	100@60	N.A.	1-4	[57]
NVP//CMS1-rGO	60@50	38@200	75.5% @ 500	Active materials	0 -2.8	*

#: CBN: B,N doped carbon; P-TiO₂: phosphorylated TiO₂

The electrochemical performance of optimized full cell is also compared with literatures as shown in **Table 6.3**. It is seen that our full cell delivers competitive cycling stability due to the utilization of stable cathode and anode materials, and the well match electrochemical kinetics between two electrodes. The limited capacity of our full cell can be related with the small voltage window limited by ether-based electrolyte and the calculation based on the total mass of cathode and anode. An increase in capacity from 60 mAh/g at 50 mA/g to 84 mAh/g can be expected if calculated based on cathode mass only. Our work provides

insights in preparing highly stable SIBs based on nanostructured layered bimetallic sulfides anodes, in which fast electrochemical kinetics and excellent cycling stability were manifested.

6.4 Conclusion

Bimetallic sulfides of hollow CMS1 nanospheres have been prepared with improved rate performance compared to the pure CMS1 nanoplates. By utilization of ether-electrolyte, the electrochemical mechanism of CMS1 was transferred from conversion-based to dominantly intercalation, thus enabling fast Na⁺ storage performances. With further introduction of reduced graphene oxide, the hollow nanospheres structure of CMS1 is maintained with smaller charge transfer resistance of the resultant CMS1-rGO, which is able to deliver further enhanced cycling stability, maintaining capacity of 205.7 mAh/g after 2000 cycles. Stable NVP-based cathodes were also developed to couple with CMS1-rGO anode for SIB full cell assembly. By carefully adjusting the weight ratio between cathode and anode, SIB full cell with stable cycling stability of 75.5% after 500 cycles and high coulombic efficiency approaching 100% can be obtained due to the well matched electrochemical kinetics between cathode and anode, and the fast and stable Na⁺ storage performances of respective cathode and anode materials. This work emphasizes the importance of nanostructuring the layered bimetallic sulfides and utilization of ether-based electrolyte, in which the electrochemical mechanism is controlled to be intercalation, so as to obtain fast and stable anode materials towards full cell SIB with extended cycling stability.

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Chapter 7

Conclusion and Future work

Metal sulfides with relatively good electronic conductivity and high theoretical capacity are promising sodium ion batteries (SIBs) anode candidates yet issues caused by volume change during electrochemical testing are still unresolved. In this thesis, approaches have been applied to prepare nanostructured bimetallic sulfides with open frameworks and incorporated with carbon materials, aiming to harvest high capacity anodes with fast electrochemical kinetics and excellent cycling stability. Our strategies were proved to be effective in obtaining high capacity and stable nanostructured bimetallic sulfides-based SIB anodes. In addition, the conversion-based electrochemical mechanism of bimetallic sulfides in carbonate based electrolyte and intercalation-dominant electrochemical mechanism in ether-based electrolyte were validated. The necessity to consider the cost, scalability and electrochemical mechanism of nanostructured bimetallic sulfides for development of SIBs for grid application are discussed. Future work includes utilizing in-situ nuclear magnetic resonance to reveal the effect of Mn-doping in Mn-doped multiphase Ni sulfides and development of flexible and stretchable SIBs based on nanostructured bimetallic sulfides will be discussed.

7.1 Summary and perspective

The purpose of this thesis is to manifest high electrochemical performance of metal sulfides while mitigating the issues induced by volume changes during electrochemical testing. In this thesis, several approaches have been employed to obtain metal sulfide based SIB anodes with high capacity, fast electrochemical kinetics and excellent cycling stability. The approaches include utilization of bimetallic sulfides with open frameworks, size reduction, creation of internal voids, incorporation of stable carbon materials and employing ether-based electrolyte. The hypothesis is that bimetallic sulfides with open framework structures provide open channels for fast and stable Na^+ storage. During electrochemical testing of bimetallic sulfides, formation of finely distributed nanocomposites composed of respective metal sulfides with reduced Na^+ diffusion length and buffering effect will alleviate stress caused by volume changes, thus delivering improved cycling stability. Through the preparation of bimetallic sulfides using NiMn layered double hydroxides (LDHs) with layered structure or CoFe Prussian blue analogues (PBs) with large interstitial sites, and through direct preparation of bimetallic sulfides Cu_2MoS_4 (CMS) nanostructures, fast and stable Na^+ storage performance have been achieved.

The preparation flowcharts of the aforementioned bimetallic sulfide materials systems are provided in chapter 3, including the principles of different physical/chemical and electrochemical characterization methods. The detailed preparation process and physical/chemical and electrochemical characterization results of bimetallic NiMn sulfides, bimetallic CoFe sulfides and bimetallic CMS have been elaborated in respective result chapters including chapter 4, chapter 5 and chapter 6, respectively.

As discussed in chapter 4, NiMn LDHs were selected as the bimetallic precursor towards formation of Mn-doped multiphase Ni sulfides (NMS) nanoparticles. With higher electronic conductivity, smaller charge transfer resistance and larger sodium ion diffusion coefficient than the monometallic multiphase Ni sulfides (NS) nanoparticles, bimetallic NMS nanoparticles deliver better rate performance and increased cycling stability. Owing to the enhanced surface area, further reduced charge transfer resistance and the buffering

effect of rGO, NMS nanoparticles anchored on the surface of rGO (NMGS) exhibit improved rate performance and cycling stability, which is further promoted by employing ether-based electrolyte. The electrochemical mechanism of NMGS in carbonate-based electrolyte and ether-based electrolyte were investigated to be conversion-based and intercalation dominant respectively.

However, the hypothesis of maintaining the layered structure of NiMn LDHs precursor with large interlayer spacings in bimetallic NiMn sulfides is disproven. As shown in Fig. 2.10, bimetallic LDHs have layered structure with large interlayer spacings of ~ 0.77 nm.^[1] Nonetheless, in LDHs structure the positively charged metal hydroxide slabs have hydrogen bonding with the interlayer anions or water molecules, thus the interlayer bonding is relatively weak, allowing the expansion of the interlayer spacings by anions exchange.^[1, 2] As a result, after the sulfidation process by hydrothermal reactions, the layered structure is no longer retained due to the reaction of NiMn LDHs with hydrolyzed thioacetamide.^[3]

Figure 7.1 Crystal structure of NiS₂. The figure is reproduced from reference [7] with permission from Wiley online library.

On the other hand, the dominant phase of pyrite NiS₂ (# 04-002-2589; cubic, space group Pa-3) in NMS has similar crystal structure with MnS₂ (pyrite structure, space group Pa-3), yet the Mn doping level in NMS is quite limited to $\sim 1.7\%$.^[4, 5] The crystal structure of pyrite NiS₂ has been provided in Fig. 7.1. The limited Mn doping level are tentatively

ascribed to the difference in crystal lattice parameters between NiS_2 ($a = 5.7 \text{ \AA}$) and MnS_2 ($a = 6.1 \text{ \AA}$) as provided in Table 2.2, and the different crystal structures between the NiMn LDHs precursor (hexagonal) and the final dominant product of NiS_2 (cubic).^[5-7]

Starting from NiMn LDHs with large interlayer spacings, bimetallic sulfide solid solution is obtained (with limited Mn-doping content) while the layered structure of precursor is not preserved, nevertheless, the as-prepared bimetallic sulfides NMS exhibited enhanced rate performance and cycling stability compared to the monometallic sulfide NS while electrochemical performance of NMGS composites are further promoted, confirming the advantage of bimetallic sulfides over monometallic sulfide when applied as SIB anode materials and the positive effect of carbon incorporation towards enhanced electrochemical performance.

Continuing with the purpose of preparing bimetallic sulfides, monometallic sulfides with similar crystal structure parameters are to be considered for bimetallic sulfide solid solution formation. Similarly with NiS_2 and MnS_2 , CoS_2 and FeS_2 also have pyrite structures (space group of Pa-3).^[8] As shown in Table 2.2 in chapter 2, CoS_2 and FeS_2 both have cubic crystal structure with similar lattice parameters ($a = 5.5 \text{ \AA}$ for CoS_2 and $5.4 \text{ \AA}$ for FeS_2).^[7] In addition, both CoS_2 and FeS_2 are more electronically conductive than NiS_2 , CoS_2 is even metallic with much lower electronic resistance of $2 \times 10^{-4} \text{ \Omega/cm}$.^[7] Thus CoS_2 and FeS_2 are targeted to form bimetallic sulfide solid solution.

Unlike LDHs with layered structure but weak interlayer bondings, PBs have three dimensional cubic crystal structure with tunable compositions and large interstitial sites that allow fast and reversible alkaline ions accommodation.^[9] Thus CoFe PBs were selected as the bimetallic precursor for preparation of bimetallic CoFe sulfides solid solution preserving the three dimensional cubic crystal structure of CoFe PBs.

In chapter 5, it is shown that bimetallic CoFe bimetallic sulfides can be obtained by sulfidizing CoFe PBs. With higher sodium ion diffusion coefficient, the optimized bimetallic sulfides PB3-1S (Co: Fe feeding ratio= 3: 1) delivers improved rate performance

than the monometallic Fe PBS (sulfidized Fe PB). By coating poly-dopamine on CoFe PBs prior to sulfidation process, hollow interiors are created in PBC1-1S (weight ratio of PB3-1: dopamine= 1: 1) while nanocube morphology of CoFe PBs are retained. Benefiting from higher surface area, smaller charge transfer resistance, and higher sodium ion diffusion coefficient, improved rate performance and higher cycling stability are realized in carbon coated PBC1-1S hollow nanocubes compared to the non-coated PB3-1S random particles. The electrochemical performance of PBC1-1S can also be boosted by utilizing ether electrolyte, while the electrochemical mechanism of PBC1-1S in carbonate-based electrolyte was also revealed to be conversion-based.

Figure 7.2 Crystal structure Co_9S_8 . (T, tetrahedral; O, octahedral) This figure is reproduced from reference [11] with permission from royal society of chemistry.

In CoFe PBs derived bimetallic CoFe sulfides (PB3-1S), Co_8FeS_8 solid solution can be obtained, maintaining cubic crystal phase. The crystal structure of Co_8FeS_8 resembles that of Co_9S_8 ,^[10] which is presented in Fig. 7.2. Co_9S_8 (space group Fm-3m) has a cubic phase ($a = b = c = 9.927 \text{ \AA}$) with atoms closely packed, in which 8/9 of the Co atoms are paired with the S tetrahedron and 1/9 of Co atoms are coordinated to the S octahedron.^[11] Since Fe prefers tetrahedral coordination with S atoms, thus in Co_8FeS_8 Co occupies the tetrahedral sites while Fe occupies the octahedral sites.^[12] By comparing the crystal structure of Co_8FeS_8 with CoFe PBs, it can be seen that although it is still cubic phase after sulfidation, large interstitial sites are no longer preserved, with formation of closely packed arrangement of atoms.

Although the bimetallic CoFe sulfide could not preserve the three dimensional cubic crystal structure of CoFe PBs precursors with large interstitial sites, the superior rate performance of bimetallic sulfide PB3-1S over monometallic sulfide Fe PBS is confirmed, due to the higher sodium ion diffusion coefficient. The advantage of carbon coating and nanostructuring to obtain carbon coated hollow PBC1-1S nanocubes is also evidenced, with higher rate performance and cycling stability than the non-coated PB3-1S random particles.

Based on the above results, formation of bimetallic sulfides can be realized by sulfidation of bimetallic precursors using NiMn LDHs and CoFe PBs precursors, nonetheless, the original crystal structures of the precursors could not be preserved. Thus instead of sulfidizing bimetallic precursors, bimetallic sulfides with open frameworks are directly prepared.

As shown in chapter 6, CMS nanoplates were transformed into hollow Cu_2MoS_4 nanospheres (CMS1) by introduction of glucose. With higher surface area and pore volume, hollow interior as well as the open framework structure of CMS1 with large interlayer spacings, it delivers enhanced rate performance and cycling stability compared to CMS. The electrochemical mechanism of CMS1 was changed from conversion-based in carbonate electrolyte to intercalation-based in ether electrolyte, allowing fast and reversible Na^+ storage. A stable SIB full cell by coupling with $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ -based cathode can be realized. These results emphasize the importance of nanostructuring the layered bimetallic sulfides and utilization of ether-based electrolyte, to obtain fast and stable anode materials towards full cell SIB with extended cycling stability.

The advantage of employing bimetallic sulfides instead of monometallic sulfides as SIB anodes has been confirmed from the improved electrochemical performance of NMS vs. NS and PB3-1S vs. Fe PBS. The electronic conductivity can be improved with heteroatom doping in monometallic sulfide as evidenced in Figure 4.12, the sodium ion diffusion coefficients are also higher in bimetallic sulfides than in monometallic sulfides as shown in Figure 4.13, Table 5.1 and Figure 5.9b. Thus the rate performance of bimetallic sulfides

are improved compared to that of monometallic sulfides as shown in Figure 4.17b and Figure 5.9a. Cycling stability of bimetallic sulfides are also superior than those of monometallic sulfides as displayed in Figure 4.17c, which can be ascribed to the buffered stress due to formation of nanosized monometallic sulfides after sodiation/desodiation. The above-mentioned superiorities of bimetallic sulfides again emphasized the potential of bimetallic sulfides as advanced SIBs anodes. In addition, importance of nanostructure design is also reflected from the enhanced rate performance and cycling stability of PBC1-1S vs. PB3-1S and CMS1 vs. CMS, while incorporation of carbon materials in different forms can also effectively improve the electrochemical performance of bimetallic sulfides, e.g. NMGS, PBC1-1S and CMS1-rGO. The electrochemical mechanism of bimetallic sulfides were investigated using various characterization methods, revealing the conversion-based mechanism in carbonate-based electrolyte and the intercalation-dominant mechanism in ether-based electrolyte.

The electrochemical performance of our optimized products NMGS, PBC1-1S and CMS1-rGO are tabulated with those reported in literatures as shown in Table 7.1. The specific capacities of our products at low current density of 50 mA/g are comparable with some reported in literatures, however, the specific capacity of our products at high current density of 5000 mA/g are quite competitive, obviously higher than some of those monometallic sulfide or bimetallic sulfide based materials.^[13, 19, 22-25]

In addition, the rate performance and cycling stability of NMGS, PBC1-1S and CMS1-rGO are also compared with those reported in literatures. As shown in Figure 7.3, the rate performance of our products are among the best, with capacity retention of 45% ~ 60% when the current density is increased from 50 to 5000 mA/g, clearly higher than those monometallic and bimetallic sulfide based materials reported in literatures.^{[13, 14, 18, 21, 22, 24-}

^{27]} The cycling stability of PBC1-1S is competitive with those metal sulfide based materials reported in literatures, while the cycling stability of NMGS and CMS1-rGO are among the best. With extended cycling number of 2000 cycles, NMGS is able to maintain more than 60% of its original capacity. The cycling stability of CMS1-rGO is more impressive, with more than 95% capacity retention after 2000 cycles, which emphasizes the potential of

bimetallic sulfides with facile ion conduction pathways as advanced sodium ion battery anode. The less competitive cycling stability of PBC1-1S is probably due to the lack of large area and conductive support, e.g. rGO, it is believed that incorporation of rGO with PBC1-1S is able to further enhance the performance of PBC1-1S.

Table 7.1 Performance comparison of NMGS, PBC1-1S and CMS1-rGO with literatures

	Specific Capacity (mAh/g @mA/g)	Rate capability (mAh/g @mA/g)	Cycling stability (% @ cycle No.)	Re f.
NMGS	388.4 @50	229.2 @5000	63.5% @2000	
PBC1-1S	316.4 @ 50	141.7 @ 5000	73.3% @ 500	
CMS1-rGO	258 @50	131.9 @5000	95.6% @2000	
NiS ₂ /rGO	382 @ 80.7	168 @1614	77% @200	[13]
Ni ₃ S ₂ /G@Ni	791 @50	284 @600	70.4% @110	[14]
NiS hollow sphere	683.8 @100	337.4 @5000	73% @50	[15]
NiS _x -rGOS	515 @200	414 @4000	96.8% @100	[16]
FeS@C	621 @100	452 @2500	67.6% @300	[17]
FeV ₂ S ₄	550 @75	350 @375	88% @10	[18]
CoS/rGO	235.6 @100	132.9 @2000	40.7% @100	[19]
Co ₉ S ₈ @HCP@rGO	738 @200	359 @5000	92.6% @500	[20]
CoS/rGO	636 @100	359 @5000	70% @1000	[21]
1T MoS ₂ -3D/G	330 @50	175 @2000	71.1% @200	[22]
MoS ₂	227 @200	148 @5000	88.6% @1200	[23]
MoS ₂ /C	400.6 @50	89 @5000	74.8% @600	[24]
MoS ₂ -G foam	449 @50	172 @200	~54% @50	[25]
CuV ₂ S ₄	473 @100	232 @2000	>100% @300	[26]
CuS	180 @50	90 @1600	95.8% @200	[27]

Figure 7.3. Rate and cycling Performance comparison of NMGS, PBC1-1S and CMS1-rGO with literatures

SIBs may not be able to challenge LIBs in terms of capacity and energy density due to the smaller voltage range and the larger and heavier Na^+ charge carrier. In certain application fields where high performances are pursued, for example, wearable electronics, LIBs are still favored. However, with merits of cost effectiveness enabled by the low cost of Na source and use of cheaper Al current collector, it is believed that SIB will find its application in large scale grid applications. In order to facilitate the development of SIBs for grid applications, electrode materials with high performance, facile and scalable synthesis, low cost and good cycling stability are to be developed. Graphite with low cost, availability, and good stability has been widely used as LIB anodes. SIB anodes with these characteristics are also desired.

Our works show that nanostructured bimetallic sulfides have high capacity and good cycling stability, while the costs and availability are not fully addressed. Bimetallic sulfides prepared based on cheap transition metals (e.g. Fe, Mn, Cu etc.) are favorable with the purpose of reducing the cost. In addition, the synthesis route towards nanostructured bimetallic sulfides are to be designed for large scale and facile production. Taking synthesis of PBC-1S as an example, the preparation of PBPDA (poly-dopamine coated CoFe Prussian blue analogues) are based on room temperature wet-chemical methods, with yield of ~ 0.2 g/batch. It can be easily scaled up to hundred grams and higher yield production of the PBPDA. Synthesis of PBC1-1S can also be facilely done using the thermal assisted sulfidation of PBPDA, which has a yield of ~ 0.1 g/ batch in our work and can be easily scaled up to hundred grams or even higher yield production of PBC1-1S.

With low cost, scalability and good cycling stability, before proceeding to grid application, the electrochemical mechanism of electrode materials are also to be fully understood in order to provide guidelines for fabricating SIBs with desired properties. For example, our work studied the different electrochemical mechanism of NMGS and CMS1-rGO in carbonate and ether-based electrolytes, thus different electrochemical performance. Cycling stability and rate performance of NMGS, CMS1-rGO are obviously higher in ether-electrolyte than in carbonate-electrolyte, associated with their intercalation-dominant mechanism in ether electrolyte. With further investigation and understanding of their

electrochemical mechanism, low-cost transition metal-based nanostructured bimetallic sulfides with facile synthesis route will be promising SIBs anode candidate, accelerating the development and commercialization of SIBs for grid applications.

7.2 Future work

7.2.1 In-situ Nuclear Magnetic Resonance for NMS

The positive effects of Mn-doping on the electrochemical performance of NS are clearly seen in the improved rate performance and cycling stability of NMS, which is related with the smaller charge transfer resistance and improved Na^+ diffusion coefficient of NMS. However, the role of Mn in NMS during electrochemical process is still unclear. In addition, the limited content of Mn ($\sim 1.7\%$) makes it difficult to detect for many characterization methods.

Figure. 7.4. Typical ${}^6,{}^7\text{Li}$, ${}^{23}\text{Na}$ NMR shifts of components in electrochemical cell. The figure is reproduced from reference [28] with permission from American Chemical Society.

Nuclear magnetic resonance (NMR) is able to detect electronic and structural properties of atoms with non-zero nuclear spin, regardless of the crystallinity of samples.[22] In NMR spectra, the signal shifts and broadening can be affected by the chemical environment of the atoms while the peak intensity is related with natural abundance of the isotopes, magnetic field strength, sample size, etc.[22] As shown in Fig. 7.3, the ${}^6,{}^7\text{Li}$ or ${}^{23}\text{Na}$ NMR signals of components in an electrochemical cell cover large range of shifts. The electrolyte and solid electrolyte interphase (SEI) signals fall into the diamagnetic shifts range of $-10\sim 10$ ppm, while the signal of metallic Na and metallic Li are Knight shifted to ~ 1100 ppm and ~ 250 ppm, respectively.[22] So by applying in-situ NMR, the electronic and structural changes of elements as well as formation/disappearance of intermediate/metastable phases

during the electrochemical process can be detected, revealing the electrochemical dynamic and mechanisms.[22]

One example is the multistep electrochemical reactions of VS_4 lithium ion battery anode revealed by in situ NMR.[23] Combining the ^6Li and ^{51}V NMR spectra, the structural and valence state change of V element with corresponding phase evolution during the electrochemical process are revealed. As a result, the electrochemical mechanism of VS_4 is proposed as shown in Fig. 7.4. With initial discharge, VS_4 is transformed into Li^+ intercalated Li_3VS_4 phase (V^{5+}), which is subsequently reduced to a mix-valence compound $\text{Li}_{3+x}\text{VS}_4$. Upon further discharging, formation of V metal and Li_2S are detected. On reverse charging, intermediate $\text{Li}_{3+x}\text{VS}_4$ phase is formed, which is further transformed into VS_4 upon further charging.[23]

Figure. 7.5. Electrochemical mechanism of VS_4 as lithium ion battery anode revealed by in-situ NMR method. The figure is reproduced from reference [29] with permission from American Chemical Society.

Considering the high natural abundance of Mn isotopes (^{55}Mn 100% vs. 1.14% of ^{61}Ni) and ^{23}Na (100%) and the higher receptivity of ^{55}Mn (0.179 vs. ^1H) than ^{61}Ni (4.09×10^{-5} vs. ^1H), [24] by monitoring the ^{55}Mn and ^{23}Na spectra, in-situ NMR is expected to reveal the Mn chemical environment change and possible phase evolutions, thus explaining the role of doped-Mn in the enhanced rate performance and cycling stability of NMS than NS.

7.2.2 Flexible and stretchable SIBs

In this thesis, SIBs electrode fabrication is based on the conventional slurry-casting method, which contains non-conductive binders as well as conductive additives. In addition, heavy metal foils (Cu foil or Al foil) are used as the current collector. These binders, additives and current collectors are electrochemically inactive, yet taking a large weight percentage of the whole device. As a result, the gravimetric/volumetric energy density of the SIB full cells will be greatly compromised when it comes to practical applications since the weight ratio of electrochemically active materials in the full cell are quite limited. Also, the fabricated SIB full cells will be rigid, heavy and bulky. [25]

With the increasing demand for wearable, flexible and portable electronics, flexible energy storage devices including flexible supercapacitors and flexible LIBs have been pursued in recently years. [26, 27] The realization of flexible energy storage devices greatly relies on the preparation of flexible electrodes with good mechanical strength, realizing light weight, thin, flexible and bendable SIB full cells. [25, 26, 28] Preparation of flexible electrodes can be achieved by incorporating active materials with flexible and conductive carbon/metal matrix. [25, 28]

Apart from flexible electrodes that have been prepared, examples of flexible full cell devices have also been reported and showcased. [26, 28, 31] For example, flexible Sb/rGO anodes based on Sb nanoparticles (< 10 nm) and flexible NVP($\text{Na}_3\text{V}_2(\text{PO}_4)_3$)/rGO anodes based on NVP nanocrystals (~ 50 nm) can be obtained, thus allowing fabrication of flexible SIB full cell (7 cm * 5 cm, thickness < 1 mm). [31] The flexible SIB full cell delivers excellent electrochemical performance and good flexibility, still lighting up a LED after

being repeatedly bended for 30 cycles.

In addition to flexible and portable electronics, there has been tremendous interests and rapid development in stretchable electronics, including conformable skin sensors, wearable communication devices, roll-up displays, and implantable medical devices.[32-34] Thus stretchable energy storage devices are to be developed that can be integrated into stretchable electronic devices. Stretchable energy storage devices have been showcased in literatures, which are realized by strategies such as embedding active material in elastic scaffold,[33] wavy/buckled/wrinkle design,[34] and helically coiled spring configuration.[35] Using sugar cube template, PDMS (poly(dimethylsiloxane)) sponge coated with rGO can be obtained, which is used as the elastomeric and conductive current collector to anchor the active materials of hard carbon and VOPO_4 . [33] After lamination and sealing, a stretchable LIB full cell can be obtained, which shows excellent stretchability, maintaining 89% of the original capacity after being stretched for 100 times at 50 % strain.

Figure. 7.6. Schematics for preparation of (a) flexible electrodes and (b) stretchable electrodes based on nanostructured bimetallic sulfides.

It is shown that the conventional slurry casting based methods for electrodes/devices fabrication find limits when it comes to future application fields including flexible and stretchable electronic devices. In this thesis, we have demonstrated the good electrochemical performance of nanostructured bimetallic sulfide based electrode materials for SIB anodes. Considering that our nanostructured bimetallic sulfides are either nanoparticles (NMS, ~ 5 nm) or hollow nanostructures (PBC1-1S nanocubes, ~ 100 nm; CMS1 nanospheres, ~ 100 nm), it is highly possible that flexible SIB anodes based on these nanostructured bimetallic sulfides can be obtained by anchoring onto light weight and conductive carbon matrices. As schemed in Fig. 7.5a, the nanostructured bimetallic sulfides can be electrospun into a flexible mat composed of polymer nanofibers. After subsequent carbonization, the flexible mat will be transformed into carbon nanofibers with nanostructured bimetallic sulfides embedded. The interconnected carbon nanofibers will

ensure charge transfer between bimetallic sulfide nanostructures and buffer the stress caused by volume change during electrochemical testing. In order to obtain optimum performance of the flexible electrode, the weight ratio of electrochemically active bimetallic sulfides should be higher although the flexibility might be compromised. Thus the weight ratio of the bimetallic sulfides will to be tuned to obtain light weight and high electrochemical performance while maintaining good flexibility so as to obtain promising flexible electrodes. To pursue further, it is envisaged that these nanostructured bimetallic sulfides based flexible electrodes can also be incorporated with elastomeric scaffolds towards fabrication of stretchable SIB electrodes. As shown in Fig. 7.5b, the flexible electrodes composed of conductive and interconnected carbon nanofibers embedded with bimetallic sulfide nanostructures will be attached onto pre-strained PDMS (poly(dimethylsiloxane)) substrate. After releasing the strain, the flexible electrodes will form curved structure on top of PDMS. This newly formed electrodes will sustain some extent of stretchability while maintaining charge storage capabilities of the top layer. In this process, the weight ratio of carbon needs to be increased again because the electronic conductivity of the top layer electrodes will be reduced during the stretching process. A higher content of carbon can maintain the electronic conductivity of the top layer electrodes when being stretched. The thickness of the bottom layer PDMS will also be optimized to ensure the stretchability while avoiding excess amount of electrochemically inactive PDMS, so as to obtain stretchable electrodes with high gravimetric/volumetric capacity.

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