Redox-active polymers as promising electrodes for rechargeable lithium batteries

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**NANYANG
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**REDOX-ACTIVE POLYMERS AS PROMISING ELECTRODES
FOR RECHARGEABLE LITHIUM BATTERIES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

REDOX-ACTIVE POLYMERS AS PROMISING ELECTRODES FOR RECHARGEABLE LITHIUM BATTERIES

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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.

...15/Jun/2018...
Date

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Xie Jian

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.

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Authorship Attribution Statement

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

Chapter 1 and 2 are published partially as (1) **J. Xie**, P. Gu, Q. Zhang, *ACS Energy Lett.* **2017**, 2, 1985-1996; (2) **J. Xie**, Q. Zhang, *J. Mater. Chem. A* **2016**, 4, 7091-7106 and (3) **J. Xie**, C.-E Zhao, Z. Lin, P.-Y. Gu, Q. Zhang, *Chem. Asian J.* **2016**, 11, 1489-1511.

The contributions of the co-authors are as follows:

- A/Prof Q. Zhang provided the initial project direction and edited the manuscript drafts.
- For paper (1), I prepared and wrote the whole manuscript draft.
- For paper (2), I prepared and wrote the whole manuscript draft.
- For paper (3), I prepared the whole manuscript draft. I, Dr C.-E Zhao, Dr Z. Lin and Dr. P.-Y. Gu co-wrote the manuscript draft.

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The contributions of the co-authors are as follows:

- A/Prof Q. Zhang provided the initial project direction and edited the manuscript drafts.
- For paper (1), I prepared and wrote the whole manuscript draft and analyzed all the data.
 - The oligomer sample was synthesized and purified by me. Characterizations including SEM, XRD, TGA and EA were conducted by me. The cell assembly and all the electrochemical studies were carried out

by me. In addition, the sample preparations for all these studies were also conducted by me.

- Dr X. Rui partially contributed to the cell assembly and electrochemical study as well as assisted in the collection of the galvanostatic charge-discharge, cycling and rate stability data. Dr P. Gu conducted the FTIR analysis and involved in the discussion on the EA results. Dr J. Wu assisted in the synthesis of the oligomer. A/Prof Q. Yan and A/Prof Z. J. Xu provided necessary discussions and glovebox for cell assembly.
- For paper (2), A/Prof Q. Zhang and Prof W. Huang conceived the idea and designed the experiments. Dr Z.-Q. Lin and I co-prepared and co-wrote the manuscript draft.
 - The nanoengineering of the COF sample was conducted by me. Characterizations including SEM, TGA and EA were conducted by me. The cell assembly and all the electrochemical studies (galvanostatic charge-discharge, CV, cycling, rate stability and EIS) were conducted by me. In addition, the sample preparations for all these studies were also conducted by me.
 - Dr. Z.-Q. Lin. and J.-N. Weng synthesized the pristine NG-COF and prepared the NG-COF samples. A/Prof Z. J. Xu provided the glovebox and battery tester for battery fabrication and testing. B. Zhang and X. Huang performed the TEM/HRTEM/STEM and EDX characterizations. H. Zhang and H. Li provided the AFM measurements. J. Li conducted the theoretical calculation. R.-B. Song contributed to the XPS and Raman test. J.-N. Weng and Y. Liu provided the BET data and porosity analysis. Z.-Q. Lin. worked on the FTIR, SEM, AFM and other characterizations.

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- A/Prof Q. Zhang provided the initial project direction and edited the manuscript drafts.
- For paper (1), I prepared and wrote the whole manuscript draft and analyzed all the data. Dr W. Chen partially contributed to and wrote the material synthesis section.
 - Characterizations including the SEM, TGA and EA were conducted by me. The solubility tests of the two samples, cell assembly, cell disassembly and all the electrochemical studies (galvanostatic charge-discharge, CV, cycling, rate stability and EIS) were also carried out by me. In addition, the sample preparations for all these studies were conducted by me.
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- For paper (1), I prepared and wrote the whole manuscript draft and analyzed all the data.
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 - I purified the as-prepared sample that was synthesized by Dr Z. Wang.
 - Dr P. Gu conducted the FTIR analysis. A/Prof Z. J. Xu provided the glovebox for cell assembly and was involved in the discussion.
- For paper (2), I prepared and wrote the whole manuscript draft and analyzed all the data.
 - Characterizations including the SEM, TGA were conducted by me. The solubility tests, cell assembly, cell disassembly and all the electrochemical studies (galvanostatic charge-discharge, CV, cycling, rate stability and EIS) were conducted by me. In addition, the sample preparations for all these studies were also conducted by me.
 - I purified the as-prepared sample that was synthesized by Dr Z. Wang.
 - Dr W. Chen and Dr S. Sun assisted in the FTIR and EDS elemental mapping analyses. A/Prof Z. J. Xu provided the glovebox for cell assembly and was involved in the discussion.

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Abstract

Electrode materials play a critical role in achieving high energy density and long cycle life rechargeable lithium batteries. The increasing concern with respect to the use of traditional inorganic electrode materials on resources and environmental issues has strongly inspired scientists to search green energy electrodes. Organic compounds are potentially sustainable and renewable materials as many of them can be obtained from natural products and biomass. To meet the ever-growing demands for the next generation versatile and sustainable energy-related devices, redox-active polymers, which have potential advantages over inorganic materials, are among the most promising types of green candidates. The properties of redox-active polymers can be tuned through the modification of the structure and incorporation of different functional moieties.

The purpose of this project is to develop novel redox-active polymers, which could be potential high-performance electrode materials for organic based rechargeable batteries. Therefore, this thesis mainly addresses the design, synthesis, characterization and electrochemical performance of several novel redox-active polymers and large aromatic molecules for lithium related rechargeable batteries.

In detail, an overall introduction for the research on redox-active polymers is provided. The rationale, hypothesis and objectives are involved. Moreover, the strategies, methods and approaches to achieve the objectives are discussed in each chapter. The literature concerning redox-active polymers, background and current situation are also included. Specifically, the history, principles and mechanisms of redox-active polymers are reviewed. Different types of redox-active polymers are classified. The working principles that the characterization techniques employed in this project are introduced.

More importantly, this thesis includes the major findings and conclusions: Firstly, two novel redox-active ladderized conjugated polymers and their nanostructures were designed and developed as high-performance negative electrode materials for Li-organic batteries. Secondly, four novel redox-active carbonyl compounds were designed and

developed as high-performance positive electrode materials for Li-organic batteries. Thirdly, a novel all-plastic-electrode battery was designed, optimized and developed on the basis of a novel designed bi-functional poly(quinone) electrode. The symmetric full battery delivers excellent electrochemical results. Lastly, a general summary of the whole project is also provided. The recommended future works to obtain advanced flexible battery systems are also introduced in the last chapter.

Lay Summary

As mentioned in the abstract, the purpose of this project is to develop high-performance novel redox-active polymers for organic based rechargeable batteries. Therefore, this thesis mainly addresses the design, synthesis, characterization and electrochemical performance of several novel redox-active polymers and large aromatic molecules for lithium related rechargeable batteries. This thesis includes the major findings that can be classified into the following paragraphs. In particular, the impact on the research communities and the outcome novelty of this thesis are discussed. The recommended future works to obtain advanced flexible battery systems are also introduced.

Firstly, two novel redox-active ladder conjugated polymers (in terms of their one-dimensional (1D) and two-dimensional (2D) structures) were synthesized through a simple one-step polymerization process, respectively. Through nano-engineering, the nanostructures of both polymers were obtained and their feasibilities as the anode materials for lithium-organic batteries were investigated. The superior electrochemical properties of these two compounds bring the battery performance of organic materials to a new level. These investigations present efficient methods to develop multi-electron redox active materials with stable electrochemical performance.

Secondly, two innovative strategies to obtain better organic cathodes were proposed by designing four novel redox-active organic cathodes. These two studies present possible and effective strategies toward more competitive capacity retentions and prolonged lifetimes of the future electrochemical cells. Both studies confirm that, through designing and modifying organic structures, organic positive electrodes with better performance can be achieved. These novel structural tailoring strategies provide alternative solutions to develop organic cathodes toward next-generation of high stability batteries.

Thirdly, a ladder-structured heterocyclic poly(quinone), was developed as a electrochemical stable anode, cathode and bi-functional electrode. Such a superior electrode material PDB shows an insoluble behavior, therefore delivering outstanding

energy density and ultra-long cycling stability as both the anode and cathode materials. Furthermore, an innovative all-plastic-electrode symmetric full-battery was fabricated with excellent electrochemical performance. This study provides an effective strategy to develop flexible and stable organic electrodes toward next-generation of high performance all-plastic batteries.

Lastly, a general summary of the whole project is presented by discussing the hypothesis and outcomes achieved in this thesis. The recommended future works, including the objectives, current situation and effective strategies to obtain advanced flexible battery systems are comprehensively discussed.

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Figure 6.14 All-plastic-electrode symmetric full-battery demonstration. (A) Proposed redox mechanism of PDB used as active bi-functional electrodes (pristine PDB as the cathode and pre-lithiated PDB as the anode). (B) Configuration of the fabricated all-PDB

based full-battery. (C) Cross-sectional SEM images of the PDB cathode and PDB anode (scale bar: 5 μm).

Figure 7.1 Schematic illustration of the two conjugated polymers discussed in chapter 4.

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Abbreviations

AFM	Atomic Force Microscopy
CMP	Conjugated Microporous Polymer
COF	Covalent Organic Framework
CV	Cyclic Voltammetry
EA	Elemental Analysis
EDS	Energy-Dispersive X-Ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier Transform Infrared Spectra
HRMS	High-Resolution Mass Spectrometry
LIB	Lithium-Ion Battery
NMR	Nuclear Magnetic resonance
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Chapter 1*

Introduction

The increasing concern about traditional inorganic electrode materials on resources and environmental issues has strongly inspired scientists to explore green electrode materials. Organic redox-active compounds are potentially sustainable and renewable materials as many of them can be obtained from natural products and biomass. Additionally, the properties of organic compounds can be tuned through the modification of the structures and the introduction of functional groups. In this chapter, the hypothesis and objectives are proposed to develop novel redox-active polymers for high-performance organic based lithium-ion batteries. The dissertation overview and outcomes are also included.

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1.1 Hypothesis

Since the first introduction of the concept of lithium-ion based rechargeable battery in 1970s,^[1-4] rechargeable lithium batteries have received great attention as the important energy storage systems in the past few decades. Considerable success has been achieved for the applications in portable electronics and electric vehicles. Recently, inorganic redox-active materials have been extensively synthesized and investigated as the electrode materials.^[5-14] However, they are still far from the requirements for practical applications. Nanostructured or microstructured transition metal oxides, metals and their alloys that possess high theoretical capacity have been developed as the anode and cathode materials.^[5, 7, 15-32] For example, the theoretical capacity of silicon (Si) can reach as high as 4200 mAh g⁻¹ and the theoretical lithium storage of LiFePO₄ is around 170 mAh g⁻¹.^[15, 17, 20] Although their electrochemical performances are much better than that of commercially used anode (graphite ~372 mAh g⁻¹) and cathode (LiCoO₂ ~140 mAh g⁻¹) materials, the lithiation processes in most of these materials result in significant volume expansion, which causes the pulverization of the materials, leading to the fracture and the loss of electric contact.

In addition, the development of eco-friendly lithium-ion batteries (LIBs) has met a bottleneck, as the large production of the transition metal based materials causes numerous concerns for resources and environmental issues. Therefore, more and more researchers are looking for potential redox-active organic compounds that can be applied for LIBs, owing to their good redox stability and high theoretical gravimetric capacities. More importantly, organic redox-active compounds that consist of low atomic weight elements (such as H, C, N, O and S) are potentially sustainable and greener as many of them can be obtained from natural products and biomass.^[33-39] In fact, a lot of redox-active organic molecules with electrochemically active carbonyl groups have been successfully reported as the electrode materials. Similar to an inorganic LIB, the charge and discharge process of an organic electrode-based LIB occurs on two active electrode materials. As shown in **Figure 1.1**, the success of organic compounds can also be

attributed to the redox reactions that involve the transfer of electrons between the positive and negative electrode materials.

Figure 1.1 The cell configuration and charge transfer process of a typical organic-based LIB. Reproduced from ref 93. Copyright Royal Society of Chemistry.

In the past two decades, several types of organic materials, such as carbonyl compounds,^[40-60] organic salts,^[34, 39, 48, 61-72] organosulfurs^[73-76] and conjugated polymers,^[77-88] have been extensively studied as electrodes for LIBs. The concept of organic materials as electrodes can be traced back to more than 40 years ago,^[89] however, much less attention has been paid to organic electrodes since the great achievement of inorganic electrodes in applications has been realized. Fortunately, researchers have never stopped the investigation on organic electrodes, because their structures and functional groups can be flexibly designed and controlled during the synthesis process, therefore, different properties of the organic compounds can be obtained through the tuning of the structures as well as the functional groups.

Organic redox-active materials have been demonstrated as suitable electrodes for advanced rechargeable batteries due to their structural diversity, reasonable sustainability, tunable properties, and possible high energy density.^[90-94] However, most of these materials (especially small molecules) encounter serious dissolution issue, causing sharp deterioration in cycling and rate stability.^[95] Various strategies have been proposed to

suppress this problem.^[96] The most common approach is to generate their enolate forms ($-\text{OM}$, $\text{M}=\text{Li}^+$, Na^+ & K^+).^[97-100] Unfortunately, such formations will cause reduced energy densities due to the relatively lower operating voltages of organic salts. In the past two decades, novel ideas have been demonstrated to realize high-performance batteries with better stability. For example, organic redox small molecules with extended structures and rigid frameworks have been proven to be effective candidates.^[101-104] In addition, the introduction of sulfur (S) atoms or electron withdrawing groups (e.g. $-\text{F}$, $-\text{CN}$ & $-\text{SO}_3\text{Na}$) can lead to enhanced stability and increased operating voltage.^[105-108] Very recently, new organic materials with redox-active centers such as $\text{C}=\text{N}$,^[109] $\text{C}=\text{S}$ ^[110] and $\text{N}=\text{N}$ ^[111] also show greatly-improved redox ability and electronic conductivity. Although these approaches deliver several promising results, the target to achieve organic rechargeable batteries with high energy density, stable cycling, and steady rate behavior remains a big challenge.

More recently, to pursue both stable cycling performance and high energy density organic materials, redox-active polymers, which are often obtained through the polymerization of redox-active small molecules, are considered to be the most promising electrode candidates due to their poor solubility, good structural diversity, reasonable sustainability, tunable properties, etc.^[97-100] Most importantly, the dissolution issue can be effectively addressed by polymerization strategy. According to the capacity calculation formula,^[112] the theoretical capacity of an electrode material can be improved from two aspects. One is through the adoption of multielectron reactions. With more active sites and electrons involved into the electrochemical reactions, the specific capacity will be increased several folds. Another is through the reduction of molecular weight (the single repeating unit for polymers). Since redox-active polymer are often consisted of low-molecular weight atoms and the structures can be designed and tailored with multielectron activities, redox-active polymers are highly desirable for better electrode materials as compared with inorganic materials. Most importantly, organic synthesis could simply allow chemists to control the structures and functional groups in a large amount.^[113] As shown in Figure 1.2, several previously reported representative redox-active polymers can be easily obtained in a few synthetic steps.

Figure 1.2 Synthesis of representative redox-active organic compounds. Reproduced from Ref 113. Copyright Elsevier Inc.

Because of these advantages, redox-active polymers are believed to be promising future electrode materials for advanced rechargeable LIBs. As shown in Figure 1.3 and 1.4, redox-active polymers can be classified into two major groups^[91] (1) redox-active group embedded polymers, including conventional conductive polymers and novel conjugated polymers and (2) redox-active pedant bearing (functional groups containing) polymers

including carbonyl polymers and radical polymers. However, radical polymers still present some disadvantages, such as low theoretical capacity values due to their large molecular weight (per repeating unit), limited reaction electrons involved and low energy density.^[114] Thus, state-of-the-art investigations have been mainly focused on conjugated polymers (conductive polymers can be also regarded as a type of conjugated polymers) as well as polymers with multiple redox-active carbonyl groups.^[115-125]

Therefore, this thesis will mainly focus on these two types of polymers. Surprisingly, recent progress showed that the electrochemical performances including energy density, power density and cycling stability of redox-active polymers are comparable to or even superior than the conventional inorganic materials.

Directly employing redox-active organic polymer as the active electrode materials is a promising approach to improve performance and stability of the future LIBs due to the following hypothesizes:

- (i) The idea of employing organic redox-active polymers will expand the resources of electrode materials and alleviate the environmental concerns.
- (ii) The usage of insoluble redox-active polymer compounds can prevent themselves from dissolving into common non-aqueous electrolyte solutions due to their poor solubility.
- (iii) Benefiting from nanoengineering, organic nanostructures can allow researchers to achieve electrode materials with high power or energy density and fast charging-discharging capability, attributing to the larger surface area and possibly higher electronic conductivity as compared with bulk materials.
- (iv) Due to their natural superior mechanical characteristics (e.g. good flexibility), polymer compounds could be excellent candidates for future flexible batteries.

Figure 1.3 Classification of redox-active polymer types. Reproduced from ref 115. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 1.4 Classification of redox-active polymer structures. Reproduced from ref 91. Copyright Elsevier Inc.

1.2 Objectives and Scope

As mentioned in the previous section, redox-active polymers are promising candidates for electrode materials, which can overcome most of the shortcomings of inorganic

materials.^[91] The organic synthesis could allow scientists to control the structures and functional groups in a large amount, and organic materials are potentially renewable since many of them can be prepared from natural products and biomass.^[33-35, 39] Although some recent works have shown that organic materials can be used as battery electrodes with good performance,^[73, 91] the investigations are not enough. Besides, polymer-based nanostructures or microstructures are still largely unexplored. The obtained knowledge from literature is still rare and hinders the ability to design high-energy density or power density organic materials. Thus, in order to improve the competence of rechargeable batteries for practical use, the stability (or cycle life) of the electrodes at high current densities is a key issue. Moreover, the use of organic redox-active polymers is considered to expand the availability of the resources of electrode materials and alleviate the environmental concerns to a certain extent.^[33] This thesis plans to lead to the understandings on how different organic polymers can achieve high battery performance.

This thesis will focus on the development of novel hetero-atoms containing redox-active polymers, which are considered as suitable candidates for the next generation of high performance rechargeable batteries. Investigations found that the presence of hetero-atoms (including oxygen, nitrogen and sulfur atoms) in the polymer structure could enhance the ability of the material to accept more lithium ions and increase the operating voltage (e.g. higher operating voltage, better electronic conductivity, lower energy for lithiation, etc.), hence improving the electrochemical performance of rechargeable LIBs. Therefore, in this project, the author and his collaborators will design and synthesize novel redox-active polymers as well as heteroatoms containing conjugated materials, and will prepare the nanostructures or microstructures of these materials. The author and his collaborators also plan to extend the redox-active polymers from one-dimensional (1D) to two-dimensional (2D) by designing and synthesizing nitrogen-rich covalent organic frameworks (COFs). These proposed polymer electrodes are expected to exhibit superior electrochemical performance in LIBs, affording high Li-storage capacity and good cycling stability.

The detailed objectives of the proposed project are listed below:

- a) Designing, synthesizing and characterizing redox-active polymers with different heteroatoms and their nanostructures or microstructures.
- b) Extending the structure of redox-active polymers from 1D to 2D frameworks, and exploring their electrochemical performance for Li-organic batteries.
- c) Investigating the feasibility of redox polymer electrodes as the negative or positive electrodes for Li-organic batteries through the fabrication of half cells. Considerations including the specific capacity, cycling stability, rate capability and energy density.
- d) Comparing different electrolytes and solvents. Selecting a compatible electrolyte system (with a proper concentration) and an optimized conductive additive ratio to perform electrode fabrication.
- e) Fabricating redox-active polymer based flexible electrode materials. In addition, achieving and optimizing well-performed all-polymer based symmetric full-batteries.

1.3 Dissertation Overview

This thesis addresses the design, synthesis, characterization and electrochemical performance of several novel redox-active polymers and large aromatic molecules for lithium related rechargeable batteries. The strategies, methods and approaches to achieve the objectives are discussed in each chapter.

Chapter 1 provides an overall introduction for the research on redox-active polymers. The rationale, hypothesis and objectives are also involved in this chapter.

Chapter 2 reviews the literature concerning redox-active polymers. The background and current situation are included. In details, the history, principles and mechanisms of redox-active polymers are reviewed. Different types of redox-active polymers are classified and divided into several sub-sections in this chapter.

Chapter 3 discusses the working principles that the characterization techniques employed in this project. The methodologies of data analysis of several techniques are also

involved. Each particular approach is appropriately briefed and the key components of necessary techniques are listed in each sub-sections of this chapter.

Chapter 4 elaborates the synthesis, characterization and electrochemical performance of two novel redox-active conjugated polymers. Both the obtained 1D and 2D redox-active ladder-structured conjugated polymers are demonstrated to show great potential as negative electrodes for lithium-organic batteries.

Chapter 5 elaborates the design and development of four novel redox-active carbonyl compounds as positive electrodes for lithium-organic batteries. In detail, two large aromatic dianhydrides based on naphthalene and perylene building blocks are investigated. In addition, two carbonyl polymers based on pyrene-4,5,9,10-tetraone building blocks are also investigated.

Chapter 6 elaborates the design and development of a unique quinone polymer as a novel, soft and flexible electrode material, which is further used as the anode, cathode and bifunctional electrode with high-performance. Moreover, the fabrication and optimization of a novel all-plastic-electrode symmetric LIB is demonstrated.

Chapter 7 provides a general summary of the whole project. The recommended future work to obtain advanced flexible battery systems (on the basis of multivalent Mg and Al-ions) is introduced.

1.4 Findings and Outcomes

This research led to major novel outcomes by:

1. Two novel redox-active ladderized conjugated polymers and their nanostructures were developed as high-performance negative electrode materials for Li-organic batteries.
2. Four novel redox-active carbonyl compounds were developed as high-performance positive electrode materials for Li-organic batteries.

3. A novel all-plastic-electrode battery was designed, optimized and fabricated on the basis of a novel designed bi-functional poly(quinone) electrode. The symmetric full battery delivers excellent electrochemical results.

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Chapter 2*

Literature Review

This chapter contains the literature studies of the state-of-the-art redox-active compounds deployed as active electrodes for rechargeable Li-organic batteries. In particular, different types of organic redox-active compounds including conductive & conjugated polymers, carbonyl polymers and redox-active small molecules or building blocks to obtain redox-active polymers are introduced. The background and current situation of redox-active polymers are included. In detail, the history, principle and mechanism of each type of redox-active compounds are reviewed. Different types of redox-active compounds are classified and divided into several sub-sections in this chapter.

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2.1 Brief Overview of Redox-Active Polymers

Tremendous investigations have recently been devoted to the design and development of high-performance, light-weight, flexible and environment-friendly rechargeable batteries.^{1,2} Among all the types of organic electrode materials, earlier approaches have been dominantly focused on organosulfide, thioether and nitroxyl radical compounds.³ Though some of them delivered noteworthy electrochemical performances, there are still many difficulties to achieve long cycle life and high energy-density organic electrode materials. For example, serious dissolution problems and slow reaction kinetics could be frequently observed in organosulfides and thioethers.⁴⁻⁵ Due to the large molecular weight (per repeating unit) and limited reaction electrons involved in the reaction, nitroxyl radical compounds often possess low theoretical capacity values.⁵

Compared to inorganic electrode materials (e.g. LiCoO_2 ,⁶ $\text{Li}_4\text{Ti}_5\text{O}_{12}$,⁷ etc.), redox-active polymers show several advantages, such as the excellent electronic conductivity and superior energy storage due to the extended π -conjugation and tunable property, which can be obtained through the modification of organic structures as well as introduction of different functional groups and redox moieties.⁸ More importantly, the serious structural alterations that often encountered with inorganic materials can be successfully avoided, because redox-active polymers can allow a simple and fast redox process.⁹ Due to these superiorities, remarkable rate performance and ultra-long cycle life rechargeable batteries can be potentially achieved based on redox-active polymers. Scheme 2.1 illustrates the electrochemical reactions of representative types of redox-active compounds, including n-type, p-type and bipolar organic compounds.^{8a} Moreover, the electrochemical reactions of novel redox-active compounds with different redox centers or functional groups like $\text{C}=\text{N}$, $\text{C}=\text{S}$ and $\text{N}=\text{N}$ are also presented in Scheme 2.2. They are promising redox-active materials for future high-performance organic electrode based rechargeable batteries.

Scheme 2.1 Illustration of the electrochemical reactions of several representative types of redox-active organic materials. Reproduced from ref 8a. Copyright Royal Society of Chemistry.

Scheme 2.2 Illustration of the electrochemical reactions of novel redox-active compounds with different functional groups. Reproduced from ref 8b,c and ref 68. Copyright Nature Publishing Group, Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

As mentioned in chapter 1, redox-active polymers can be classified into two major groups, the first group is the redox-active group embedded polymers, including conventional conductive polymers and novel conjugated polymers. The second group is the redox-active pedant bearing (functional groups containing) compounds, mainly consisting of carbonyl-containing polymers and organic salts. Since this thesis is focusing on these two types of polymers, the details with regard to both groups are reviewed below.

2.2 Redox-Active Conductive and Conjugated Polymers

Conductive and conjugated polymers have attracted tremendous attentions as effective electrode materials for anion-based battery designs in combination with negative metal electrodes (e.g. lithium (Li), sodium (Na), etc.).¹⁰ Metal-ion based battery designs are nowadays the most popular type of rechargeable battery systems. In particular, Li-ion batteries are widely known for their high energy and power density. Redox-active organic materials have shown great potential on rechargeable Li-ion, Na-ion and even dual-ion batteries as either positive or negative electrodes, since successful developments have been demonstrated in the past two decades.¹¹⁻¹² With further explorations of conductive and conjugated polymers on novel battery designs, future all-organic batteries or all-solid based flexible batteries with high performance are expected to be obtained. Due to the accessible redox states, high surface area and fast kinetics of nanostructured conjugated polymers; they are also potential high power-density candidates for electrochemical capacitor (e.g. pseudocapactor & supercapacitor) applications.¹³⁻¹⁵

Research on conductive and conjugated polymers has become an emerging topic since the first discovery of the conductive polymer polyacetylene (PAC) in the 1970s.¹⁶⁻¹⁷ Typical examples of conductive polymers including polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT), polyparaphenylene (PPP), and polyindole (PI) have been extensively investigated in the past ten years as pure active electrode materials for rechargeable batteries.¹⁰ However, rechargeable batteries based on pure conventional conductive polymer electrodes have already reached the bottleneck of their performance, attributing to their low doping

availability during the electrochemical reactions. To overcome this issue, several effective strategies have been proposed to improve the electrochemical performance of conjugate polymers.

Figure 2.1 A brief illustration towards high performance conjugated polymer electrodes. Reproduced from ref 109. Copyright American Chemical Society.

A brief illustration of the key parameters and effective strategies to achieve high performance conjugated polymer batteries is shown in Figure 2.1. Among all the strategies, one was to employ nanostructured conductive polymers.¹⁸ Owing to the advantages of nanostructures, for example, the enlarged surface area, enhanced electrochemical reactivity, and shortened pathway for charge transportation, nanostructured conductive polymers could deliver improved performance as the active electrode materials as compared to bulk conductive polymers.¹⁹ Continuing on with this strategy, conductive polymer nanocomposites in the form of hydrogels, combining the advantages of organic and inorganic materials were developed.²⁰ More recently, a new type of heterocyclic conjugated polymer representatives includes poly(benzobisimidazobenzophenanthroline) (BBL) and poly(1,6-dihydropyrazino[2,3g]quinoxaline-2,3,8-triyl-7-(2H)-ylidene-7,8-dimethylidene) (PQL), with ladder-like heterocyclic structures, delivered noteworthy performance as the active electrode materials for rechargeable Li-ion batteries.²¹⁻²² To be noted that, by extending the structures of organic compounds from one-dimension (1D) to two-dimensional (2D), conjugated microporous polymers (CMPs), covalent organic frameworks (COFs) in terms

of their redox-active organic structures can also deliver promising results as effective electrode materials for rechargeable metal-ion batteries.²³⁻²⁹

To give a summary of the above-mentioned strategies and the representative demonstrations, Figure 2.2 lists the structures of several nanostructured conjugated polymers that have been successfully employed as electrode materials for metal-ion rechargeable batteries. These materials will be further discussed in the following sub-sections. To highlight that, the theoretical capacity values and number of electrons (per repeating unit) in Figure 2.2 are calculated based on their structures alone (before doping) with respect to the highest electron transportation capability from the literature studies. Table 2.1 compares and lists the key properties and performances of typical electrode materials, including commercial inorganic materials and representative organic materials.

Figure 2.2 Structures and theoretical capacity calculations of typical conjugated polymers, including conventional conductive polymers and novel conjugated polymers.

Table 2.1 Comparison table includes the key properties of outstanding inorganic and organic electrode materials.

Types	Electrode Material (electrolyte doping species)	Nanostructures (diameter in nm)	Electronic Conductivity ($S\ cm^{-1}$)	Initial Reversible Capacity ($mAh\ g^{-1}$)	Working voltage (V)	Cyclability ($mAh\ g^{-1}$)	Rate Capability (at maximum current density)
Commercial Inorganic Materials	$LiCoO_2$ ⁶	-	8.5×10^{-6}	141	4.3-3.6	137 after 100 cycles	at 0.1 C
	$Li_4Ti_5O_{12}$ ⁷	-	10^{-13}	150	2.0-1.2	145 after 250 cycles	73 $mAh\ g^{-1}$ at 3.2 A g^{-1}
Organosulfide	PDMcT ^d	-	10^{-7}	240	3.8-1.8	10 after 10 cycles	at 20 mA g^{-1}
Thioether	PTBDT ⁵	-	-	~240	4.2-1.4	~560 after 20 cycles (large polarization observed)	at 50 mA g^{-1}
Nitroxyl Radical	PTMA (Li^+ & PF_6^-) ³⁰	-	-	77	4.0-3.0	~68 after 500 cycles	At 0.1 mA cm^{-2}
Conventional Conductive Polymers	PANI (ClO_4^- & Li^+) ³¹	50-100 Bulk forms	7.1 5×10^{-1}	75.7 ~170	3.9-2.0 4.25-2.5	75.7 after 80 cycles ~176 after 400 cycles	at 20 mA g^{-1} at 1 C
	PI (PF_6^-) ³²	50-100	1.9×10^{-3}	~73	4.0-2.0	55.0 after 100 cycles	at 0.1 mA
	PPy (SO_4^{2-}) ³³	200-400	-	52.2	1.5-0.1	~30 after 130 cycles	at 0.1 C
	PPP (PF_6^- & Li^+) ³⁴	Irregular shapes	-	80 (p-doping) 400 (n-doping)	4.6-3.0 3.0-0.0	70 after 100 cycles ~580 after 90 cycles	at 40 mA g^{-1} at 40 mA g^{-1}
	BBL (Li^+) ²¹	~30	-	1787	3.0-0.0	1181 after 50 cycles & 496 after 1000 cycles	461 $mAh\ g^{-1}$ at ~5.9 A g^{-1}
Novel Conjugated Polymers (including 1D & 2D)	PQL (Li^+) ³⁵	40-60	2.1×10^{-3}	1444	3.0-0.0	1770 after 100 cycles & ~500 after 1000 cycles	303 $mAh\ g^{-1}$ at ~9.1 A g^{-1}
	PDA (Li^+) ³⁶	~500	-	1818	3.0-0.0	1414 after 580 cycles & 500 after 1024 cycles	~900 $mAh\ g^{-1}$ at 3.2 A g^{-1}
	Microporous HATN-CMP (Li^+) ³⁷	~100	-	147	4.0-1.5	91 after 50 cycles	50 $mAh\ g^{-1}$ at 1.0 A g^{-1}
	BPOE (ClO_4^- & Na^+) ²³	~300	4.09×10^{-6}	55 (p-doping) 185 (n-doping)	4.1-1.3	~200 after 50 cycles & ~160 after 1000 cycles	~45 $mAh\ g^{-1}$ at 5.0 A g^{-1}

2.2.1 Principles and Essential Parameters

In an typical electrochemical cell construction, when a conjugated polymer is used as an active electrode material, it can accept or release ions during the electrochemical oxidation and reduction.³⁸ This ion accepting or releasing movement is known as the polymer doping or dedoping process, during the same time, the electric energy is stored via the movement of the ions within the π -systems along the polymer chains.³⁹ Moreover, doping is a reversible process that makes the conjugated polymers positively or negatively charged, enabling the energy storage applications.⁸ Conjugated polymers are classified into three different groups: p-, n-, and bipolar type (Equation 1 & 2, bipolar type encounters both p- & n-doping), depending on the types of ions (anions, cations or both ions) that are incorporated into the organic structures.⁴⁰

p-doping (PF_6^- as an anion example):

n-doping (Li^+ as a cation example):

x is the doping level

The maximum charges (in terms of anions and cations) that can be stored in an electrode are represented by a parameter named theoretical capacity (C_{th}).⁴¹ Equation 3 shows the calculation of the theoretical capacity of an electrode material. It can be derived that such a parameter (C_{th}) can be improved from two aspects. The first way is through the adoption of multielectron reactions. With more active sites and electrons involved into the electrochemical reactions, the specific capacity will be increased several folds. The second way is through the reduction of molecular weight. Since organic materials are often consisted of low-molecular weight atoms (e.g. C, H, O, N, and S) and the structures can be designed and tailored with multielectron activities, organic materials are highly desirable for future high capacity electrode materials.¹¹

$$C_{th} = \frac{n \times F}{M_w} = \frac{n \times 96485 \text{ (C mol}^{-1}\text{)}}{M_w \text{ (g mol}^{-1}\text{)}} = \frac{n \times 26801}{M_w} \text{ (mAh g}^{-1}\text{)} \quad (3)$$

To measure the maximum energy that an electrode can provide, theoretical energy density (E_{th}) is the parameter, which is determined by theoretical capacity and operating voltage as shown in Equation 4. A battery with a promising energy density requires both high specific capacity (C_{th}) and high voltage (V). In Equation 4, the voltage of an electrochemical cell (V) is termed as the voltage difference between cathode (V_c) and anode (V_a) ($V = V_c - V_a$ (volt)), thus in a battery fabrication, the operating voltage of a cathode material should be as high as possible, whereas for an anode material it should be as low as possible. As for power density, high values can be obtained enabling the application of fast charge-discharge rechargeable batteries, especially for those materials that can provide high capacity values at high current rates.

$$E_{th} = C_{th} \times V \text{ (Wh g}^{-1}\text{)} \quad (4)$$

Since most of the conductive polymers were developed in their p-doped states through oxidation polymerization, early studies have proven the capability of conductive polymers to be preferably employed as active cathode materials.⁸ Jean Roncali et al. summarized the synthesis and bandgap control of conjugated polymers.⁴² The most attractive advantage of conductive polymer cathodes is their high operating voltage upon charging and discharging, usually ranging from 3-4 V.^{8, 43} Mostly, the anions from the electrolyte solution can be continually “doped” into the polymer structures at a high voltage to achieve their semi-oxidation or oxidation state (known as charging). A plenty of anion electrolyte species including PF_6^- , ClO_4^- , BF_4^- and AsF_6^- , etc., have been successfully “doped” into conductive polymer structures.¹⁰ Nevertheless, due to the poor intrinsic electronic conductivity and low doping availability (at most $x \sim 0.3$ to 0.5), it is essentially difficult for conductive polymers to achieve their full oxidation states.⁴⁰ This challenge has been widely recognized on conductive polymers.

High levels of doping will lead to permanent destruction of the polymer chains and subsequently result in unsatisfied electrochemical performance.⁴⁴⁻⁴⁶ In the 1980s,

investigation have already revealed that, upon charging beyond a certain voltage limit, the electroactivity and charge state of conjugated polymers would be destroyed, known as overoxidation.⁴⁴ Conditions including solvent and electrolyte species also have impact on this process and could cause different levels of doping. As a result, the life time of rechargeable batteries will be shortened. Polymer compounds including PAc, PPy, PEDOT, etc. were observed to suffer from this degradation process, though the exact chemical changes of these materials were not extensively studied.⁴⁵⁻⁴⁷ To get a deeper understanding, D. Aurbach and M.D. Levi summarized several effective strategies to improve the doping availability (e.g. by introduction of different electron-withdrawing groups).⁴⁸ Moreover, one recent investigation observed the morphological and crystallinity changes on PEDOT film upon overoxidation.⁴⁶ From the perspective of ionization or doping, the more a conjugated polymer chain is doped, the more “charge island” overlap and delocalize over the material, thus improving the electronic conductivity of conjugated polymers.^{39, 49} Of course, factors including charge carriers, counterion species and reaction kinetics, etc. should be considered to get a high electronic conductivity and performance. In addition to doping, the charge transfer and polaron formation of conjugated polymers should also not be neglected.^{39, 50}

2.2.2 Conventional Conductive Polymers

Despite the above-mentioned disadvantages, one of the greatest advantages of conductive polymers is the excellent electronic conductivity (upon pre-doping) as well as the good flexibility, particularly at their nanoscopic sizes. Pioneering demonstrations have been carried out to study the performance of nanostructured conductive polymer as active electrodes.⁵¹ As mentioned in section 2.2, attributing to the increased electroactive surface area and the enhanced electronic conductivity of nanostructures, the electrochemical performance of nanostructured conductive polymers can be obviously improved. This strategy was confirmed by a comparison study between ClO_4^- pre-doped PANI bulk powders and nanotubes.⁵² With an almost six-time-higher electronic conductivity, ClO_4^- pre-doped PANI nanotubes (~ 300 nm, 7.1 S cm^{-1}) delivered a significantly-improved specific capacity compared to the unmodified ClO_4^- pre-doped

PANI powders (1.2 S cm^{-1}) (Figure 2.2a&b). Other than PANI, a study on Cl^- pre-doped PI nanoparticles (50-100 nm) also presented a considerable electronic conductivity and cycling stability.³² However, the practical capacity of the obtained PI was only moderate and might be further improved through optimizing the synthetic conditions. Moreover, a full battery (assembled with LiCoO_2) was achieved by involving an aqueous solution (Li_2SO_4) electrolyte into SO_4^{2-} pre-doped PPy nanoparticles (200-400 nm)⁵³. Nevertheless, a low working voltage of only around 0.9 V was delivered by such a demonstration. The result is unsatisfactory for the requirement of a promising full battery (preferably $>1.5 \text{ V}$). To investigate the possibility of bipolar conductive polymers as active electrode materials, PPP stands out due to its unique p- and n-dopable property.⁵⁴ Due to this excellent property, PPP showed a large operating voltage ($>2.4 \text{ V}$) with a potential high energy density (Figure 2.2c). Therefore, a full battery was successfully fabricated by employing bipolar PPP nanoparticles as both the anode and cathode materials.⁵⁵ Although the fabricated cell displayed a noticeable capacity gap between the charge (p-type) and discharge (n-type) capacity values (Figure 2.2d), this was one of the few earliest attempts to develop an all-organic battery.

Figure 2.3 Charge-discharge profiles of (a) ClO_4^- doped bulk PANI & (b) ClO_4^- doped PANI nanotubes (inset is the TEM image of ClO_4^- doped PANI nanotubes). (c) Cyclic voltammetry (CV) profiles of PPP at the n-dopable (0-3 V) and p-dopable (3-4.6 V) regions (inset is the SEM image of PPP aggregates). (d) Charge-discharge profiles of an

all-organic battery employing PPP as both the anode and cathode at 40 mAh g⁻¹. Reproduced from refs 52 and 55. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Copyright Royal Society of Chemistry.

Nanostructured conjugated polymers as pure active cathode materials are still rarely investigated. As mentioned, conductive polymers with pre-doped nanostructures show obvious advantages over their bulk forms. However, the maximum doping level of conductive polymers has not been effectively improved. As a result, the practical capacities of conductive polymers are quite low and far behind their theoretical capacities. Although the electronic conductivity of conductive polymers can be improved through morphology modification and nanoengineering, it is extremely difficult to further enhance the doping availability of conductive polymers, because they easily become unstable when over-doped, attributing to the serious charge repulsion among their structural units.⁸

2.2.3 Conductive Polymer Composites

After realizing the advantages and disadvantages, investigations on nanostructured conjugated polymers draw tremendous attention to the utilization of their hybrid and composite forms. State-of-the-art developments show successful experience on the fabrication of conductive polymer based three-dimensional (3D) conductive hydrogels.⁵⁶⁻⁵⁹ The unique cross-linked networks possess not only large surface areas and good structural flexibilities, but also high conductivity and rapid charge transportation behaviors. More importantly, a great number of free spaces can be provided by such cross-linked flexible frameworks, to compensate the significant volume expansions of the inorganic electrode materials.

Relying on this concept, nanostructured conductive polymer in their hydrogel forms have been greatly investigated. A 3D porous PANi-Silicon (PANI-Si) hydrogen nanocomposite (60-100 nm) (Figure 2.4a) was developed with a foam-like network as the anode material.⁵⁶ This demonstration exhibited an ultra-stable cycling performance and

no significant capacity fading can be observed after 5000 cycles (Figure 2.4b). Following this direction, a PPy-Si-carbon nanotube (PPy-Si-CNT) ternary network was developed (Figure 2.4c) with an outstanding battery performance.⁵⁷ More recently, a nanocomposite hydrogel PPy-Fe₃O₄ anode (Figure 2.4d, right) was developed. The structure of this hydrogel framework could be well maintained after 50 cycles of reversible cycling (Figure 2.4e).⁵⁹ In future, more nanocomposite based electrodes with high performance are believed to be obtained by using these strategies, to overcome the challenges (e.g. volume expansion, short cycle life and low capacity retention) of the traditional metal or metal oxide based inorganic electrode materials.

Figure 2.4 (a) TEM image of PANI-Si. The Si nanoparticles (blue arrow) are coated with uniform PANI layers (red arrow). (b) Ultra-long cycling of PANI-Si nanocomposite electrode between 0.01 and 1.0 V at 1 A g⁻¹. (c) SEM of PPy-CNT-Si nanocomposite ternary electrode. (d) Illustration of a traditional electrode system (left) and a novel nanostructured PPy-Fe₃O₄ conductive hydrogen electrode system (right). (e) SEM image of PPy-Fe₃O₄ electrode after the cycling test. Reproduced from refs 56, 57 and 59. Copyright Nature Publishing Group. Copyright American Chemical Society. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

Although conductive polymer based nanocomposites present promising electrochemical performance as electrode materials, the capacity contributions are mainly from the active

inorganic materials. By reviewing these studies, conductive polymers in their composite structures solely dominate as the coatings or networks to promote electron transportation as well as ion diffusion. The demonstrations on highly-performed batteries using single nanostructured conjugated polymers are still rare and yet to be discovered.

2.2.4 Novel Heterocyclic 1D Conjugated Polymers

To achieve sustainable organic-based batteries with high performance, more experiments should be carried out regarding the deployment of single nanostructured conjugated polymers as the active electrode materials. It is well known that conventional conductive polymers prefer to stay in their p-doped state, either through pre-doping or electrochemical oxidation to a certain voltage. Therefore, they are usually deployed as the active cathode materials. Although few conductive polymers showed n-dopable behaviors, where the cations can be n-doped into the organic structures,⁴⁰ much less developments have been carried out on exploring the electrochemical performance of conjugated polymers in their n-doped states. Apart from employing conventional conductive polymers, designing and developing novel conjugated polymers that are n-dopable with good performance is therefore highly desirable. For conventional conductive polymers, the doping process occurs through delocalization of the ions (mostly cations) along the polymer backbone.³⁸ However, for novel conjugated organic materials, they could show high energy storage through the insertion of metal cations (e.g. Li^+ , Na^+ , etc.) onto the atoms with lone pair electrons (e.g. oxygen and nitrogen) and the unsaturated carbon atoms. Sun et al first discovered this novel mechanism on a small conjugated molecule NTCDA. This mechanism was further confirmed by several groups.⁶⁰⁻⁶³ Nevertheless, even though the small molecules like NTCDA and PTCDA could accept a large amount of cations (e.g. Li^+ and Na^+), their high capacity storage capability can only be sustained at the initial cycles. These molecules still show poor cycling stabilities, suffering from the serious dissolution problems.

Considering from the aspect of molecular design, developments from the author's group found that conjugated ladder polymers could be good candidates for high performance

and fast storage electrode materials.^{21, 64} Additionally, we also found that nanostructured conjugated polymers can show high electronic conductivity even without pre-doping.²² Previously, the author's research group demonstrated the design and development of several heterocyclic nanostructured conjugated polymers as anode materials for lithium-organic batteries. Our studies showed that lithium cations (Li^+) could be effectively inserted onto the conjugated polymer structures between 3.0-0 V. Superior to small organic molecules that show serious dissolution behavior, conjugated polymers could not be easily dissolved into the non-aqueous organic electrolytes, due to their large aromatic backbones and repeatable units. By adopting a simple one-pot synthesis, novel ladder-conjugated polymers can be synthesized.²¹⁻²² Traditional methods to obtain polymer nanostructures contains oxidation polymerization, electrochemical polymerization, self-assembly, etc.,⁶⁵ Different from these methods, the nanostructures of novel heterocyclic conjugated polymers can be obtained through a simple precipitation method (Figure 2.5a). The rigid ladder-like structures with extended π -conjugations are believed to be beneficial to the charge transfer during the electrochemical reactions.⁶⁶ Moreover, the electrochemical reactivity of organic materials can be enhanced due to the presence of oxygen and nitrogen heteroatoms in the conjugated backbones.^{60, 67} Therefore, the overall battery performance in terms of specific capacity, cycling stability and rate performance can be improved.

Figure 2.5b&c show the nanoparticles of two novel conjugated polymers: BBL and its derivative SBBL, which were obtained with diameters of around 30 and 70 nm, respectively.²¹ These nanostructured BBL and SBBL deliver much improved electrochemical performance as compared with their as-prepared microsized aggregates. In details, BBL and SBBL nanoparticles can accept a large amount of around 22.3 and 15.2 Li^+ , respectively (per repeating unit), attributing to the large π -conjugated backbone and heteroatom-rich multi-aromatic system. These remarkable high Li^+ storage led to a large initial reversible capacity of 1787 and 1603 mAh g^{-1} of BBL and SBBL, corresponding to a high value of 93.1% and 84.9% of their theoretical capacity values. Nevertheless, the cycling performance of both materials showed rapid declination with only 66% and 58% capacity retentions after 50 cycles. The low polymerization of the two

compounds with large backbones might be responsible for the fast deteriorations. Therefore, further studies from the author's research group focused on conjugated polymers that could be obtained by small backbone reactants.

Figure 2.5 (a) Schematic illustration of a simple precipitation method. Step I: The conjugated polymer/acid solution is added dropwise into a rapid-stirring solvent. Step II: The nanostructured conjugated polymers are rapidly precipitated out from the solvent. (b) SEM image of BBL nanoparticles. (c) SEM image of SBBL nanoparticles. (d) Cycling performance of PQL nanoparticles at 100 mAh g⁻¹ (Inset is the SEM image). (e) Charge-discharge profiles of PPCQ nanoparticles for the first two cycles at 100 mAh g⁻¹ (Inset is the SEM image). (f) Long-term cycling of PDA electrode at 500 mAh g⁻¹ (Inset is the SEM image of as-prepared PDA). Reproduced from refs 21, 22, 64 and 36. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Copyright American Chemical Society.

To design organic materials with better cycling ability, one promising type of conjugated polymers synthesized by small backbone reactants is the heterocyclic conjugated polyazaacene, which possesses a rich number of nitrogen atoms. To investigate the doping availability of this type of conjugated polymer, a novel polyazaacene PQL was designed and synthesized.²² PQL nanoparticles showed significantly improved electronic conductivity ($2.1 \times 10^{-3} \text{ Scm}^{-1}$) than its pristine state ($1 \times 10^{-5} \text{ Scm}^{-1}$), confirmed by the four-point conductivity measurement. From both the electrochemical cell fabrication and

density functional theory (DFT) theoretical study, 13.6 Li^+ could be practically accepted by PQL nanoparticles (with diameters of ~ 50 nm), corresponding to a high theoretical capacity of 1822 mAh g^{-1} . Due to the kinetic reaction limitation, the practical capacity could not reach the maximum theoretical capacity, however, it still belongs to one of the highest values for organic anodes (1444 mAh g^{-1}) (Figure 2.5d). Other than the superior battery performance at room temperature, to be highlighted that, BBL, SBBL and PQL nanoparticles could exhibit better performance at a higher temperature of 50°C , showing the possibility of developing high-temperature organic batteries in future.

Above mentioned conjugated BBL, SBBL and PQL were composed of six-membered rings. In the following works, by introduction of a five-membered ring, a nanostructured oligomer poly(1,4-dihydro-11H-pyrazino[2',3':3,4]cyclopenta[1,2-b]quinoxalin-11-one) (PPCQ) (>100 nm) was synthesized. This compound showed a high initial lithiation with about 13 Li^+ ($\sim 1678 \text{ mAh g}^{-1}$) were accepted by the conjugated structure (Figure 2.5e).⁶⁴ Inspired by the redox availability of catechol/o-benzoquinone, a study regarding the biodegradable polydopamine (PDA) as both the binder and active anode materials was conducted.³⁶ The PDA microspheres (~ 500 nm) could accept about 10 Li^+ at a high current density of 500 mAh g^{-1} . Such a high Li^+ storage could be well maintained with a high retention of 93% after 580 cycles (Figure 2.5f). To summarize, all above-mentioned nanostructured conjugated polymers showed excellent cycling stability and high capacity retentions even after ultra-long cycles of charging and discharging. These investigations on novel nanostructured heterocyclic conjugated polymers demonstrate a potential way to develop organic rechargeable batteries with high performance.

For recommendation, detail understanding of the Li^+ doping and solid electrolyte interphase (SEI) formation mechanisms through in-situ or ex-situ studies become essentially important, especially considering the poor solubility and amorphous state of polymer electrodes. Prior to study the mechanisms, of course, the exact information of conjugated polymers, including the molecular weight, number of repeating units, structural defects, and so on, should be obtained through advanced polymer

characterization instruments. Though it is quite challenging, a better understanding of the electrochemistry of such a promising type of material is highly desirable.

2.2.5 Novel Heterocyclic 2D Conjugated Polymers

Two-dimensional (2D) conjugated structures could also be suitable electrode materials for rechargeable batteries. Particularly, nanostructured conjugated polymers including CMPs, COFs and similar aromatic frameworks could be promising high performance electrode materials with high specific capacity, long cycles and high power density. Several unique features can be found on 2D conjugated polymers, such as the poor solubility in most of the common solvents, large surface area and high structural stability. More importantly, the synthetic diversity (by selecting different organic building blocks) provides chemists a bright future to develop various 2D conjugated polymers with different structures. Demonstration showed that microporous hexaazatrinaphthalene-based CMP (HATN-CMP) could be a good redox-active cathode material (Figure 2.6a &b) with the power density ranges from 70 to 706 W kg⁻¹.³⁷ The redox mechanism of such a type of material was further confirmed by a recent study on a single-crystal based small-molecule HATN (or so-called triquinoxalinyne (3Q)),⁶⁸ which shows an excellent reversibility of Li⁺ doping. This material delivered a high specific capacity (395 mAh g⁻¹) (Figure 2.6c) and a super-high stability of 10000 cycles at 8 A g⁻¹, and the power density was as high as ~8 kW kg⁻¹. Several nanostructured triphenylamine (TPA)-based CMPs (OPTPA, SPTPA and YPTPA) with high surface areas were synthesized by Jiang et al.²⁴ (Figure 2.6g). These materials used as active cathodes exhibited good rate stability and fast charge-discharge capability. The shuttling ions were PF₆⁻ anions, which can be reversibly doped into the TPA-based CMPs during the electrochemical reactions. Among these materials, YPTPA can provide an ultra-stable capacity of ~93 mAh g⁻¹ after 1170 cycles at 2 A g⁻¹ (Figure 2.6h). The power density of YPTPA could reach ~6.4 kW kg⁻¹. For the investigation of CMP-based anode materials, a CMP named PDCzBT with a high reversible capacity of 1042 mAh g⁻¹ (vs. Li⁺) and a good rate performance was developed by Cui et al.²⁵ All these outstanding results revealed successful developments of CMPs to be used as effective electrode materials for organic rechargeable batteries.

Figure 2.6 (a) Molecular structure of HATN based conjugated polymer (HATN-CMP). (b) SEM image of HATN-CMP. (c) Initial charge-discharge profiles of a small-molecule hexaazatrinaphthalene (or triquinoxalinylene 3Q) between 1.2 and 3.9 V at 400 mAh g⁻¹. (d) Structure of an aromatic porous-honeycomb conjugated polymer (BPOE). (e) TEM image of BPOE showing a sheet-like morphology. (f) Ultra-long cycling performance of BPOE as the electrode for a sodium-ion battery between 1.3 and 4.1 V at 1.0 A g⁻¹. (g) Structures of the three COFs. Reproduced from refs 37, 68, 24 and 23. Copyright Royal Society of Chemistry. Copyright Nature Publishing Group. Copyright Elsevier Ltd.

The development of crystalline or semi-crystalline organic structures with strong covalent bonds is also of great potential and a lot of COFs have been developed by Jiang and coworkers.⁶⁹ COFs are known as porous materials with a precisely-defined network structure of building blocks.⁶⁹ Through chemical modification, nitrogen atoms can be incorporated onto the COF structure and naturally fitted into the strong covalent network of carbon atoms.^[70] The introduction of nitrogen can result in an improved

electrochemical reactivity of the COF materials. It is believed that the nanopores in the interconnected holey structure can serve as reservoirs for Li ions, therefore accommodating a large amount of Li during lithiation and delithiation process. As a result, the energy density and cycling stability of COFs could be improved. By choosing different starting materials or reactants, COF structures with different properties can be produced in large scale. Figure 2.7 displays a representative of nitrogen-containing COF network that has been precisely characterized and studied.^[70]

Figure 2.7 Preparation and characterization of a representative COF structure. (a) Reaction between hexaaminobenzene trihydrochloride and hexaketocyclohexane. (b) As-prepared COF crystal. (c) Atomic-resolution scanning tunnelling microscopy (STM) topography image. (d) Simulated image. Reproduced from ref 70. Copyright Nature Publishing Group.

Apart from the investigations on electrode materials, a recent study revealed that COFs could also be suitable materials for solid-state electrolyte applications, due to the fast lithium-ion conductivity.^[71] However, investigations on COFs as electrolytes are still rare due to the poor solubility of COFs. Since this thesis is focusing on electrode materials, the electrolyte applications of conjugated polymers will not be comprehensively covered.

So far, the reports on nanostructured conjugated polymers (e.g. PAc and PPP) as bipolar or bifunctional electrodes (can be either n-dope or p-doped) in an assembled

electrochemical cell are still in the early stage. Demonstrations showed that bipolar COFs including their nanostructures might be good substitutes for bipolar electrode materials with high energy storage.^[23, 72] To be highlighted, an aromatic porous-honeycomb conjugated polymer (BPOE) (Figure 2.6d) with a size of around 300 nm (Figure 2.6e) was obtained. It exhibited both p-dopable and n-dopable properties (vs. ClO_4^- and Na^+ , respectively), sustaining a long cycle life (80% of the initial capacity value⁷²) of 7000 cycles (Figure 2.6f).²³ Moreover, BPOE has a remarkably power density of 10 kW kg^{-1} . Nevertheless, BPOE displayed a capacitive behavior at a high current density. Such a capacity behavior could be probably resulted from the pseudo-Faradaic reactions that occurred at the surface of this material.⁷³ Although several studies have been reported on COFs, their nanostructures were rarely explored and investigated as electrode materials for Li-organic battery applications. To fill in this gap, it is desirable to synthesize novel nitrogen-rich graphene-like conjugated frameworks with 2D conjugated ladder-like structures. Such doped organic materials could be of high performance electrodes for next generation rechargeable lithium batteries. The well-defined porous structure of graphene-like COFs will not only afford a high-energy storage, but also will provide a stable network during cycling procedure.

Therefore, owing to the advantages of conjugated polymers, for example, inherent stable structure, large π -conjugation and good electrochemical stability, 1D and 2D conjugated ladder-like polymers are able to show excellent performance in rechargeable Li-organic batteries. These redox-active polymers could become future substitutes for high energy and power density rechargeable Li batteries.

2.3 Redox-Active Carbonyl Polymers

2.3.1 Background and Reaction Mechanism

According to the theoretical capacity calculation,^[41] the specific capacity of electrode material can be significantly improved by adopting multiple electron reactions. Therefore, it is highly desirable to design and synthesize organic materials with the ability to provide multiple electrons during the redox reactions. Carbonyl-containing (C=O) organic materials are among the most investigated electrode materials due to their redox ability during the charge and discharge process.^[9] The redox mechanism of electrochemically reactive electron carbonyl compounds (including both small molecules and polymers) can be simply explained by the enolation reactions on the carbonyl group, which can be stabilized by the conjugated backbones. Each carbonyl group in the organic structure can reversibly accept one lithium ion to form the lithium enolate^[9]. Due to this mechanism, a lot of organic structures with multiple redox-active carbonyl groups were designed and synthesized. Among them, quinones were among the most investigated electrodes.^[74] However, organic electrode materials like traditional designed quinones, which only have two carbonyl groups (two-electron reactions) without any heteroatoms could not satisfy the emerging requirement for high capacity electrode. In order to improve the specific capacity of organic electrodes, the most efficient way is by incorporating more active carbonyl groups into the organic structures or by incorporating heteroatoms. Following this way, organic structures which have four and even eight carbonyl groups were designed.^[76, 77] Amazingly, all the carbonyl groups were found to be involved in the redox-reactions, resulting in excellent reversible capacity results.

In 2012, a novel lithium ion insertion model for organic materials was proposed to explain the mechanism of the redox reactions of organic materials with multi-electron reactions (more than two electrons).^[66] It was found that anhydride, carbonyl or carbonyl-containing groups in the conjugated systems could significantly lower the free energy for lithium ion addition process. Thus, each C₆ ring in multi-ring aromatic compounds can reversibly accept up to six lithium ions to form a Li₆/C₆ additive complex. NTCDA and

many other multi-ring aromatic compounds were employed to study how many lithium ions can be inserted onto the fused C₆ ring systems.^[66] The electrochemical process of NTCDA revealed that it has the ability to reversibly accept total eighteen lithium ions, corresponding to a specific capacity of 1800 mAh g⁻¹. As shown in Figure 2.8, the proposed mechanism of the electrochemical process was explained by a two-step reaction. The first step was the enolization reaction at the carbonyl oxygen of the material, and the second step was the electrochemical reaction on the unsaturated carbons of the C₆ and anhydride ring systems. To further confirm this mechanism, 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) **1** was also taken as an example to be investigated and showed similar result.^[66] This mechanism offer opportunities to design and develop high storage Li-ion batteries on the basis of redox-active organic compounds.

Figure 2.8 Proposed mechanism of the electrochemical insertion of lithium ions onto the NTCDA structure. Reproduced from ref. 66. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

2.3.2 Carbonyl Building Blocks and Small Molecules

Before stepping into redox-active carbonyl polymers, it is critical to realize some typical redox-active carbonyl-containing small molecules that have been deployed as active electrode materials (Table 2.2). Some representative small molecules have also been frequently used as the building blocks to obtain redox-active carbonyl polymers. Nonylbenzo-hexaquinone (NBHQ) was among the earliest redox-active organic cathode materials.⁷⁸ This study revealed that during the electrochemical reaction, lithium ions can

be inserted or deinserted reversibly at the oxygen atoms when the carbonyl groups are reduced or oxidized.

Based on this proposed mechanism, many organic compounds with two or multiple carbonyl groups were designed and investigated as the electrodes for LIBs. For example, according to the evaluation of polyketons with N-cyclic structures, the redox potential can be tuned by the incorporation of two intracyclic nitrogen atoms.⁷⁹ Pyromellitic diimide **2** is among one of the popular small molecules or building blocks.⁸⁰ Investigations indicated that this compound was able to uptake of nearly two lithium ions at two of the carbonyl groups, displaying an initial capacity of 220 mAh g⁻¹. This compound still provided a reversible capacity of 200 mAh g⁻¹ after 25 cycles at a current rate of 0.05 C. A simple molecule anthraquinone (AQ) **3** has been investigated as the cathode.⁸¹ The two carbonyl groups involved in the redox reaction during the charging and discharging process gave an initial discharge capacity of 251 mAh g⁻¹. However, the capacity declined rapidly during the cycling process and the Coulomb efficiency was found to be very low. The poor cycling performance was attributed to the dissolution of AQ **3** since the color of the electrolyte was observed to be changed after several cycles.

Table 2.2 Electrochemical performance of representative carbonyl small molecules and building blocks used to obtain carbonyl polymers.

Number [Reference]	Structure	Redox Potential Window (V versus Li/Li ⁺)	1 st cycle capacity, last cycle capacity No. of cycles, current density (mA g ⁻¹ or C rate)
1 [66]		1.5-4.6	~127, ~70, 80, 25
2 [80]		1.3-3.0	220, 200, 25, 0.05 C
3 [81]		1.4-3.5	251, ~90, 50, 50
4 [82]		1.8-3.5	~237, ~212, 100, 0.1 C
5 [82]		1.8-3.5	~220, ~137, 100, 0.1 C
6 [82]		1.8-3.5	~210, ~162, 100, 0.1 C
7 [83]		1.5-3.5	173, NA, NA, 0.2 C
8 [83]		1.5-3.5	191, NA, NA, 0.2 C
9 [83]		1.5-3.5	350, 253, 50, 0.2 C

Continuing on this direction, a series of AQ-based heteroatoms-containing carbonyl compounds have been prepared and evaluated as the cathode materials, including benzofuro[5,6-*b*]furan-4,8-dione (BFFD) **4**, benzo [1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (BDTD) **5** and pyrido[3,4-*g*]isoquinoline-5,10-dione (PID) **6**.⁸² Compared with AQ **3** that does not contain heteroatoms, these compounds showed better electrochemical performances in terms of both specific capacity and cycling capability. In addition, by replacing half of the carbon additive with graphene, the cycling performance of all the compounds could be significantly improved due to the suppression of dissolution of these electrode materials. Further investigation found that BFFD **4** possessed the best electrochemical performance among all the compounds (Figure 2.9). Even when charged and discharged at a current rate of 100 C, a reversible capacity of 181 mAh g⁻¹ could still be obtained, which retained 70% of BFFD's initial capacity. This work revealed the possibility of achieving high rate organic electrode materials by incorporation of heteroatoms (e.g. O, N and S) into the organic molecular designing.

Figure 2.9 Cycling performance of AQ and several AQ based heterocyclic organic materials (BFFD, BDTD and PID) tested at 0.1C. Reproduced from ref 82. Copyright Royal Society of Chemistry.

Since carbonyl groups play an important role in determining the specific capacities of organic compounds, it seems that the capacity of all organic compounds can be improved

by increasing the amount of carbonyl groups. However, the investigations indicated that experimental capacities of most structures with more than two carbonyl groups were not as high as expected, attributing to the low utilization of active carbonyl groups. Therefore, to develop high efficiency organic compounds with full utilization of carbonyl functional groups, a research on designing of different organic structures has been conducted.⁸³ N,N'-diphenyl-2,3,5,6-tetraketopiperazine (PHP) **7**, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) **8** and pyrene-4,5,9,10-tetraone (PTO) **9** were evaluated as each of them contain four carbonyl groups. The results suggested that only in PTO **9**, all the four carbonyl groups could be involved in the reversible reaction with lithium, resulting in a higher specific capacity (the first cycle) of 360 mAh g⁻¹. However, for PHP **7** and NTCDA **8**, when they were simulated to be involved into the four-electron reduction, the highest occupied molecular orbitals (HOMOs) of PHP⁴⁻ and NTCDA⁴⁻ failed to retain within the structure (Figure 2.10), indicating that the backbones of these two compounds could not support so much negative charge. Further density functional theory (DFT) calculations showed that, compared with PHP **7** and NTCDA **8**, PTO **9** experienced a more negative free energy change from the dilithiated state to the tetralithiated state. This more negative energy change provided a larger driving force for the further reduction reaction (from dilithiated state to the tetralithiated state) to occur, which was the reason that all the four carbonyl groups could be involved in the reversible reaction of PTO.

Figure 2.10 HOMO investigations of PHP, NTCDA and PTO with different extents of reductions. Reproduced from ref 83. Copyright Royal Society of Chemistry.

2.3.3 Carbonyl Salts

Most of the redox-active carbonyl small molecules encounter serious dissolution issue, causing sharp deterioration in cycling and rate stability.^[40] The most common approach to address this issue is to generate their enolate forms ($-\text{OLi}$).^[84, 88, 89, 91] Many organic salts were designed and investigated as the electrode materials (Table 2.3). Tarascon's group reported two organic salts $\text{Li}_2\text{C}_6\text{H}_4\text{O}_4$ (Li *trans-trans*-muconate) **10** and $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ (Li terephthalate) **11** that can be used as the anode materials for lithium ion batteries.^[84] Especially, $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ **11** was capable of accepting two lithium ions to give an initial reversible capacity of 300 mAh g^{-1} at 1 C. The reversible capacity slowly decayed during the cycling process but still retained 234 mAh g^{-1} after 50 cycles. It was worthy to note that the redox potential of $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ **11** versus Li/Li^+ is 0.8 V, which is much lower than that of the previously reported inorganic anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (1.5 V).^[85-87] Such a low potential of $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ **11** provides a chance for organic materials to be used as high energy density LIB batteries. Li *et al.* reported a novel organic salt $\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4)$ **12**.^[88]

This compound was synthesized by dehydration of $\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4) \cdot \text{H}_2\text{O}$, which was obtained through the reaction between 1,5-dihydroxy anthraquinone and LiOH . The cyclic voltammogram (CV) of the electrode showed two oxidation and reduction peaks separately, confirming a two-step reaction of lithium ions with two carbonyl groups. The stability of this compound was good since it still retained 95% of its initial capacity after 50 cycles of charging and discharging. Nevertheless, the potential window of $\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4)$ **12** was in the range of 1.5 V to 3.0 V, which was higher compared to the anode material and hence should be further tuned.

Table 2.3 Representative organic salts with carbonyl groups and their electrochemical performances.

Number [Reference]	Structure	Redox Potential Window (V versus Li/Li^+)	1 st cycle capacity, last cycle capacity No. of cycles, current density (mA g^{-1} or C rate)
10 [84]		1.2-2.5	~210, 125, 80, 0.1 C
11 [84]		0.7-3.0	~370, 234, 50, 0.1 C
12 [88]		1.0-3.8 1.0-3.8	126, 120, 50, 22 115, 100, 50, 111
13 [89]		0.6-3.0	~470, ~200, 100, 25
14 [91]		0.9-2.0 0.9-3.0	~95, ~70, 100, 1 C 246, 170, 20, 0.1 C

It was reported that the chemical stability of organic materials could be enhanced by a larger conjugated aromatic core, due to the decreased solubility. Therefore, in order to obtain organic electrodes with better cycling performance, a new material $\text{Li}_4\text{C}_{24}\text{H}_8\text{O}_8$ **13**

was investigated as the anode.^[89] To be noted that, this salt was synthesized on the basis of the previously reported PTCDA **2**, which has also been demonstrated as the electrode material but exhibited very poor cycling stability.^[90] Superior to PTCDA **2** and those earlier reported smaller organic compounds, $\text{Li}_4\text{C}_{24}\text{H}_8\text{O}_8$ **13** showed a reversible capacity of 195 mAh g^{-1} after 100 cycles, retaining 95% of its initial capacity, which show great improvement as compared with PTCDA **2**. This better electrochemical performance indicated that by introducing a larger conjugated structure of perylene ring, the chemical stability of organic compound in electrolyte could be improved by the suppressed solubility.

Organic electrode materials with poor conductivity might have low electrochemical performance. Regarding this issue, adding carbon additive to increase the conductivity is a common and useful method. However, adding too much carbon additive will result in a lower energy density of the electrode. Therefore, exploring an efficient way to utilize the advantage of carbon additives is urgent. A demonstration was carried out on the effect of carbon coating in the liquid state.^[91] Due to the low conductivity of dilithium trans–trans benzene diacrylate **14**, it was a good model to be investigated. The electrochemical results suggested that dilithium trans–trans benzene diacrylate prepared by this *in situ* method (dispersing carbon SP directly into the reaction solution as it is chemically inert) was almost twice the value as compared to the compound prepared by the classical ball-milling method. By utilizing this novel *in situ* synthesis strategy, the conductivity and the electrochemical performances of organic electrodes could be improved.

Considering from the perspective of molecular design, improving the conductivity of the molecule can be achieved by extending the π -conjugated system. Therefore, a faster charge transportation and collection of the molecules can be achieved. The extended π -conjugated system can also stimulate the intermolecular interactions. Recently, Lei *et al.* designed an extended structure sodium 4,4-stilbene-dicarboxylate (SSDC) based on the widely reported small molecule sodium benzene-dicarboxylate (SBDC).^[92, 93] Although SSDC was mainly designed for sodium ion batteries, the reversible capacity of 204 mAh g^{-1} after 50 cycles at a current density of 50 mA g^{-1} was also among the best

performances for lithium-ion batteries. Even at a high current density of 1 A g^{-1} , SSDC could also deliver a reversible capacity of 112 mAh g^{-1} . The stable cycling performance at high current density indicated that SSDC was a good candidate for fast charge and discharge battery. The success through molecular design of organic salts provided an efficient route for improving the battery performance.

2.3.4 Carbonyl Polymers

As mentioned in chapter 2.3.2, earlier investigations have been focused on redox-active carbonyl-containing small molecules. However, most of the carbonyl-containing small molecules encounter dissolution issues and thus deliver poor or moderate cycling performances, which usually are less than 100 cycles. It is widely known that decreasing the solubility of organic compounds can be realized through polymerization. Although the solubility issue can be addressed by generating the enolate forms of carbonyl small molecules, unfortunately, such formations will cause reduced energy densities due to the relatively lower operating voltages of organic salts. Therefore, polymers containing carbonyl groups have been mostly considered due to their stable structures and poor solubility in electrolyte. Table 2.4 shows the representative examples of high performance carbonyl polymers containing as the active electrode materials.

Table 2.4 Representative carbonyl polymers and their electrochemical performances.

Number [Reference]	Structure	Redox Potential Window (V versus Li/Li ⁺)	1 st cycle capacity, last cycle capacity No. of cycles, current density (mA g ⁻¹ or C rate)
15 [94]		1.5-3.5	300, 200, 17, 20
16 [95]		1.4-3.5	198, 178, 200, 50-500
17 [96]		1.4-3.4	90, ~100, 200, 0.1 C-5 C
18 [97]		1.5-3.6	350, 184, 100, 15
19 [98]		1.5-4.0	231, 193, 500, 1 C
20 [99]		1.5-3.0	248, 243, 1000, 1 C
21 [99]		1.5-3.0	~230, ~160, 160, 0.2 C-20 C

Poly(5-amino-1,4-naphthoquinone) (PANQ) **15** was one of the earlier reported carbonyl-containing polymers.^[94] The average redox potential of PANQ **15** was 2.6 V, suggesting it might be a good cathode material. Although this compound has been demonstrated to show a reversible capacity of 220 mAh g⁻¹, only 17 cycles of the material was evaluated. Together with the investigation on anthraquinone (AQ) **3**, Song *et al.* tested the electrochemical performances of Poly(anthraquinonyl sulfide) (PAQS) **16** as the cathode material.^[95] Charge-discharge curves showed the redox potential of PAQS **16** was between 1.8 and 2.1 V. Different current densities were performed to test the rate performance of PAQS **16**. After 200 cycles, the capacity of PAQS **16** kept almost same as its initial reversible one. Such a good cycling performance of PAQS **16** indicated that polymers with thioether bond (C-S-C) could effectively avoid unwanted dissolution issue. Continuing searching PAQS **16**, it was found that different substitution positions of sulfur on the anthraquinone structure could significantly affect the electrochemical performances of PAQS **16** in terms of capacity and cycling stability.^[96] Poly(1,5-anthraquinonyl sulfide) (P15AQS or PAQS) **16** and poly(1,8-anthraquinonyl sulfide) (P18AQS) **17** were synthesized and evaluated separately, the results revealed that P15AQS **16** with less steric hindrance at the substitution positions displayed a higher capacity and longer cycling life.

As it was reported that thioether bond could improve the electron transfer due to the π -electron delocalization between the lone pair electrons of sulfur and the aromatic rings,^[90] poly(2,5-dihydroxyl-1,4-benzoquinonyl sulfide) (PDBS) **18**, which also contains thioether bond, has also been assessed as the cathode material.^[97] Similar to PAQS **16**, PDBS **18** did not show a very flat plateau, instead, it showed a sloping plateau between 1.75 and 2.35 V. When it was tested to 100 cycles, it still retained a reversible capacity of 184 mAh g⁻¹ at a small current density of 15 mA g⁻¹. Continuing on this research, PAQS **16** was synthesized through *in situ* polymerization with functionalized graphene sheets.⁵¹ This as-prepared composite was tested between 1.5 V and 3 V. After 100 cycles, it still retained 79% of its theoretical capacity. In addition, with the increasing amount of graphene loading, PAQS showed much improved rate performance. This result confirmed

the hypothesis that higher content of graphene would lead to higher conductivity of the electrode.

Yoshida *et al.* examined the effect of ring size according to different studies including LUMO studies, nucleus-independent chemical shifts (NICS), and DFT calculations.^[98] These results showed that the compound with six-membered rings was more stable than the compound with five-membered or four-membered rings during the redox reactions. For this reason, polymer-bounded pyrene-4,5,9,10-tetraone (PPYT) **19** was chosen to be investigated as the electrode. Thermal analysis revealed the high thermal stability of PPYT **19**. Due to this stability, PPYT **19** was able to deliver a reversible capacity of 193 mAh g⁻¹ after 500 cycles at a high current rate of 1 C (Figure 2.11a). Even at an extremely high current rate of 30C (corresponds to a time of 2 min to fully discharge), the capacity was still about 90% of that at 1 C (Figure 2.11b). Moreover, the average Coulombic efficiency was 99.96%, which is higher than most of small molecules.

More recently, according to the previous experience on PAQS,^[95] poly(1,4-anthraquinone) (P14AQ) **20** and poly(1,5-anthraquinone) (P15AQ) **21** were synthesized through a simple one-step polycondensation respectively.^[99] P15AQ **21** showed a faster decay upon cycling as it was observed dissolved in the electrolyte. Due to this, it was only cycled for 100 cycles. However, P14AQ **20** had poor solubility in the electrolyte and a long cycling performance at the current density of 1 C or 2 C with the reversible capacity at 248 mAh g⁻¹ or 235 mAh g⁻¹ was investigated. More importantly, as shown in **Figure 2.11c**, no significant decay could be observed even after 1000 cycles. This excellent ultra-long cycling performance (99.4% capacity retention at 1000 cycles) suggested that P14AQ **20** was among the best cycling performance organic electrodes.

Figure 2.11 (a) Cycling performance of **PPYT 16** at the current rate of 1 C. (b) Discharge rate performance of **PPYT 16** at various rates (1 C-30 C). (c) Long-term cycling profiles (1000 cycles) of **P14AQ 17** at a current rate of 1 C or 2 C. Reproduced from refs 98 and 95. Copyright American Chemical Society. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

One of the drawbacks for carbonyl polymers is that, many of them actually show an undesirable sloping behavior (Figure 2.12a) due to the generation of a broad distribution of redox states during the electrochemical reactions. To overcome this issue, a novel strategy was proposed by designing π -conjugated redox polymers that combine the advantages of conjugated units and redox-active sites (Figure 2.12b).^[100] As a result of this strategy, a high performance redox-active & conjugated carbonyl polymer P(NDI2OD-T2) with a flat plateau, a reduced polarization and a significant high level of doping (n-type, vs. Li⁺) has been obtained. The reversible doping was maintained for 3000 cycles with a high capacity retention of 96%.

Conjugated poly(2,5-dimethoxyaniline) PDMA and cross-conjugated quinones relying on this strategy also delivered high battery performance.^[101-103] Even 2D conjugated or non-conjugated polyimide-based COF and CMP structures with redox-active carbonyl groups

were developed, providing stable performances.^[27-28, 104] Very recently, a promising study on redox-active macrocycles was conducted by Stoddart JF et al.^[105] They suggested that, by controlling the conformational dispositions of redox-active units in the obtained macrocycles, the electron repulsion can be minimized. Different voltage profiles of pyromellitic diimide (PMDI) derivatives were obtained (Figure 2.12c). Other than the multi-plateau behaviors observed in other derivatives, the triangular ((-)-3PMDI- Δ) macrocycle exhibit a through-space electron delocalization with a well-defined single plateau. If possible, it will be quite interesting to investigate the nanostructures of these materials through future studies. All these strategies provide opportunities to achieve high performance organic-based rechargeable batteries.

Figure 2.12 (a) Different behaviors of voltage curves during the discharge. (b) Design strategy of conjugated redox polymers. (c) Voltage profiles and structures of the three PMDI derivatives. Reproduced from refs 100 and 105. Copyright American Chemical Society.

2.3.5 Bi-functional Carbonyl Compounds

Bi-functional organic materials, which can be used as both the anode and cathode materials were rarely investigated. Table 2.5 lists several representative bi-functional redox-active organic compounds that have been successfully involved into all-organic-

electrode LIBs. The first all-organic LIB was reported by Poizot group in 2009.^[106] The tetralithium salt of 2,3,5,6-tetrahydroxy-1,4-benzoquinone ($\text{Li}_4\text{C}_6\text{O}_6$, THQ,) **22** was evaluated that can be both reduced to $\text{Li}_2\text{C}_6\text{O}_6$ and oxidized to $\text{Li}_6\text{C}_6\text{O}_6$. Under a current rate of 0.1 C, $\text{Li}_2\text{C}_6\text{O}_6/\text{Li}_6\text{C}_6\text{O}_6$ cell was able to provide an initial capacity of 200 mAh g^{-1} (equals to a two-electron reaction with the two carbonyl groups) between 0 V and 2 V, and still retained a reversible capacity of 120 mAh g^{-1} after 50 cycles (Figure 2.13a). However, this all-organic battery is still far from the real applications due to its low working potential.

Table 2.5 Representative bi-functional electrodes and their electrochemical performances.

Number [Reference]	Structure	Redox Potential Window (V versus Li/Li^+)	1 st cycle capacity, last cycle capacity, No. of cycles, current density (mA g^{-1} or C rate)
22 [106]		0.0-1.9	200, 130, 50, 0.1 C
23 [107]		1.0-4.0	~180, ~135, 60, 40
24 [108]		1.0-2.7	225, ~200, 20, 0.2 C

In order to search for high working potential electrodes, Yang *et al.* investigated a nanostructured conjugated bipolar polyparaphenylene (PPP) **23** as both the anode and cathode.^[107] The CV in Figure 2.13b revealed that PPP **23** can be either p-doped (at a high potential of 4 V) or n-doped (at a low potential of 1.2 V). The discharge and charge measurement of PPP **23** showed a reversible capacity of 80 mAh g^{-1} and 350 mAh g^{-1} at the anode and cathode, separately. The constructed all-organic battery of PPP **23** delivered an average working potential of 3 V with a reversible capacity of about 80 mAh g^{-1} after 60 cycles. This large potential gap and redox reversibility enable it to be used as a potential electrode for all-organic batteries.

Figure 2.13 (a) Voltage-composition profile for galvanostatically cycled $\text{Li}_2\text{C}_6\text{O}_6/\text{Li}_6\text{C}_6\text{O}_6$ all-organic cell at a current rate of 0.1 C. Inset is the cycling performance for 50 cycles. (b) CV measurements of PPP at n-dopable and p-dopable potential regions. Reproduced from refs 106 and 107. Copyright American Chemical Society. Copyright Royal Society of Chemistry.

In 2013, 2D nanosheets of an organic tetralithium salt of 2,5-dihydroxyterephthalic acid ($\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$, Li_4DHTPA) **24** were investigated.^[108] The proposed mechanism (Figure 2.14a) showed the occurrence of the reversible two-electron reactions on the carbonyl groups with redox couples of $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6/\text{Li}_2\text{C}_8\text{H}_2\text{O}_6$ in the cathode and $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6/\text{Li}_6\text{C}_8\text{H}_2\text{O}_6$ in the anode, respectively. As shown in Figure 2.14b&c All-organic LIBs were constructed and displayed a reversible capacity of about 200 mAh g^{-1} (at 0.2 C) with an average working voltage of 1.8 V. Continuing on the work, this tetralithium salt ($\text{Na}_4\text{C}_8\text{H}_2\text{O}_6$, Na_4DHTPA) was also used as the electrode in all-organic sodium ion batteries and exhibited good electrochemical performances.^[109]

Figure 2.14 (a) The changes of structures and the redox reactions between $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$ (Li₄DHTPA) and $\text{Li}_2\text{C}_8\text{H}_2\text{O}_6$ (Li₂DHTPA)/ $\text{Li}_6\text{C}_8\text{H}_2\text{O}_6$ (Li₆DHTPA). (b) Charge and discharge profiles. (c) Cycling capability and Coulombic efficiency of symmetrical LIBs with organic $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$ nanosheets at the current density of 48.2 mA g^{-1} . Reproduced with permission from ref 108. Copyright American Chemical Society.

2.4 PhD in context of literature

In this chapter, the literature concerning redox-active polymers and their background and current situation are also included. Specifically, the history, principles and mechanisms of redox-active polymers are reviewed. Different types of redox-active polymers are classified in to several subsections. The working principles that the characterization techniques employed in this project are also introduced.

On the basis of the literature studies, this thesis concluded the major findings outcomes: Firstly, two novel redox-active ladderized conjugated polymers and their nanostructures were designed and developed as high-performance negative electrode materials for Li-organic batteries. Secondly, four novel redox-active carbonyl compounds were designed and developed as high-performance positive electrode materials for Li-organic batteries. Thirdly, a novel all-plastic-electrode battery was designed, optimized and developed on the basis of a novel designed bi-functional poly(quinone) electrode. The symmetric full

battery delivers excellent electrochemical results. Lastly, a general summary of the whole project is also provided. The recommendations to obtain advanced flexible battery systems are also introduced in the last chapter.

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Chapter 3

Experimental Methodology

This chapter discusses the working principles that the characterization techniques employed. In detail, the morphology & crystallographic (SEM, TEM, XRD and AFM), chemical structure & elemental composition (TGA, FTIR, NMR, HRMS, EA and XPS) and electrochemical characterizations (galvanostatic charge-discharge, CV, and EIS) are separately discussed in each sub-sections. In addition, the methods of data analysis of these techniques are involved. Each particular approach is appropriately briefed and the key components of necessary techniques are also listed.

3.1 Rationale for selection

In this thesis, several novel redox-active compounds including conjugated polymers and carbonyl polymers were synthesized. In particular, their nanostructures were obtained. Therefore, characterization techniques should be carefully selected to investigate the properties of the obtained samples. For example, to check the morphologies (e.g. size, diameter and thickness) and crystallographic structures of the as-prepared samples, SEM, TEM, XRD and AFM are critical techniques. Since almost all the discussed polymers in this thesis show poor solubilities, the chemical structures and elemental compositions of the as-prepared samples are usually investigated by solid-state TGA, FTIR, NMR, HRMS, EA and XPS. Most importantly, since this thesis is focusing on the applications of redox-active polymers as electrode materials for Li-based rechargeable batteries, electrochemical characterization techniques including galvanostatic charge-discharge, CV, and EIS are frequently deployed in this project. The detailed principles and methodologies of these techniques are discussed below.

3.2 Materials Characterization

3.2.1 Scanning Electron Microscopy (SEM)

The morphology characterization of materials through SEM is essentially important to reveal the microstructure features and morphologies of materials. SEM is a useful technique that scans a sample (either organic or inorganic) with high-energy electrons. The electrons interact with the atoms can make the sample to produce signals that contain information about the sample's properties (e.g. size, shape and diameter). During the experiment, the specimen surface is scanned by a focused beam of electrons by sweeping it across a rectangular shaped area (called "Raster"), the signals generated from electron sample interaction forms an image on the screen. SEM is different from optical microscope for its better resolution, larger depth of field, higher magnification and etc. SEM uses a beam of highly energetic electrons to examine the sample on a very fine scale. Compared to optical microscope, SEM is more complex and advance.

The most common used source in SEM is thermionic electron emission gun. Figure 3.1 illustrates the key components inside a SEM instrument.^[1] The filament in thermionic gun is heated to emit electrons and gives the electrons enough energy to overcome the work-function energy barrier of the material and escape from the material. For SEM, images are generated by scanning of the specimen and collecting of the electrons that are emitted out (the image is formed step by step).

SEM uses the secondary electrons and the back scattered electrons to generate images. Back scattered electrons have higher energy, they come from electron beams that are deflected by the specimen, hence they are generated in a high amount and can be easily collected by the detector that is placed above the specimen. On the other hand, secondary electrons have lower energy (kinetic energy) as they are kicked out from the atoms by electrons. Secondary electrons are very sensitive to topographical change since they can only be emitted out from the surface or near the surface of specimen, they can be used to observe the topography and morphology of a specimen. Due to this reason, they must be collected by using grid that has high positive potential and connects to the detector. The detector is usually placed beside the sample and will transform the electrons into photons, and then pass to photomultiplier which converts photons to electron pulse. After being amplified, the signals will be passed to a cathode ray tube display for examination. Specimen interaction is what makes electron microscopy possible. The energetic electrons strike the sample and activate different reactions. Different interactions and detectable signals can be generated.

Figure 3.1 Schematic illustration of an example of a SEM instrument.^[1] The model is JEOL JSM 5410. Copyright Springer Science & Business Media 2007.^[1]

When electrons strike on the sample, the interactions between the electrons and the atoms in the sample include above electrons, visible light and X-rays. During the characterization, there are many factors influence the contrast and image resolution, such as electron scattering, atomic number, thickness of the specimen, condenser lens current, stigmatism, working distance and accelerating voltage. The advantages of SEM include the ability of imaging not only thin films but also bulk materials and their 3D morphologies. SEM can be applied to almost all kinds of specimens including both conducting and non-conducting specimens. It provides variety of analytical modes (e.g. EDX, SEI & BEI) to measure the composition of a specimen. For the disadvantages of SEM, it usually requires a conductive coating, and the resolution of SEM is not sharp or

high enough to be able to detect individual atoms. Most of the time, SEM can only reflect the surface features of a sample but not at the atomic scale.

3.2.2 Transmission Electron Microscopy (TEM)

TEM is also a useful and common microscopy technique to characterize the morphology and crystal structure of ultra-small samples. Similar to SEM, an image can be obtained from the interaction between a sample and the generated electron beams. However, superior to SEM, the image with morphology information shows much higher resolution due to the smaller wavelength of electrons. Such a characteristic allows TEM to capture very small samples or even a single atom. Typical TEM components consist of major components, including lenses for different purposes (e.g. condenser lenses, objective lenses and projector lenses). Moreover, vacuum system, specimen stage, electron gun, electron lens and apertures are critical components for TEM equipment. A TEM quality mesh is usually used as the sample support to hold the samples. Since TEM is not a frequently-used technique to characterize polymer compounds with amorphous structures, here the introduction on TEM is not discussed in detail. Figure 3.2 shows an example including the key components of a TEM instrument.^[2]

Figure 3.2 Schematic illustration of an example of a TEM instrument.^[2] Copyright Springer 1996.

3.2.3 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) results were performed on Shimadzu powder with Cu α -radiation ($\lambda = 1.5418$) to study the crystallographic structure of samples. Generally, the characterization and analysis process consist of two steps. The first step is the preparation of samples and collection of X-ray diffraction pattern: Mount the sample powders in the X-ray diffraction holder taking care to place the specimen precisely in the centre of the goniometer circle. Collect data at a step size of 0.02 degrees (2-theta) within a range. Set the collection time a fixed value. For sample preparation, the position of the samples is located between the primary and secondary optics. When waves fall upon the sample, the

ones that reflected from the upper sheet have a shorter optical path than those reflected from the lower sheet. If the glancing angle is equal to θ and the planes are spaced distance d apart then $ND = 2d\sin\theta$. For reinforcement, the path difference must be a whole number of wavelengths hence the condition for diffraction is

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

Below are essential requirements during the sample preparation process:

- a) It should have many samples in random orientations. If some of the samples are not randomly distributed, they will not be exposed to the X-ray.
- b) The particle size is very important. The sample with the particle size less than 10 μm is the optimum size.
- c) The sample surface, and the receiving slit axes should be parallel to each other and all perpendicular to the plane of the diffractometer circle. The surface of the specimen should be coincident with the diffractometer axis. The receiving slit should lie on the diffractometer circle.

The second step is the qualitative interpretation of the X-ray diffraction pattern: Use the software (e.g. Match! Software) on the diffractometer computer to identify the phases present in each sample. XRD is a technique in crystallography in which the pattern produced by the diffraction of X-rays through the closely spaced lattice of atoms in a crystal is recorded and then analysed to identify and characterize unknown crystalline materials. The crystal lattice structure can be determined by using Bragg's law. XRD uses diffracted x-ray to obtain the information on crystal structures, orientations, grain size, crystallinity, and crystal defects. Figure 3.3 shows a schematic illustration of the diffractions of x-rays.^[3] The intense peaks in XRD correspond to constructive interferences of monochromatic beams deflected from layers of atoms in the crystal, satisfying to the Bragg's law ($2d_{hkl} \sin \theta = n\lambda$, $n = 1, 2, 3, \dots$). If the Bragg's law is not satisfied, then the interference will be destructive in the nature, the beams will cancel each other and no intense beam occurs. A suitable filter with selective absorption is used

to generate a parallel, monochromatic and coherent (in phase) beam of x-ray. In XRD, the layers of atoms in the crystal serve as the spacing slits. Hence, when monochromatic x-ray passes through the interplane, a diffraction phenomenon occurs and gives rise to x-ray scattering pattern.

Figure 3.3 Diffraction of X-rays from a crystal.^[3] Retrieved from <http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html>

When the x-ray of wavelength λ is incident on the crystal at angle θ to the atomic plane with regularly packed atoms, the x-ray will be diffracted. By collecting the intensities of peaks, it is able to know the interplanar spacing of an unknown material. Besides, the relative peak intensities are generally proportional to the number of grains in a preferred orientation. Thus, XRD also gives a structural fingerprint of the unknown materials. However, the diffracted pattern is highly dependent on the arrangement of atoms in the crystal. Amorphous materials (e.g. most oligomer or polymer compounds) and liquids lack of a systematic and regular arrangement of atoms over relatively large atomic distances, the x-ray scattering is therefore superimposed by all the peaks and shown in only one broad maximum.

3.2.4 Atomic Force Microscopy (AFM)

AFM is a high-resolution tool that can be used to evaluate the morphology of both organic and inorganic samples, including their thicknesses, dimensions and shapes. Figure 3.4 shows the working principle of AFM.^[4] The sample is scanned by a sharp tip,

which is located at the end of the cantilever that is 100 to 200 μm long. Forces between the tip and the sample surface cause the cantilever to bend, or deflect. And then a detector is used to measure the cantilever deflection when the tip is scanned over the sample. Finally, the measured cantilever deflections allow a computer to generate a map of surface topography.

AFMs are widely used to study insulators and semiconductors as well as electrical conductors. Generally, there are three modes of operation, such as contact, non-contact and tapping mode. The most popular mode is the tapping mode. For this mode, a stiff cantilever is oscillated close to the sample. Part of the oscillation extends into the repulsive regime, so the tip intermittently touches or “taps” the surface. Forces between the tip and the sample surface cause the cantilever to bend. Because the atomic force microscope relies on the forces between the tip and sample, knowing these forces is important for proper imaging. The force is not measured directly, but calculated by measuring the deflection of the lever, and knowing the stiffness of the cantilever. Hook’s law gives $F = kz$, where F is the force, k is the stiffness of the lever, and z is the distance the lever is bent. Deflection signal is directly proportional to interaction force. Angular displacement of cantilever results in one photodiode collecting more light than the other photodiode, producing an output signal (the difference between the photodiode signals normalize by their sum) which is proportional to the deflection of the cantilever.

Figure 3.4 The working principle of an example of an AFM instrument.^[4] Retrieved from https://simple.wikipedia.org/wiki/Atomic_force_microscope.

3.2.5 Fourier Transform Infrared Spectra (FTIR)

Fourier transform infrared spectra (FTIR) equipment is a very important tool to characterize the structure of organic compounds, and also to confirm the realization of polymer materials. By characterizing different functional groups, the chemical structure of organic compounds can therefore be confirmed. Before characterizing the samples, a blank KBr sample (background spectrum) is usually prepared to be used as the reference sample. To analyze organic samples, they are first mixed with KBr powders and compressed into a thin pallet. The pallet is then loaded into the FTIR spectrometer for characterization. In order to obtain a high quality FTIR spectrum, the amount of samples should not be overloaded and the scanning duration should be increased with the increased number of scans. The finally obtained spectrum is characterized according to the peak locations with regard to the wave numbers and the peak shapes.

For the working principle and instrumental process of a normal FTIR, generally, after loading the samples into the machine, the infrared energy will be emitted from the source to generate a beam, which will pass through an aperture and enter the interferometer, where the encoding process takes place. The beam will then enter the sample compartment and transmitted through or reflected off of the surface of the sample. Finally the beam will be passed to the detector for measurement. In the following process, Fourier transformation process will take place where the computer will analyze all the measured signals. The finally obtained spectrum will be used for interpretation to analyze the organic structure.

Different molecules have different and specific frequencies at which they vibrate. The types of vibration modes are listed in Figure 3.5.^[5] They are divided into three groups: (1) In-plane stretching, where the change occurs in bond length; (2) In-plane bending, where the change occurs in bond angle; and (3) Out-of-plane bending, where the change occurs in bond angle. To further classify the vibrations modes, they are divided into six sub-modes, asymmetric stretching, symmetric stretching, scissoring, rocking, twisting and wagging.

Figure 3.5 Different types of molecular vibrations.^[5] Copyright Elsevier 1997.

FTIR possesses many advantages over other dispersive techniques. For example, the speed of data analysis is quite fast. The sample can be measured and characterized even in several minutes. The sensitivity of FTIR is high since the optical throughput is high, resulting in low noise levels. In addition, the fast scans enable the coaddition of multiple scans, hence the random measurement noise can be minimized or reduced. These advantages along with its mechanical simplicity and internal calibration capability make FTIR measurements accurate and repeatable.

3.2.6 ^1H Nuclear Magnetic resonance (NMR) and ^{13}C NMR

^1H NMR is the most common technique to determine the chemical or molecular structure of a compound. It is frequently used in organic chemistry by identifying the carbon-hydrogen bond of an organic compound. The samples should be soluble since ^1H NMR spectra are measured in solvents. To prevent the interference from the solvent protons, deuterated (^2H or D) solvents are preferred. Examples including deuterated water, chloroform, acetone, methanol, dimethyl sulfoxide, etc. ^1H NMR spectra of an organic compound are identified by chemical shifts (in ppm) as well as spin-spin coupling between protons. The existence of individual protons is characterized by the integration area under the peaks from the chemical shifts.

^{13}C NMR is the application of NMR with respect to carbon. The principle is similar to ^1H NMR. Just like ^1H NMR allows the identification of hydrogen atoms, ^{13}C NMR can identify carbon atoms in organic compounds. Since ^{12}C has zero net spin, ^{13}C NMR can only detect ^{13}C (at $\sim 1.1\%$ natural abundance), therefore ^{13}C NMR is less sensitive to carbon than ^1H NMR to hydrogen. The same principles of ^1H NMR can be applied to the chemical shifts of ^{13}C NMR, however, the chemical shifts values are about 20 times larger than those for ^1H NMR.

For the working principle, it is known that the nucleus is a spinning charged particle that can generate a magnetic field. Nucleus with even number of protons and neutrons experience no spin. Only those with odd numbers (like ^1H and ^{13}C) have integer spins. These spins align in random directions if there is no external magnetic field applied. However, by applying an external field, the spins can be aligned in the same direction (α -spin state) or against the direction (β -spin state) of the external magnetic field (Figure 3.6).^[6] Therefore, an energy difference ΔE is generated between both states on the basis of the applied external magnetic field. Under radiation, the nuclei will undergo relaxation and electromagnetic signals will be emitted and then received by the spectrometer. These signals will finally be reflected by a plot containing signal intensity and chemical shift.

Figure 3.6 Schematic illustration of the energy difference generated by the α - and β -spin states under an external magnetic field.^[6] Retrieved from <http://www.process-nmr.com/nmr1.htm>.

3.2.7 High-Resolution Mass Spectrometry (HRMS)

HRMS is a powerful technique to identify unknown chemical compounds or quantify known compounds. Normal mass spectrometry and low resolution mass spectrometry could usually measure the molecular weights of compounds as whole numbers. As a more advanced technique, HRMS can provide a more accurate and exact molecular weight values resulted from the measured compounds. A typical high-resolution mass spectrum plot contains the information that X-axis presents the mass to-charge-ratio and Y-axis presents the ion signal intensity. During the experiment, the tested sample produces gas phase ions upon electron ionization. These ions are termed as charged fragments and will be separated according to their mass-to-charge ratio through the acceleration of a magnetic field. The charged fragments with the same mass-to-charge ratio encounter the same deflection. Therefore a mass spectrum of the compound with the molecular weight information can be produced.

The key components of a HRMS instrument include a sample introduction system, an ion source, an analyzer, a detection system and a computer control system. Figure 3.7 shows the detailed layout of a typical mass spectrometry instrument.^[7] Firstly, the sample is introduced into the inlet of the instrument to be studied under a high vacuum atmosphere. Then, the ion source produces gas phase ions from the tested compound. The analyzer is used to allocate and separate the ions according to their characteristics (mass-to-charge ratio). Finally, the detector can detect the ions and record the relative abundance of each separated ion species. The computer system is used to control the whole instrument, in addition, to manipulate and compare the obtained spectra.

Figure 3.7 The layout and typical components of a typical mass spectrometry instrument.^[7] Retrieved from <https://byjus.com/chemistry/mass-spectrometry/>.

3.2.8 Elemental Analysis (EA)

Elemental analyzer is an important tool to determine the elemental composition of organic materials, which usually contain carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) elements. Both the quality and quantitative information of an organic or polymer compound can be obtained. For example, the elements and their mass percentage of an organic material can be directly determined, therefore giving a clear information on the structure and purity of an unknown organic compound. In particular, EA is known as a useful and frequently used technique to characterize polymer samples with poor solubility.

Figure 3.8 shows the brief procedures of an EA experiment.^[8] EA is performed through a combustion process at a high temperature ($\sim 1000\text{ }^{\circ}\text{C}$). During this process, a sample is usually burned in an atmosphere of oxygen and different traps, collecting the combustion products in the form of carbon dioxide (CO_2), water (H_2O), sulfur dioxide (SO_2), nitric oxide (NO_x) and etc. A flow of inert gas such as high purity helium will move the combustion products from the combustion chamber to a quartz tube filled with reduced

copper at a high temperature (500-700 °C). The purpose of this process is to remove all unreacted oxygen and convert nitric oxides to nitrogen gas (N_2). Apart from CO_2 , H_2O , SO_2 and N_2 , all the other species will be adsorbed by the copper. Eventually CO_2 , H_2O , SO_2 and N_2 are absorbed at appropriate traps to be analyzed. The composition of the sample (e.g. C, H, O and N elements) can therefore be calculated by analyzing the masses of the combustion product species through a gas chromatographic system.

Figure 3.8 A chart shows the brief procedures of an EA experiment.^[8] Retrieved from http://www.rsc.org/images/CHNS-elemental-analysers-technical-brief-29_tcm18-214833.pdf. Copyright Royal Society of Chemistry 2008.

3.2.9 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a technique known as an electron spectroscopy for chemical analysis of organic and inorganic sample surfaces (usually top 0-10 nm). The sample is irradiated with a beam of X-rays and the kinetic energies of the generated photoelectrons are measured (Figure 3.9).^[9] Therefore, XPS can help in identifying the elemental composition present in a material. Moreover, it can also identify the oxidation state of the elements. XPS equipment consists of key instruments including an X-ray source, an electron energy analyzer, an ultrahigh vacuum system, an electron detector system, a computer system, a set of stage manipulators, etc. For a typical XPS profile, the X-axis presents the binding

energy of the detected electrons and the Y-axis presents the number of electrons. Each element can produce a set of XPS peaks at different binding energies, corresponding to the electron configuration within the atoms, for example, $1s$, $2s$, $2p$, $3s$, etc. The obtained XPS signals will be corrected with regard to the signal intensity and normalized over all the detected elements, providing structural information of the measured sample.

Figure 3.9 Schematic illustration of the photoelectric effect.^[9] Retrieved from <https://www.ifw-dresden.de/institutes/ikm/research-teams-and-topics/micro-and-nanostructures/available-methods/xps/>.

3.2.10 Energy-Dispersive X-Ray Spectroscopy (EDS) Elemental Mapping

The elemental distribution and chemical characterization of a sample can be measured by EDS elemental mapping.^[10] It is an analytical technique depending on the interaction between the X-rays generated by the electron beam and a sample, either organic or inorganic. For the excitation process, an electron is ejected from the inner shell by the incident beam, and a hole is created. Such a hole will be filled by the electron from an outer shell with higher energy, and the difference in energy between these two shells is released in the form of an X-ray, which is further measured and analyzed by an energy-dispersive spectrometer. Most of the time, EDS elemental mapping is performed to check the existence of the desired elements as well as their distribution in a particular sample. EDS is usually conducted with SEM or TEM characterization. Since the principles for SEM and TEM have been discussed in their sections, the details for EDS will not be discussed here.

3.2.11 Thermogravimetric Analysis (TGA)

To realize the thermal property of organic samples, thermogravimetric analysis (TGA) could be conducted under nitrogen or air atmosphere at a constant heating rate. In order to conduct a thermogravimetric analysis, the first step is to turn on the gas, choose either purified nitrogen or air. Next step is to turn on the flow meter. Before burning the sample, need to check whether there exists any liquid inside the furnace chamber or not. After which, tare the sample and open the software. After filling in all the essential parameters and heating procedures, the sample can be placed into a platinum pan to be heated to temperatures range from room temperature to a high temperature up to 1000 °C. When the heating process terminates, the furnace will be cooled down to room temperature. To analyze data, the software can be used to generate TGA plots.

The purpose of doing TGA is to measure the physical and chemical properties of samples, which are measured as a function of the loss in weight with the increasing of temperature. There is no restriction on the samples regarding whether they are inorganic or organic samples. The decomposition temperature and the thermal stability of a sample can be obtained through the analysis of the data.

Figure 3.10 Schematic illustration of the physical structure of a typical TGA instrument.^[11] Retrieved from <http://polymerinnovationblog.com/wp-content/uploads/2014/06/TGA-Balance1.jpg>.

The internal structure of a typical TGA instrument was shown in Figure 3.10.^[11] To characterize a sample, the powders were weighed and placed into the platinum pan with

nitrogen gas or air purged into the furnace chamber at a constant flow rate. The sample will undergoes degradation process reflected by the reduction of the weight of the total sample. The decomposition temperature and the thermal stability of samples can be then obtained and explained.

Figure 3.11 An example of a TGA profile (silver-filled polymer ink).^[12] Retrieved from <http://polymerinnovationblog.com/wp-content/uploads/2014/06/TGA-Composition1.jpg>.

An example above shows the TGA curve of a sample consisted of silver-filled polymer ink (Figure 3.11).^[12] The composition of the sample can be obtained from the two distinct plateaus. From the curve in the range from room temperature to around 250 °C, information including the percentage of the absorbed moisture, residual solvents, and oligomers can be obtained. From 250 to around 400 °C, the percentage and decomposition temperature of the polymer binder can be obtained. The percentage of silver can also be obtained from the TGA curve, since there is no any further degradation of the sample in terms of weight. Advantages of TGA involve easy to use, accurate data, minimal sample preparation. Disadvantages include time consuming, limited range of samples and sensitive.

3.3 Battery Fabrication

For the preparation process of an electrochemical cell, necessary components are needed. Figure 3.12 shows the components used to assemble a CR2032 coin cell.^[13] Normally, a coin cell is composed of a positive case, a negative case, a non-conductive gasket, a

stainless steel spring, a stainless steel spacer, a working electrode, a separator, a counter electrode and a positive case. A copper or aluminium foil is usually used as the current collector.

Figure 3.12 Assembly process of a CR2032 coin-type cell.^[13] Copy right The Electrochemical Society (ECS) 2011.

All the components (exclude the separator and the lithium foil) of the coin-type cells are usually cleaned with ethanol and dried in vacuum oven. The parts are then assembled in a glove-box filled with argon gas. The moisture and oxygen levels in the glove-box are normally kept below 1 ppm. The electrodes are obtained by mixing of certain amount of active materials, carbon additives and binders into an organic solvent that can well disperse them. The viscous slurry is then pasted onto the current collector (copper foil for anode and aluminium foil for cathode). The electrodes are dried in vacuum to be used as the working electrodes. For half-cell fabrication, lithium sheets are usually applied as the counter electrodes. For full-cell fabrication, active materials made from organic polymers are applied as the positive and negative electrode. For the electrolyte solutions, different electrolytes (e.g. ether and ester based electrolytes) can be used according to the compatibility of between the electrolyte solutions and the electrodes.

3.4 Electrochemical Characterization

3.4.1 Galvanostatic Charge-Discharge

The term of galvanostat refers to a process that an electrode material is measured at a constant current in an electrolyte. It is an electrochemical mode applied to analyze the kinetics and reaction mechanisms that occur on an electrode material based on the control of the current. This technique is mostly conducted to measure electrochemical reactions within an electrochemical cell. For an electrochemical reaction, it is an electrochemical process associating with the flow of electrons between an anode and a cathode surrounded by an electrolyte solution. This flow can trigger an electric current between the two electrodes, resulting in a reduction and oxidation reaction (redox reaction). An oxidation occurs on the electrode material that losses electrons, whereas a reduction occurs on the electrode material that gains electrons.

For a typical cell testing process, discharge corresponds to the process that the electrode is reduced, and charge corresponds to the process that the electrode is oxidized. Galvanostatic charge-discharge can make the polarization of electrode materials occur in electrolytes, enabling observation of the anodic and cathodic reactions. During a galvanostatic charge-discharge process, the change is recorded by the potential (or voltage) versus time at a constant current, generating a charge-discharge profile wherein the X-axis is often the specific capacity in mAh g^{-1} (by taking into account of both the current and time duration), and Y-axis is often the potential in Volt (V). By repeating the galvanostatic charge-discharge process, the Coulombic efficiency, cycling stability and rate performance of an electrochemical cell can be obtained. Figure 3.13 shows an example of the charge-discharge profile of an organic polymer.

Figure 3.13 An example of the charge-discharge profile of an organic polymer poly(2,3-dithiino-1,4-benzoquinone) PDB.

3.4.2 Cyclic Voltammetry (CV)

CV is a powerful electrochemical technique to investigate the electrochemical properties (e.g. working potential, electrochemical redox reaction, diffusion coefficient, etc.) of a sample in electrolyte. For a typical CV experiment, the potential of the working electrode is ramped linearly with respect to time. Superior to linear sweep voltammetry, when the potential in a typical CV experiment reaches the set potential, it will go toward the opposite direction and returns to the initial point. Hence, repeated cycles with more information can be obtained from CV as compared with linear sweep voltammetry. Before conducting a standard CV experiment, a cell with three electrodes (working, counter and reference electrodes) is usually prepared. However, in a typical button cell, the reference electrode can be also regarded as the counter electrode; such a simplified system is called a two-electrode system and often employed for the CV study of an electrochemical cell. The electrodes and electrolyte solution in the cell system will determine the potential window that is measured in a CV experiment.

Regarding a CV scan, the scan rate is defined by the voltage change over time during the phase (Figure 3.14a).^[14] The potential is usually measured between the working and reference electrode, and the current is measured between the working and counter electrode. Depending on these parameters, a CV profile is therefore plotted by potential (E) versus current (i) (Figure 3.14b).^[14] During the forward or reverse scans, at some

points when the reduction or oxidation of a reversible redox-active material is reached, the cathodic or anodic currents (or the peak currents) will decrease as the concentration of the active material is depleted. Mostly, the reversibility of an active electrode material will give a similar oxidation peak in shape to a reduction peak. These peaks are regarded as a characteristic of the occurrence of an electrode reaction. Parameters like scan rate and electrolyte concentration will influence the width and intensity of the peaks.

Figure 3.14 Schematic illustration^[14] of (a) An example CV waveform. (b) A typical CV profile. Retrieved from https://en.wikipedia.org/wiki/Cyclic_voltammetry.

3.4.3 Electrochemical Impedance Spectroscopy (EIS)

EIS is known as a powerful technique for detailed investigation of the electron-transfer behavior and kinetics of electrode materials. It is a non-destructive method that has been widely applied to evaluate the impedance values of cells and batteries. Similar to resistance, impedance reveals the ability of a circuit to resist the current flow. However, the difference between resistance and impedance is the current supply. Resistance is measured by applying a direct current, whereas electrochemical impedance is measured by applying an alternative current, which is represented as z . The expression for impedance consists of a real and an imaginary part. It is a complex quantity with a magnitude and a phase shift depending on the frequency of the signal. A Nyquist plot can be obtained if X-axis shows the real part and Y-axis shows the imaginary part. Note that the impedance values in the Y-axis are usually negative and each single point represents a value at one specific frequency. The frequency range applied in an electrochemical study is normally 100 kHz-0.01 Hz.

The EIS profile for a standard electrochemical cell is composed of a semi-circle in the high frequency range and a tail in the low frequency range (Figure 3.15).^[15] The electrolyte resistance (or ohmic resistance) could be obtained from the initial impedance value. The well-defined semi-circles at high frequencies correspond to the charge-transfer resistances at the electrode-electrolyte interfaces, giving information on the kinetic reaction between the electrode and the electrolyte. In addition, the tail (oblique line) observed at low frequencies, which represents the Warburg resistance, shows the ion diffusion capability within the electrode. Generally, a cell with a small semi-circle and a small tail reveals a fast charge-transfer capability and a good electric response.

Figure 3.15 An example of a typical EIS profile.^[15] Retrieved from <http://lacey.se/science/eis/>.

3.5 Overview of Methodologies

In summary, this chapter discusses the working principles that the characterization techniques employed. In detail, the morphology & crystallographic (SEM, TEM, XRD and AFM), chemical structure & elemental composition (TGA, FTIR, NMR, HRMS, EA and XPS) and electrochemical characterizations (galvanostatic charge-discharge, CV, and EIS) are separately discussed in each sub-sections. In

addition, the methodologies of data analysis of these techniques are involved. Each particular approach is appropriately briefed and the key components of necessary techniques are also listed.

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Chapter 4*

Novel Nanostructured Conjugated Polymers as High-Performance Negative Electrodes for Li-Organic Batteries

Among all redox-active polymers, conjugated ladder-structured polymers have been demonstrated to show great potential due to their extended π -conjugation, good electronic conductivity, and high chemical stability. The double-stranded structure endows ladder polymers with rigid backbone property and poor solubility that can offset the serious dissolution issue encountered by most organic electrode materials. In this chapter, taking over the merits of heteroatoms doping and utilizing ladder polymers' rigid backbone structure, two novel nanostructured conjugated ladder polymers in terms of their 1D and 2D structures are presented as effective negative materials for lithium-organic batteries.

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4.1 Introduction

Developing high performance rechargeable LIBs is of great interest to achieve the ever-increasing energy storage demands for electronic devices and electric vehicles. For a long time, investigations were mainly focused on inorganic materials due to their great achievements in applications.¹ However, with the growing anxieties about environmental and resource issues regarding the metal-based inorganic electrodes, more and more efforts have been input on organic materials.^{2, 3} Although the research on organic electrode materials have been conducted as early as inorganic materials, it was still very challenging to design both efficient and eco-friendly organic electrode materials with promising battery performance.

Ladder-structured π -conjugated polymers are good candidates to be employed as active electrode materials due to their extended π -conjugations, good electronic conductivities and high electrochemical stabilities.⁴⁻⁶ In particular, the unique double-stranded structure endows ladder polymers with rigid backbone properties (inherent stability) and poor solubility that can offset the serious dissolution issue, which is the main problem of most organic electrodes. Moreover, redox-active π -conjugated polymers with multi-electron reactions can deliver excellent specific capacities as well as energy densities.^{7, 8} Owing to these advantages, π -conjugated ladder polymers are considered as promising electrode materials for rechargeable LIBs.

Recent investigations revealed that the electronic conductivity and electrochemical activity of polymer electrodes can be greatly improved with the presence of nitrogen heteroatoms,⁹ resulting in the increment of lithium-ion storage within conjugated polymers. Taking over the merits of hetero-atoms doping and utilizing ladder polymer's rigid backbone structure, previous studies from the author's research group also showed that one-dimensional (1D) nanostructured conjugated ladder polymers with a rich number of oxygen and nitrogen heteroatoms could be promising anode materials for LIBs.^{10, 11} In addition to those 1D organic structures, current investigations on two-dimensional (2D)

anode materials for rechargeable LIBs are mainly centered on graphene, because of its inherent stable structure, good cycling stability, high electronic conductivity and low lithiation voltage. However, the specific capacity of graphene is quite limited by its theoretical value (734 mAh g⁻¹). Owing to this limitation, it is extremely interesting to explore the possibility of novel 2D conjugated ladder polymers as potential anode materials, especially, the heteroatom-doped (e.g. nitrogen) 2D conjugated polymers including CMPs, COFs and similar aromatic frameworks with superior electrochemical performance.

Building on the previous experience regarding conjugated ladder polymers, in this chapter, a novel 1D nanostructured conjugated ladder-structured oligomer, poly(1,4-dihydro-11H-pyrazino[2',3':3,4]cyclopenta[1,2-b]quinoxalin-11-one) (PPCQ), is presented here with excellent electrochemical performance. Since microporous graphene-like electrode materials are highly desirable for energy storage, the author and his collaborators also extend the ladder conjugated polymers from 1D to 2D structure by designing and synthesizing a novel nitrogen-rich grapheme-like holey conjugated polymer (NG-HCP). These two novel conjugated polymers exhibit superior electrochemical performance in Li-organic cells, affording high Li-storage capacity and extraordinary cycling stability as active anode materials. These findings would open new opportunities to develop promising organic materials for high performance energy storage devices.

4.2 Synthesis, Characterization and Measurement

4.2.1 Synthesis of PPCQ

To synthesize PPCQ, 50 g 115% polyphosphoric acid (PPA) was filled into a 100 mL two-necked flask fitted with a magnetic stirrer and nitrogen inlet and outlet. In order to remove away the oxygen in the PPA solvent, the PPA was heated to 110 °C with nitrogen bubbling through the stirred acid overnight. Under a nitrogen atmosphere, 1 mmol 1,2,4,5-tetraaminobenzene tetrahydrochloride (TAB·4HCl) was added into the

deoxygenated PPA at 50 °C and the temperature was increased to 110 °C. By keeping TAB·4HCl at 110 °C overnight, all HCl were thermally removed away. Then, 1 mmol 4,5-dihydroxycyclopentenetrione (croconic acid) was added into the solution at 70 °C. The temperature of the mixture was slowly increased to 190 °C at a heating rate of 2 °C/min and maintained at 190 °C for 10 hrs with a magnetic stirring. The resulting viscous solution was cooled down to room temperature and precipitated into DI water. After precipitation, the black precipitates were ultrasonicated, centrifuged and washed many times by DI water and methanol separately. After washing the precipitates by methanol with soxhlet extractor, the finally obtained black powders (pristine PPCQ) were placed in a vacuum oven to be dried.

PPCQ nanoparticles were obtained by dissolving pristine PPCQ into the high-purity methanesulfonic acid (MSA). In details, 20 mg PPCQ was dissolved into 100 mL MSA by ultrasonication and magnetic stirring. The polymer solution was added dropwise into a rapid stirring 250 mL DI water and black precipitates were formed immediately. The precipitates were washed with DI water and ethanol many times until the MSA solvent was removed away. The finally obtained PPCQ nanoparticles were dried in vacuum oven at 100 °C for 12 hrs and the dried powders were to be characterized and tested.

4.2.2 Characterization and Measurement of PPCQ

Materials characterization: FESEM characterizations were performed on JEOL/JSM-6340F with an accelerating voltage of 5 kV. Fourier transform infrared spectra (FTIR) were recorded on PerkinElmer Spectrum GX FTIR spectrometer. Thermogravimetric analysis (TGA) was recorded by TA Instruments TGA Q500 under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. X-ray Diffraction (XRD) patterns were measured by Shimadzu powder with Cu α -radiation ($\lambda = 1.5418$).

Electrochemical cell fabrication and measurements: The coin-type cells were assembled in an argon-filled glove-box, where both moisture and oxygen levels were less than 1 ppm. The electrodes were fabricated by mixing of 70 wt% PPCQ with carbon

nanotubes (20 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) in *n*-methyl-2-pyrrolidone (NMP) solvent, and then pasted onto the copper foils. The electrodes were cut into circular disks with diameters of 12 mm and thicknesses of 8-15 μm (excluding the thicknesses of the current collectors). Lithium foils were used as the counter electrodes and the electrolyte solution was made of 1M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1, w/w). The cells were tested on a NEWARE multi-channel battery test system with galvanostatic charge and discharge between 3.0 and 0.0 V. Cyclic voltammetry (CV) was performed on an electrochemical analyzer (CH Instrument CHI604e) between 3.0-0.0 V at a scan rate of 0.2 mV s^{-1} .

4.2.3 Synthesis of NG-HCP

In a 50 mL degassed flask, 1 mmol HKH (312 mg) and 1.5 mmol TAB $\cdot$ 4HCl (426 mg) were added and mixed. To dissolve both reactants, 30 mL degassed *N*-methyl-2-pyrrolidone (NMP) solvent was injected at 100 $^{\circ}\text{C}$ in an oil bath. Upon cooling to the room temperature, ice bath was replaced. To avoid the oxidation of reagents, around 500 μL H_2SO_4 was added slowly. After string for 1 hr at room temperature, the mixture was heated to 180 $^{\circ}\text{C}$ in oil bath for 8 hrs. After cooling down, the solution was quenched with 200 mL methanol, and dark brown precipitates were collected. The as-prepared crude product was rinsed with methanol, NaHCO_3 aqueous solution and DI water for 3 times (to nearly neutrality) through a centrifugation with 10000 rad min^{-1} , respectively, followed by a seven-day Soxhlet purification in methanol. The NG-HCP black powders were dried for 3 days at 60 $^{\circ}\text{C}$ in a vacuum oven, and 246 mg final product was obtained.

To obtain nanostructured NG-HCP, 200 mL methanesulfonic acid (MSA) was prepared to dissolve 40 mg as-prepared NG-HCP. The black solution was sonicated for 2 hrs, stirred overnight and then added dropwise into 500 mL DI water with vigorous string. After placing for 12 hrs, the precipitations were then centrifuged and purified with ethanol and DI water for several times, respectively, to ensure that MSA is completely removed. The finally obtained product was vacuum dried at 60 $^{\circ}\text{C}$.

4.2.4 Characterization and Measurement of NG-HCP

Simulation and materials characterization: The simulation of single layer NG-HCP was conducted in Materials Studio 8.0 software and then fully optimized by Compass II force field in Forcite module. To perform further geometrical optimization in CASTEP module, GGA/PBE method was employed. The pseudopotentials is Norm conserving, with the energy cutoff of 400 eV, the K-points of $4 \times 4 \times 1$ and SCF tolerance of 5.0×10^{-7} . To calculate band structure of NG-HCP, the same conditions were used. Moreover, FESEM, HRTEM, STEM, AFM images, FTIR, XPS, CV, XRD, UV-vis-NIR, TGA, BET, Raman profiles and NLDFT calculation were also performed. Detailed preparation methods can be found in the author's published paper related to NG-HCP.^[12]

Electrochemical cell fabrication and measurements: The coin-type cells (CR2032) were fabricated in a glove box filled with argon. Both the moisture and oxygen contents were kept below 1 ppm. NG-HCP electrode materials before and after nano-engineering were prepared by mixing of 70 wt% NG-HCP, 20 wt% MWCNTs, and 10 wt% PVDF. The viscous slurry was then pasted onto a copper foil current collector. The electrodes were cut into circular disks with the diameters of 12 mm and thicknesses of 8-15 μm (excluding the thicknesses of the current collectors). To thoroughly remove away the NMP solvent, the electrodes were dried in a vacuum oven at 60 °C overnight. Lithium foils were used as the counter electrodes and the electrolyte solution was made of 1M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1, w/w). The cells were tested on a NEWARE multi-channel battery test system with galvanostatic charge and discharge in between 3.0 and 0.005 V (vs. Li/Li^+). CV of NG-HCP was performed on an electrochemical analyzer (CH Instrument CHI604e) between 3.0 and 0.005 V, at a scan rate of 0.2 mV s^{-1} . EIS studies were conducted on the same electrochemical analyzer with the frequencies applied in the range of 100 KHz-1 Hz.

4.3 Results and Discussion

4.3.1 Results and Discussion of PPCQ

As described in the synthesis section, PPCQ was obtained from a simple one-step polymerization reaction between 4,5-dihydroxycyclopentenetrione and TAB·4HCl in 115% PPA at 190 °C for 10 hrs (Figure 4.1). The finally obtained black powders (pristine PPCQ) were insoluble in almost all commonly-used organic solvents. Therefore, to obtain PPCQ nanoparticles, pristine PPCQ was dissolved into strong MSA. The resulted dark color solution was then dropwisely added into DI water under a rapid stirring. The precipitates were sonicated, centrifuged and washed with DI water and methanol respectively and later dried. The finally obtained PPCQ nanoparticles were performed as an anode material.

Figure 4.1 Synthesis of PPCQ through a simple one-step polymerization.

Figure 4.2 FESEM images of PPCQ nanoparticles. (A) At low-magnification ($\times 10000$) and (B) at high-magnification ($\times 30000$). FESEM images of PPCQ anode. (C) At low-magnification and (D) at high-magnification.

Figure 4.2A&B show the morphologies of the as-prepared PPCQ nanoparticles. The PPCQ nanoparticles are observed to be with an average size larger than 100 nm. The FESEM images of the composed PPCQ anode with the addition of carbon additives (CNTs) were presented in Figure 4.2C&D. It can be clearly seen that the CNTs are interconnected with PPCQ nanoparticles after mixing and grinding. Figure 4.3 below shows the TEM image and elemental mappings of as-prepared PPCQ nanoparticles. The presence of carbon, nitrogen and oxygen elements can be observed and they are homogeneously distributed in the skeleton of as-prepared PPCQ.

Figure 4.3 Structural characterization of PPCQ nanoparticles. (A) TEM image. Elemental mapping of the surface of PPCQ nanoparticles. (B) Element carbon. (C) Element nitrogen. (D) Element oxygen.

To get a deeper understanding of the chemical structure of PPCQ, elemental analysis (EA) was performed. From the obtained EA results (Table 4.1), the measured content of C, H and N element in PPCQ is, respectively 52.69%, 2.79% and 19.11%, indicating that the C/N molar ratio is 2.76. Based on this result, the author could possibly infer that the obtained PPCQ is an oligomer with an average degree of polymerization (n) equals to approximately four, and the terminal groups of PPCQ are mainly consisted of OH groups. The proposed exact chemical structures of PPCQ oligomers are presented in Figure 4.4, which contain different structural possibilities (with monomeric units $n = 3, 4, 5$ and etc.) with variable contents of water molecules. Because of the strong hydrogen bond (O-

H $\cdots$ O) between H₂O and PPCQ, each carbonyl group (C=O) could be associated with one H₂O to form the proposed mixtures of the oligomer structures of PPCQ.

Table 4.1 Elemental analysis and calculated molar ratio of PPCQ oligomers.

Structures/Element Content	C%	H%	N%
Measured	52.69	2.79	19.11
Structure 1 ($n=3$)	52.95	2.63	18.30
Structure 2 ($n=4$)	54.42	2.64	20.04
Structure 3 ($n=5$)	55.27	2.65	21.05

Figure 4.4 Proposed oligomer structures of PPCQ according to the EA results.

The XRD spectrum of PPCQ nanoparticles was displayed in Figure 4.5A, and in agreement with the studies in conjugated polymers,^{13, 14} the distinctive diffraction peak observed at around 26° is explained by the π - π stacking between the conjugated main chains. To further confirm and verify the successful polymerization of the targeted compound, the chemical structure of PPCQ was characterized by Fourier transform infrared spectroscopy (FTIR) (Figure 4.5B). The absorption peak of the carbonyl groups

C=O is observed at 1696 cm^{-1} .^{8, 15} The weak peak at around 3300 cm^{-1} and the peak at 1220 cm^{-1} could be attributed to the stretching vibration of the N-H bonds and C-N bonds respectively.¹⁶ The peaks observed between 1628 and 1446 cm^{-1} are ascribable to the C=N stretchings,¹⁶ indicating the successful reaction and cyclization between the two reactants to form the ladder-structured oligomer. A large and broad peak between 3400 and 2000 cm^{-1} could be observed and should be resulted from the O-H stretching and water,^{17, 18} further indicating the existence of O-H groups and water molecules in the product. This result is tally with the EA results and could reasonably explain why there is a large and broad peak between 3400 and 2000 cm^{-1} due to the existence of the O-H groups and water molecules. Thermal stability of PPCQ nanoparticles was investigated by thermogravimetric analysis (TGA) (Figure 4.5C), which shows that PPCQ nanoparticles loss approximately 5% of its weight below $200\text{ }^{\circ}\text{C}$ caused by the water loss. This 5 wt% of water is close to the percentage of water content in the proposed chemical structures, further confirming the formation of the proposed oligomer structures for PPCQ. Owing to the existence of the mixtures of oligomers, PPCQ nanoparticles show continuous degradation upon heating up to $700\text{ }^{\circ}\text{C}$, nevertheless, approximately 70% of the weight could still be maintained, revealing a good stability of PPCQ at high temperatures.

Figure 4.5 Characterizations of as-prepared PPCQ nanoparticles. (A) XRD. (B) FTIR. (C) TGA.

To understand the battery performance of PPCQ nanoparticles, various electrochemical investigations were performed. The galvanostatic charge and discharge capability of PPCQ nanoparticles was evaluated at 100 mAh g^{-1} between 0.0 and 3.0 V. As shown in Figure 4.6A, the curves of the first two cycles were presented. There are two small plateaus observed at about 2.7 and 1.6 V, followed by a sloping plateau below 1.0 V, which are ascribed to the acceptance of lithium-ions onto the carbonyl group,¹⁹ nitrogen atoms^{10, 11} and C₆ aromatic rings,²⁰ respectively. It can be noticed that PPCQ displayed a high capacity of 4098 mAh g^{-1} at the first discharge with a reversible capacity of 1678 mAh g^{-1} in the following charge process. The initial reversible capacity corresponded to a Coulombic efficiency (CE) of 41%. The large capacity loss was ascribed to the formation of a solid electrolyte interface (SEI) layer associated with a series of irreversible reactions. The formation of SEI is a very common phenomenon in the first cycle of anode materials for LIBs.^{21, 22} Although the CE of the first cycle was not high, it could be rapidly increased after the second cycle and stabilized at around 97% over 120 cycles (Figure 4.6C).

To verify and confirm this irreversible lithiation in PPCQ, CV was carried out in the range of 0.0-3.0 V at a scan rate of 0.2 mV s^{-1} . The initial three cycles were examined as shown in Figure 4.6B. A large and broad tail below 1.1 V was observed at the 1st cathodic sweep, confirming the large contribution of the irreversible capacity resulted from the SEI film during the first discharge process. The completely disappeared peak at 1.1 V and the decreased intensity of the current in the 2nd and 3rd cycles confirmed the irreversible reactions caused by the SEI during the 1st cycle. To step into the details of the reactions, in the first cathodic sweep, the small peak in the range of 1.4-1.6 V was associated with the addition of lithium-ions onto the unsaturated nitrogen atoms.^{10, 11} The lithiation process accomplished with a sharp declination of the current from 1.0-0.0 V, which might be due to the addition of lithium ions onto the C₆ aromatic rings along with the formation of the SEI.²⁰ On the reverse anodic sweep, the peak started at 1.4 to 1.75 V corresponded to the delithiation of lithium ions from nitrogen atoms. The oxidation peak centered at about 2.5 V was related to the occurrence of the enolation process, where the carbonyl

group formed due to the reoxidation of the lithium enolate.¹⁹ The peaks were in good agreement with the potential plateaus observed in the charge and discharge profiles.

Figure 4.6 Electrochemical characterization of the PPCQ anode. (A) Charge and discharge profiles for the initial two cycles. (B) Cyclic voltammetry (CV) curves. (C) Cycling performance and Coulombic efficiency for 120 cycles. (D) Rate performance (each rate consists of ten cycles).

The excellent electrochemical stability of PPCQ can also be realized from the cycling test. Figure 4.6C shows that even after 120 cycles, PPCQ can still deliver a high reversible capacity of 972 mAh g⁻¹. From the author's understanding, most of the organic materials have been preferred to be the cathode materials. Up to present, seldom pure organic anode materials have been reported, especially organic anodes with high lithium storage. As far as the author knows, this capacity performance of PPCQ is better than most reported organic anodes, including lithium salts^{23, 24} and carbonyl compounds.^{25, 26} It is worthy to note that such a good result is comparable to or even better than the metal-based inorganic anodes that reported with high capacity performances, for examples, SnO₂ (580 mAh g⁻¹ after 100 cycles),²⁷ α-Fe₂O₃ (945 mAh g⁻¹ after 30 cycles)²⁸ and Co₃O₄ (970 mAh g⁻¹ after 30 cycles).²⁹ If consider that one lithium ion per formula unit of PPCQ contributes to 129 mAh g⁻¹, the reversible capacity of 1678 mAh g⁻¹, referring

to a utilization of 93.1% of its theoretical capacity ($\sim 1802 \text{ mAh g}^{-1}$) indicates that PPCQ is capable of accepting nearly thirteen lithium-ions.

The small sized nanoparticles, which are closely packed to carbon additives, provide large surface areas for electron transfer among PPCQ nanoparticles. Thus, a good rate performance should be expected. Figure 4.6D shows that under various current densities of 0.2, 0.5, 1.0, 2.0, 5.0 A g^{-1} , PPCQ could achieve reversible capacities of 963, 667, 509, 419, 329 mAh g^{-1} , respectively. Even when cycled at an extremely high rate of 10 A g^{-1} , a specific capacity of 269 mAh g^{-1} could still be achieved. It is noted that a moderate capacity of 396 mAh g^{-1} (the average of the 10 cycles at 0.2 A g^{-1}) was attained when the current rate was reset to 0.2 A g^{-1} . Such a capacity was relatively low as compared with its capacity at 0.2 A g^{-1} during the initial ten cycles. The decay of capacity might be due to (1) the structure of PPCQ was not stable or it was dissolved to some extent during the cycling process at such high rates (up to 10 A g^{-1}), since most of the reported organic compounds including polymers could only endure low current rates;³⁰ and (2) the ring-size effect could be another reason that affected the rate performance of PPCQ, since it was found that compound with five-membered rings display worse stability during the reactions compared with those with six-membered rings.³¹

Figure 4.7 Electrochemical performance of PPCQ nanoparticles at 2.5 A g^{-1} . (A) Charge and discharge profiles at different cycles. (B) Coulombic efficiency for 1000 cycles. (C)

Corresponding ultra-long cycling performance in terms of charge and discharge capacities.

Nevertheless, to further understand the stability of PPCQ during the cycling process, PPCQ was tested at a consistent high current rate of 2.5 A g^{-1} for 1000 cycles. Notice that in the charge and discharge profiles of PPCQ nanoparticles (Figure 4.7A), even at such a high rate, PPCQ could still maintain at 489 mAh g^{-1} after 1000 cycles, exhibiting a high capacity retention of 87.8% with respect to its initial reversible capacity (the 2nd discharge, 557 mAh g^{-1}). Figure 4.7B shows that the average Coulombic efficiency (exclude the 1st cycle) of PPCQ is as high as 99.8%, which is among the best efficiencies of the reported organic electrodes. The overall ultra-long cycling profile is also presented (Figure 4.7C), where the performance is quite stable and consistent during the 1000 cycles. This extraordinary excellent performance confirms the superiority of PPCQ and indicates that PPCQ is stable enough to be used at high current densities.

4.3.2 Results and Discussion of NG-HCP

NG-HCP was obtained as black powders by a direct polycondensation between hexaketocyclohexane (HKH) octahydrate and 1,2,4,5-Tetraaminobenzene (TAB) tetrahydrochloride in N-methyl-2-pyrrolidone (NMP) with sulphuric acid as a catalyst (Figure 4.8A). The alternating connection between pyrazine and benzene rings forms an extended 2D structure with homogeneous honeycomb-like pores (Figure 4.8B), where excessive carbonyl and amino groups existed at the edge.

Figure 4.8 Dehydration-condensation in NMP solution and schematic representation of pristine **NG-HCP** structure (A). Molecular configuration (B) of a single layer **NG-HCP** with 11.65 Å in micropores and a packing distance of 3.34 Å.

To further understand the detailed structure, the ideal crystalline structure of a NG-HCP single layer was fully optimized by Compass II force field³² in Forcite module (Materials Studio 8.0) and then followed by DFT method (GGA/PBE) in CASTEP module³³. The ideal NG-HCP single layer is constructed with the parameters of $a = b = 16.70$ Å, $\gamma = 120^\circ$ (regardless of the out-of-plane), where uniform pores with the diameter of 11.65 Å are obtained (Figure 4.9A). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) at γ point are determined as -6.250 and -5.270 eV, respectively (Figure 4.9B&C). The predicted pore size of NG-HCP is 11.653 Å as shown in Figure 4.9D. The electronic structure of the ideal NG-HCP crystal was also calculated by first-principles. The results show that single layer NG-HCP is a direct band gap semiconductor with a finite gap of 0.958 eV at the γ point (Figure 4.9E).

Figure 4.9 Simulation result of NG-HCP in ideal crystal. Unit cell of NG-HCP single layer (A) with long-range order, $a = b = 16.70 \text{ \AA}$, $\gamma = 120^\circ$. An iso-surface plot of the Kohn–Sham orbital at the gamma point: (B) Conduction-band minimum state; (C) Doubly degenerate valence-band maximum state, corresponding to the calculated HOMO and LUMO level of NG-HCP single layer, respectively. (D) Band structure from the zone center to the M point of the 2D triangular lattice. (E) Structural representation of $a \times 2$, $b \times 2$ unit of NG-HCP single-layer.

To confirm the precise structure of NG-HCP unit, X-ray photoelectron spectroscopy (XPS) measurement is performed to investigate the valence states of elements in NG-HCP. The XPS spectrum exhibits 3 peaks centered at 283.6 eV, 397.8 eV and 530.5 eV, corresponding to C1s, N1s and O1s, with the contents of 50.04, 13.96 and 33.87 at%, respectively (Figure 4.10A). By analyzing the binding energy (BE) values obtained from high-resolution XPS, the nature of the binding between carbon, nitrogen and oxygen can be confirmed.^{34, 35} XPS of C 1s ranges from 280 to 290 eV is shown in Figure 4.10B. Generally, there are several different types of C groups in NG-HCP, which are confirmed by the appearance of several spectral peaks with different relative contents: C=C at

284.53 eV (32.75 at%), C-OH at 286.73 eV (13.65 at%) and C=O at 288.1 eV (0.86 at%). No N-O or O-C=O (at 289.0 eV) could be observed, indicating the absence of nitro- or carboxylic- group.

Figure 4.10 Composition and bandgap. (A) XPS survey spectrum of the as-prepared NG-HCP. High-resolution XPS spectra of (B) C1s and (C) N1s of NG-HCP. (D) Optical band-gap measurements in UV-vis-NIR and a plot of the absorbance squared vs. photon energy ($h\nu$). Inset shows the UV-vis-NIR absorption curve.

Interestingly, a new BE peak of 283.45 eV is obtained with a content as high as 52.75 at%. The lower BE value might be due to the delocalization of the lone pair of electrons of N atoms to form a larger aromatic system, which is strongly supported by the formation of a closed ring structure of NG-HCP with a ~ 1.16 nm pore size as predicted in Figure 4.9D. Similarly, another peak with a lower BE value was also obtained in N 1s (Figure 4.10C), where a BE value of 397.24 eV (17.03 at%) is derived from the C=N of the pyrazine moiety. The other two N- elements BE peaks locate at 398.21 (80.71 at%) and 400.4 eV (1.53 at%), correspond to the signals from the pyridine and amino-group (or

pyridone). No imine-N (C=N, at ~ 399.7 eV), quarter-N (at ~ 401.3 eV), graphitic nitrogen (at ~ 400.7 eV) and only a very small amount of amino-group is observed, which reveals the domination of the pyrazine nitrogen in the 2D skeleton of NG-HCP has better aromaticity than other N-doped graphene materials. The rather weak signal from C 1s at 288.1 eV (C=O) may arise from the resonance between the ketone and phenolic hydroxyl groups. Therefore, the formation of 2D NG-HCP skeleton with well-defined structure could be confirmed from the alternating pyridine and benzene rings, which are connected by the conjugated carbon nitrogen double bonds (C=N). The UV-vis-NIR spectroscopy (Figure 4.10D) is performed to investigate the direct bandgap of NG-HCP compressed pellet. The value of the bandgap is approximately 1.25 eV from the edge of its absorbance at ~ 989 nm, which is much narrower than the previously investigated nitrogen-doped holey graphene.³⁴⁻³⁷ The high conductivity of such **NG-HCP** in pellet is confirmed by four-point-probe method as $3.55 \pm 0.4 \times 10^{-2} \text{ S cm}^{-1}$, which is much higher than most conductive COFs,^{38, 39} and could be resulted from the precise graphene-like units and the narrow bandgap of NG-HCP.

The FTIR of NG-HCP (Figure 4.11A) exhibits two broad vibration bands at 3359 and 3214 cm^{-1} , which may be derived from the resonance hydroxyl and amino groups, respectively, accompanied with several subtle peaks from the aromatic skeleton in the range of 1620 $\sim$ 1040 cm^{-1} (1619, 1584, 1475, 1341 and 1043 cm^{-1} et al). The thermal stability of **NG-HCP** is revealed by TGA (Figure 4.11B). No significant decomposition of **NG-HCP** before 220 $^{\circ}\text{C}$ (5 % weight lost) was observed from the TGA curve and about 65 % of its weight remains maintained even at a high temperature of 800 $^{\circ}\text{C}$. Powder XRD result of the as-prepared NG-HCP (Figure 4.11C) shows a remarkable diffraction peak at 26.60° , which indicates a highly ordered packing out-of-plane and readily high crystallinity. The position of the peak corresponds to an interlayer distance (d-spacing) of 3.34 Å (right corner of Figure 4.8B), which is in good agreement with the (002) diffraction peak of graphite. The details of O 1s (Figure 4.11D) suggests that the O atom is consistent with the BE values of the quinone (or very little pyridone groups) and ketone (C=O) at 530.06 and 531.34 eV, respectively, with nearly the same atomic content (49.27 and 50.73 at%), respectively.

Figure 4.11 Structural characterization of NG-HCP. (A) FTIR spectrum of as-prepared NG-HCP. (B) DSC measurement of NG-HCP pellet after vacuum oven dried at 60 °C, with a heating rate of 5 °C min⁻¹. (C) Powder XRD pattern of compressed NG-HCP pellet. (D) High-resolution XPS spectra of O 1s of the as-prepared NG-HCP.

The morphology of **NG-HCP** was observed through SEM characterization (inset of Figure 4.12A). By dispersing **NG-HCP** into low a concentration DMSO solvent (ca. 0.05 mg mL⁻¹), well-dispersed sheet-like structures with thickness of tens of nanometers can be obtained. Nitrogen sorption experiments were carried out and revealed a close-correlation porous structure of the resulting NG-HCP between surface area and pore volume with an ideal crystallinity of NG-HCP. The experiment is performed at 77 K, after degassing of the as-prepared NG-HCP at 150 °C for 12 hrs. A type I isotherms observed in Figure 4.12A indicates the microporous structure of NG-HCP with an apparent Brunauer-Emmett-Teller (BET) surface area of 72.56 m² g⁻¹ (calculated $p/p_0 = 0.05 \sim 0.11$ in the adsorption branch) and a pore volume of 0.2548 cm³ g⁻¹. Furthermore, the distinct adsorption of the sorption isotherms below $p/p_0 = 0.1$ emphasizes the very well-defined porosity of NG-HCP. The pore size distribution based on non-local density functional theory (NLDFT) method (Figure 4.12B) indicates the presence of both meso-

and micro-pores in NG-HCP. On the basis of the surface area result, the size of micropores is centered at 11.8 Å, which is reasonably close to the predicted pore size (11.6 Å). A small portion of the mesopores in the range of 5 ~ 110 nm could be observed from the pore size distribution, which might be derived from the interlayer distance between NG-HCP layers. The cumulative surface area shows that the micropores, with dimensions smaller than 16 Å, contributes ~60 % surface area and dominate the absorption at the surface. The BET result reveals that NG-HCP possesses large surface areas but small pore volumes, indicating the formation of closed porous structures in NG-HCP 2D nanostructures.

Figure 4.12 Porosity and nanosheets of NG-HCP. (A) Nitrogen adsorption/desorption isotherms and (B) Pore size distributions of NG-HCP. (C) AFM image of NG-HCP single- or multi-layer nanosheets dispersed in DMSO. (D) Corresponding cross-sectional measurements of NG-HCP nanosheets. (E) Raman spectrum of as-prepared NG-HCP.

AFM characterization was performed to characterize the morphology of layered NG-HCP obtained from diluted DMSO solution. As shown in Figure 4.12C, the round-shaped NG-HCP nanosheets with rough surfaces are well-dispersed on silica substrate with the size

in the range of 100 ~ 500 nm. The height profiles of the 2D NG-HCP layers show a thickness at ca. 1 nm. Typically the thicknesses are measured to be 1.0 ± 0.2 nm as shown in the cross section of the white line (Figure 4.12D), corresponding to a single-layer of NG-HCP. This result is well consistent with that of exfoliated graphene on SiO_2 substrate, instead of a theoretical single atomic thickness, which may due to the side groups and small molecular adsorption at the surface.^[40] It is even thinner than graphene oxide (~ 2 nm)^[41] and some other 2D carbon nitride.^[42]

Raman spectroscopy is another powerful tool for the characterization of graphene-like materials. The authors and collaborators involved in this study observe a series of vibration bands that are similar to graphene, including the G (1528 cm^{-1}), D (1348 cm^{-1}) band, G' and 2D ($2500 \sim 2800 \text{ cm}^{-1}$) broad band in NG-HCP powder sample (Figure 4.12E). The G-band Raman feature, which is commonly observed in all sp^2 carbon systems, is assigned to the in-plane bond-stretching motion of the pairs of C-sp^2 atoms. Interestingly, NG-HCP exhibits a large downshift comparing with the pristine graphene ($1583\text{-}1588 \text{ cm}^{-1}$).^[35] Such a downshift in G-band caused by N-doping has been observed in other N-doped graphene-like counterpart (only $\sim 10 \text{ cm}^{-1}$), which might be attributed to the phonon energy renormalization arising from the electron-phonon coupling.^{43, 44} The Raman spectrum has a high intensity of D-band with the intensity ratio of D-band/G-band (I_D/I_G) 0.94, indicating that a large amount of topological defects is introduced by N doping. Whereas, the D band presents an upshift of 13 cm^{-1} ($\sim 1335 \text{ cm}^{-1}$ in pristine graphene) instead, which is attributed to the appearance of new types of disorders with the introduction of new fine structures as pyrazine in the 2D skeleton.^{34, 43} The upshift and downshift of D-band and G-band provide solid evidence for the modification of phonon and electron structures within NG-HCP caused by N doping.

Figure 4.13 TEM/HRTEM images of NG-HCP nanosheets. (A) TEM image of NG-HCP nanosheets from DMSO suspensions. (B) and (C) HRTEM of NG-HCP nanosheets in different region. FFT of the (D) red and (E) purple square region in (B) and (C), respectively. Right inset of (D), the distance measured between the vertexes of inner hexagon in (D). (G) AB....stacking configuration of two NG-HCP layers derived from inset of (B). (F) Lattice fringe distance measurement of cyan line in inset of (B).

The morphology and precise honeycomb microstructure of NG-HCP was further investigated by TEM. The wrinkled paper-like morphology is further confirmed by low magnification images (Figure 4.13A) from diluted DMSO suspensions. A polycrystalline NG-HCP with crystal domain size of about 3 nm can be clearly seen in the high resolution TEM (HRTEM) results from Figure 4.13B, C and F. Therefore, a typical AB....stacking between two NG-HCP single layers is proposed by the lattice analysis (Figure 4.13G). Half-cell lattice offset of NG-HCP single layer along the diagonal

direction leads to a spacing of 8.993 Å of c axis with angle $\alpha = \beta = 62.342^\circ$ in a unit cell. Enlargement of the HRTEM image of the corresponding red square region in Figure 4.13B indicates a well-ordered crystalline domain with large cell parameters (inset of Figure 4.13B). In order to identify the well-defined honeycomb micropores in NG-HCP, electron diffraction patterns are obtained through fast Fourier transform (FFT) of different lattice fringes to study the layer stacking and packing motifs within NG-HCP. Two significant concentric hexagonal patterns are obtained through the FFT (Figure 4.13D). The diagonal line between the two vertexes of inner hexagon is determined as 3.31 ± 0.3 1/nm (inset of Figure 4.13D). The spots 1 and 2 possess a d-space of 6.04 ± 0.64 and 3.16 ± 0.16 Å, respectively, corresponding to the diffraction of (1,0,0)s and (2,0,0)s facets of NG-HCP based on its simulated unit cell. The FFT of the purple square region in Figure 4.13C generates two spots marked as 3 and 4 (Figure 4.13E), which are assigned to (2,-4,0) and (4,-8,0) facets, respectively. No typical spots or lattices of graphene (100)s (or 2.46 Å) could be obtained, suggesting a total difference in aromatic ring of the backbone of NG-HCP as compared with graphene. The cyan line in inset of Figure 4.13B exhibits a series of regular periodic peaks with distance of 14.46 Å (4 peaks) as the typical d-spacing of (1,-1,0)s facets (Figure 4.13F), corresponding to the distance between two diagonal lines of the unit cell (red dash line in Figure 4.13G). All these results strongly support the generation of precise honeycomb pores with graphene subunits as proposed in Figure 4.8B.

Figure 4.14 Electrochemical performance of NG-HCP nanosheets/CNT electrode. (A) CV curves of NG-HCP nanosheets/CNT anode at a scanning rate of 0.2 mV s^{-1} in the voltage range of 3~0 V vs. Li^+/Li . (B) Galvanostatic charge-discharge profile of NG-HCP nanosheets/CNT anode at a current rate of 20 mA g^{-1} in the voltage range of 3~0 V vs. Li^+/Li . (C) Cycling performance of NG-HCP nanosheets and pristine NG-HCP electrode hybrid with CNT at a current rate of 0.1 A g^{-1} . (D) Rate performance of NG-HCP nanosheets/CNT electrode at various current densities in the range of $0.1 \sim 2.5 \text{ A g}^{-1}$. (E) Ultra-long cycling performance of NG-HCP nanosheets/CNT electrode at a current rate of 1.2 A g^{-1} . (F) SEM image of the NG-HCP anode.

The cyclic voltammetry (CV) curves of NG-HCP as an anode material are presented and show typical curves of the carbonaceous anode materials⁴⁵ (Figure 4.14A). In the first cycle, a pronounced reduction peak is observed at ca. 1.1 V, attributing to the formation of a solid electrolyte interface (SEI) film on the surface of NG-HCP. This peak disappears in the following cycles, suggesting an irreversible reaction caused by the formation of the SEI film, which is a common phenomenon in the 1st cycle. For the 2nd

and 3rd cycles, the peak centered at ca. 1.4 V can be attributed to the addition of lithium-ions onto the nitrogen atoms.^{10, 11} The second and third cycles were almost overlapped, suggesting a good reversibility of NG-HCP during the discharge and charge cycling. Figure 4.14B shows the galvanostatic charge-discharge profiles of NG-HCP at a current rate of 20 mA g⁻¹ in the voltage range of 0 ~ 3 V vs. Li⁺/Li. The first discharge profile shows a stage at ca. 1.1 V, indicating the formation of the SEI film, which is well in accordance with the CV curves. The initial specific discharge and charge capacity reaches 2497 and 1319 mAh g⁻¹, respectively, with a Coulombic efficiency of 52.8%. The capacity loss (~ 1178 mAh g⁻¹) is mainly attributed to the irreversible reactions from the formation of the SEI film, which is a common phenomenon in the first cycle of LIB anodes. After 170 cycles, the reversible capacity of NG-HCP is sustained at a high value of ~975 mAh g⁻¹ under a current rate of 0.1 A g⁻¹ (Figure 4.14C). This performance is better than the state-of-the-art heteroatom-doped graphene^{46, 47} and even comparable with most of the porous graphene materials (e.g. 1040 mAh g⁻¹ for the mesoporous graphene nanosheets,⁴⁸ 956 mAh g⁻¹ for the N-doped holey graphene⁴⁹). The specific reversible capacity of NG-HCP is stabilized at 935, 665, 480, 341, 295 and 257 mAh g⁻¹ (Figure 4.14D) when cycled under different current densities of 0.1, 0.5, 1, 1.7, 2.0 and 2.3 A g⁻¹, with Coulombic efficiency over 99%. Even at a high current density of 2.5 A g⁻¹, a reversible capacity of 237 mAh g⁻¹ is still obtained. Notably, after 70 cycles of testing at various current densities, the capacity is retained at 928 mAh g⁻¹ when the current density is reset to 0.1 A g⁻¹. A superior long-term cycling performance is obtained (Figure 4.14E) with a stable capacity range of 423~510 mAh g⁻¹ for 600 cycles at a high current density of 1.2 A g⁻¹. The Coulombic efficiency remains approximately 100% at the 600th cycle, revealing an excellent electrochemical stability of the NG-HCP anode.

The remarkable high capacity and ultra-stable cycling performance of NG-HCP could be explained by its novel porous structure with the introduction of an extraordinary high-level of nitrogen atoms. The micro-pores in the formed interconnected NG-HCPs holey structure can serve as reservoirs for lithium-ion storage, therefore providing a large number of channels for electron transportation during lithiation and delithiation.⁴⁵ The NG-HCP nanosheets are well-sustained by the CNT networks to provide large surface

area (Figure 4.14F). Especially, after nanoengineering, the smaller sizes of NG-HCP with large surface areas could provide a much reduced diffusion length that both electrons and lithium-ions need to travel, promoting the charge-transfer reaction.⁵⁰ In addition, the electrochemical and electrical reactivity of NG-HCP was enhanced by introducing hetero-atoms into the conjugated COF structure, resulting in a superior battery performance of the electrode material. These excellent battery performance of NG-HCP open a window for the investigation of COF-structured polymers as anode materials.

4.4 Conclusions

In conclusion, two novel ladder conjugated polymers have been synthesized through a simple one-step polymerization process, respectively. The superior electrochemical properties of these two compounds bring the battery performance of organic materials to a new level. Ladder-structured conjugated ladder polymers, especially their nanostructures, containing heteroatoms (e.g. N and O) are superior anode materials for rechargeable lithium batteries. Such double-stranded 1D and 2D conjugated structures might exhibit better thermal, mechanical and electrochemical stability compared with conventional conjugated polymers. The fully coplanar backbones of ladder-structured conjugated polymers might provide coherent pi-conjugation, fast intra-chain charge transport and strong pi-pi stacking interactions. Moreover, considering their easy synthesis, low temperature reactions and non-metal containing structures, they are potential green resources for future eco-friendly and sustainable energy storage devices.

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Chapter 5*

Novel Carbonyl-Containing Large Aromatic Molecules and Polymers as High-Performance Positive Electrodes for Li-Organic Batteries

The decisive factor to realize high-capacity and energy density rechargeable batteries is the positive electrode material. Compared to negative electrode materials in Li-ion batteries, the research on positive electrode materials is far behind and their capacities are much smaller. Thus, in order to address these issues, redox-active carbonyl-containing materials are believed to be a good solution. In this chapter, four novel carbonyl-containing compounds are presented and demonstrated as positive electrodes for lithium-organic batteries. These structure designing strategies provides alternative solutions to develop organic cathodes toward next-generation of high stability batteries.

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5.1 Introduction

Beyond anode materials, the intention for high energy density Li batteries requires the cathode materials to have relatively high average potentials *versus* Li/Li⁺. The decisive factor to realize high-capacity rechargeable batteries is the cathode. Since the experimental capacity of inorganic cathodes is usually less than 200 mAh g⁻¹, searching new cathode materials to boost the capacity is highly desirable. In order to achieve high capacity and good reversibility for LIBs, cathode materials of light elements such as C, H, O and N have to be explored.

Redox-active organic compounds with carbonyl groups (C=O) are quite popular for this direction because they are easy to produce and modify. Due to the environmental friendliness, design flexibility, high working voltage and multi-electron redox ability, they have recently attracted tremendous investigations as potential high-performance green cathode materials.^[1-5] It is well known that carbonyl bonds or heteroatom-doped conjugated rings are promising candidates for reversible lithiation and delithiation during discharging and charging.^[6-10] Particularly, multiple carbonyl-functionalized organic cathodes with inherent stabilities were shown to be superior to the state-of-the-art inorganic cathode materials (e.g. LiCoO₂, LiFePO₄ & LiMn₂O₄).^[11, 12] By virtue of the diverse functionalities, carbonyl-containing cathodes have the opportunity to provide storage capabilities not only in the applications of lithium-ion (Li⁺) batteries, but also sodium (Na⁺),^[13] magnesium (Mg²⁺),^[14-16] and even potassium (K⁺)^[17, 18] -ion batteries. In addition, the mechanism of the lithiation and delithiation process has been thoroughly investigated and explained.^[19] Compared with the traditional inorganic cathodes that usually based on the first-row transition metal oxides (e.g. LiCoO₂, LiMn₂O₄ and LiFePO₄), the specific capacity and cycling stability of organic materials can be further improved by the introduction of different redox centres into the organic structures.

Over the last two decades, tremendous studies have been conducted to prepare suitable organic materials as cathodes with improved electrochemical properties.^[20] These studies

indicated that carbonyl groups play a critical role in determining the specific capacities of organic compounds. Thus, it is urgent to develop effective organic compounds with utilization of carbonyl functional groups. It is highly desirable to ensure that all the carbonyl compounds to be effectively involved into the reversible reaction to provide a high specific capacity and a high average potential. It is widely known that small organic molecules are facing severe dissolution issues, which usually result in low reversible capacity and poor cycling performance of the electrodes when cycled.^[21, 22] In order to solve this problem, the common approach is to increase the stability of the organic compounds by increasing the molecular length or polymerization.^[23, 24]

In this chapter, taking into consideration the above-mentioned points, the author and his collaborators design and develop four novel active organic cathode materials with enhanced theoretical Li capacity and improved cycling stability. Firstly, the author propose an effective method through the construction of two stable ladder-like non-polymeric dianhydride structures: NDA-4N and PDA-4N, on the basis of the naphthalene and perylene large building blocks. This approach was initiated based on the hypothesis that large aromatic building blocks with rigid ladder-like structures could enhance the stability of organic cathodes, thus improving the cycling performance of the electrochemical cells. Later, the author and his collaborators develop two novel organic polymer cathodes, poly(pyrene-4,5,9,10-tetraone) (PPTO) and poly(2,7-ethynylpyrene-4,5,9,10-tetraone) (PEPTO). Due to their four Li^+ intake characteristics, both two polymer cathodes show high specific capacities and energy densities. In particular, benefiting from the enhanced conjugation and planarity, PEPTO with $\text{C}\equiv\text{C}$ bonds as bridges shows effectively-improved rate and long-term stability. These studies propose effective opportunities to achieve next-generation of organic cathode materials through designing redox-active small molecules and polymers.

5.2 Synthesis, Characterization and Measurement

5.2.1 Synthesis of NDA-4N and PDA-4N

NDA-4N and PDA-4N were synthesized through a two-step reaction from the starting materials of compound **2** or **4**. To be specific, by mixing compound **2** or **4** with 1,2,4,5-Tetraaminobenzene tetrahydrochloride in pyridine solvent, tetra-ester compound **3** or **5** were obtained in the form of mixtures (including both cis and trans isomers). Through further refluxing of **3** or **5** with *p*-toluenesulfonic acid monohydrate (TsOH·H₂O) in toluene solvent at 110 °C, the as-prepared NDA-4N and PDA-4N compounds were obtained. After drying these two materials overnight in a vacuum oven under the temperature of 80 °C, they are ready to be used as the active cathode materials. To be noted that, compound **4** was prepared according to the previous work.^[25] For the characterizations of NDA-4N, FTIR: 1781, 1700 cm⁻¹ (anhydride). Elemental Analysis calculated: C 67.78%, H 1.67%, N 9.30%; measured: C 66.91%, H 2.29%, N 8.66%. For the characterizations of PDA-4N, FTIR: 1760, 1680 cm⁻¹ (anhydride). Elemental Analysis calculated: C 76.24%, H 2.13%, N 6.59%; measured: C 73.45%, H 2.23%, N, 6.49%. The detailed synthetic routes of the starting materials and the intermediate compounds **1**, **2**, **3** and **5** are provided in APPENDIX A.

5.2.2 Characterization and Measurement of NDA-4N and PDA-4N

Materials characterization: HRMS results were collected by a Waters ACQUITY UPLC® System. NMR spectra were obtained from a Bruker AV 300 Spectrometer at 300 MHz (¹H NMR) and 75 MHz (¹³C NMR). FTIR spectra were obtained by PerkinElmer Spectrum Frontier FTIR spectrometer. Elemental analysis was conducted on a PerkinElmer 2400Series II CHNS/O elemental analyzer. TGA investigations were conducted under a nitrogen atmosphere on a TA Instruments TGA Q500 at 10 °C min⁻¹ between room temperature and 800 °C. All SEM images were obtained by JEOL/JSM-6340F performed at an accelerating voltage of 5 kV.

Electrochemical Cell Fabrication and Measurements: Homogeneous electrode slurries were obtained after mixing the active materials (NDA-4N and PDA-4N, separately) with carbon additives (CNTs) and binders (polyvinylidene fluoride (PVDF) with a weight ratio of 3:5:2 in N-methyl-2-pyrrolidone (NMP) solvent. The slurries were uniformly pasted onto the battery grade aluminium (Al) foil current collectors. The as-prepared electrodes were dried at 60 °C for 12 hrs and then punched into circular disks with diameters of 12 mm and thicknesses in the range of 9-11 μm (excluding the thicknesses of the current collectors) to be used as the cathodes. For half-cell fabrication, lithium foils were used as the counter electrodes. The optimized electrolyte system consists of 1 mol/L (M) LiTFSI in the DOL/DME solvent (1/1, w/w) with 1% LiNO_3 as the additive. Celgard 2400 separators were used and CR2032 coin-type electrochemical cell construction was applied. The cells were prepared in a glovebox filled with pure inert gas (argon gas) wherein the oxygen and moisture levels both maintained below 1 ppm. The cells were finally assembled and placed for 12 hrs to be tested. Charge-discharge profile, rate stability and long-term cycling stability of NDA-4N and PDA-4N were obtained under room temperature on a NEWARE multichannel battery tester in the voltage range of 2.0 to 3.9 V. Different current densities of 66, 100, 166, 333 and 1000 mA g^{-1} were applied for different investigations. CV and EIS studies were conducted on an electrochemical analyzer (CH Instrument CHI604e). The scan rate of CV analysis was 0.2 mV/s and the frequency range of EIS study was set between 100 kHz and 10 mHz.

5.2.3 Synthesis of PPTO and PEPTO

2,7-Dibromo-pyrene-4,5,9,10-tetraone (**1**) was prepared according to the reported procedures.^[26] However, directly performing coupling reaction with compound **1** faces two issues: a) the degree of polymerization would be extremely small due to the poor solubility of **1**; and b) the ortho-diketones might deactivate the catalyst during the coupling reaction through chelating interaction.^[27] Therefore, in order to avoid these problems, a protection-deprotection strategy was adopted to prepare PEPTO and PPTO. Compound **1** was transformed into the tetraone-protected precursor **2** in a refluxing ethylene glycol solution with the catalysis of $\text{TsOH} \cdot \text{H}_2\text{O}$. PPTO was successfully

synthesized in a yield of 38% by hydrolyzing the desired product obtained through a nickel-catalytic self-polymerization of **2**.^[28] Following the same strategy, PEPTO was obtained by hydrolyzing the desired coupling product, which was made from **2** and bis(trimethylstannyl)acetylene in a yield of 76%.^[29] The detailed synthesis procedures of PPTO and PEPTO are provided in APPENDIX B.

5.2.4 Characterization and Measurement of PPTO and PEPTO

Materials Characterization: NMR spectra were recorded with a Bruker AV 300 Spectrometer at 300 MHz (¹H NMR) and 75 MHz (¹³C NMR). HRMS results were recorded on Waters ACQUITY UPLC® System. EA was conducted on a PerkinElmer 2400Series II CHNS/O elemental analyzer. FTIR spectra were recorded on a PerkinElmer Spectrum Frontier FTIR spectrometer. TGA profiles were obtained from a TA Instruments TGA Q500 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. SEM images were obtained by JEOL/JSM-6340F performed at an accelerating voltage of 5 kV.

Computational Methodology: The geometry structure of the trimers was optimized by using DFT calculations (B3LYP/6-31G*),^[30, 31] and the frequency analysis was followed to assure that the optimized structures were stable states.

All calculations were carried out using *Gaussian 09*.^[32]

Electrochemical cell fabrication and measurements: The as-prepared PPTO and PEPTO samples (each 9 mg) were mixed with carbon additives (multi-wall carbon nanotubes) (15 mg) and polymer binders (polyvinylidene fluoride) (6 mg) with a weight ratio of 3:5:2, separately. The mixture powders were ground with a pestle for 50 mins with the addition of a few droplets of N-methyl-2-pyrrolidone solvent. Homogeneous PPTO and PEPTO electrode slurries were separately obtained and uniformly pasted onto the battery grade aluminum foils. The as-prepared electrode films were dried at 60 °C overnight in a vacuum atmosphere and then taken out. Finally, PPTO and PEPTO electrodes with diameters of 12 mm and thicknesses in the range of 9-11 μm (excluding the thicknesses of the current collectors) were separately punched and to be used. To investigate the

electrochemical performance of PPTO and PEPTO, lithium foils were used as the counter electrodes. The electrolyte system consists of 1 mol/L (M) lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) in 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME) solvent (1/1, v/v). Celgard 2400 membrane was applied as the separator and CR2032 coin-type electrochemical cell construction was applied. The cells were prepared in a glovebox filled with pure argon gas wherein the oxygen and moisture levels were both maintained below 1 ppm. The cells were finally assembled and placed for an equilibration time of 12 hrs to be separately tested. The cells were tested on a NEWARE multichannel battery test system (at room temperature) with the galvanostatic charge and discharge in the ranges of 3.5-1.5. CV was performed on an electrochemical analyzer (CH Instrument CHI604e) at a scan rate of 0.1 mV s^{-1} . EIS analysis was conducted by the same instrument between 100 kHz and 10mHz.

5.3 Results and Discussion

5.3.1 Results and Discussion of NDA-4N and PDA-4N

The syntheses of NDA-4N and PDA-4N are displayed in Figure 5.1. The chemical structures of both compounds were confirmed by EA as shown in the synthesis section. To further confirm the successful synthesis of NDA-4N and PDA-4N, they were studied by Fourier transform infrared spectroscopy (FTIR) measurements. As displayed in Figure 5.2A&B, both the intermediate compounds **3** and **5** exhibit single typical peak from the ester functional groups (1711 cm^{-1} and 1706 cm^{-1} respectively). Moreover, two peaks located at $\sim 2900 \text{ cm}^{-1}$ suggest the existence of $-\text{CH}_3$ and $-\text{CH}_2$ functional groups. These results further indicate the correctness of the structures of compounds **3** and **5**. Regarding compounds NDA-4N and PDA-4N, it could be observed that all the peaks related to the ester functional group disappeared. Meanwhile, the typical double peaks of the anhydride functional groups appeared (1781 cm^{-1} and 1700 cm^{-1} for NDA-4N, 1760 cm^{-1} and 1680 cm^{-1} for PDA-4N), indicating the complete transformation of NDA-4N and PDA-4N from esters to anhydrides. The structures of NDA-4N and PDA-4N were further studied by thermogravimetric analysis (TGA). As shown in Figure 5.2C, both NDA-4N and

PDA-4N show good thermal stability under a nitrogen atmosphere. The results indicate a much more improved inherent stability of them as compared with single NDA and PDA units.^[33, 34] In detail, NDA-4N starts to decompose at a temperature approximate to 520 °C, while PDA-4N with a larger backbone structure shows a better thermal stability with a higher decomposition temperature close to 600 °C. The morphologies of both NDA-4N and PDA-4N were examined by SEM as shown in Figure 5.2D&E. The as-prepared NDA-4N and PDA-4N form aggregates with spheroidal-shaped nanoparticles. It is believed that such small sized materials could provide large contact areas, thus improving the lithium-ion transportation between the electrode and the electrolyte.^[35] Figure 5.2F shows the solubility test of the as-synthesized NDA-4N and PDA-4N in electrolyte. As-synthesized NDA-4N shows obvious dissolution in electrolyte, while there is almost no colour change of PDA-4N.

Figure 5.1 Synthesis of (A) NDA-4N and (B) PDA-4N, starting from compounds **2** and **4**.

Figure 5.2 FTIR spectra of (A) NDA-4N (red) & Compound **3** (black) and (B) NDA-4N (red) & Compound **5** (black). (C) TGA profiles of both NDA-4N (black) and PDA-4N (red). SEM morphology characterization of as-prepared (D) NDA-4N and (E) PDA-4N. (F) Solubility test of as-synthesized NDA-4N and PDA-4N. 2 mg of NDA-4N and PDA-4N was each added into 0.5 ml electrolyte and placed for 12 hrs.

To thoroughly evaluate the electrochemical properties of NDA-4N and PDA-4N, coin-type half-cell fabrication containing a lithium metal foil was applied. The galvanostatic charge-discharge profiles were shown in Figure 5.3A&B. Both NDA-4N and PDA-4N were assessed at a current density of 66 mA g^{-1} , in the potential range of 2.0 to 3.9 V (vs. Li^+/Li). NDA-4N and PDA-4N show a reversible specific capacity of 141.8 mAh g^{-1} and 116.3 mAh g^{-1} , respectively, at the first charge. The initial three reversible discharge and charge capacities of both NDA-4N and PDA-4N were achieved with an excellent average Coulombic Efficiency (CE) of approximately 100%, respectively. Considering that each unit formula of NDA-4N and PDA-4N could provide 44.5 and 31.5 mAh g^{-1} of their specific capacities, NDA-4N and PDA-4N could uptake maximum ~ 3.2 and ~ 3.7 lithium ions, per unit formula respectively. For the voltage profiles of NDA-4N, the 1st plateau is observed between around 2.18 and 2.40 V, and the 2nd plateau is located between around 2.40 and 2.80 V. These two plateaus were associated with the reduction process that lithium-ions were accepted by NDA-4N to form lithium enolate.^[36,37] Whereas for PDA-

4N, one general plateau was observed between 2.23 and 2.76 V during the reduction process.^[38-40] Both NDA-4N and PDA-4N exhibit a high average working potential approximate to 2.4 V.

Figure 5.3 Charge-discharge curves (the initial three cycles) of (A) NDA-4N and (B) PDA-4N at a current density of 66 mAh g⁻¹. CV measurements (the first three cycles) of (C) NDA-4N and (D) PDA-4N at a scan rate of 0.2 mV/s.

Cyclic voltammetry (CV) studies of NDA-4N and PDA-4N were performed between 2.0 and 3.9 V at a scan rate of 0.2 mV/s. Both NDA-4N and PDA-4N display two pairs of redox peaks as shown in Figure 5.3C&D, indicating a possible two-step mechanism for NDA-4N and PDA-4N, respectively. The results are in agreement with the electrochemical activity of NDA and PDA based cathode materials, which are usually explained by the occurrence of reversible two-electron transportation, respectively, during the reduction and oxidation. In detail, the first pair of redox peak of NDA-4N centers at 2.29 & 2.72 V and can be attributed to the insertion/deinsertion of the first two lithium-ions, and the other two lithium-ions are inserted/deinserted at 2.16 & 2.36 V.^[36]

^{37]} However, for PDA-4N, the reduction process occurs very fast as it could be noticed that the two cathodic peaks (at 2.12 and 2.18 V) are quite close (enlarged profile, inset of Figure 5.3D). The first lithiation/delithiation process of PDA-4N occurs at 2.18 & 2.61 V followed by the second lithiation/delithiation at 2.12 & 2.37 V.^[39, 40] All these reduction and oxidation peaks of NDA-4N and PDA-4N associate with the enolation processes at the carbonyl groups, are in good agreement with the plateaus as observed in their charge-discharge profiles. Moreover, the CV profiles of both NDA-4N and PDA-4N during the second and third cycles are almost overlapped, reconfirming the good reversibility of the reactions. Therefore, on the basis of the amount of lithium ions that NDA-4N (~3.2 Li⁺) and PDA-4N (~3.7 Li⁺) have accepted, along with the explanations of their electrochemical activities, a four-electron mechanism of NDA-4N and PDA-4N could probably be expected, respectively between 2.0 and 3.9 V as shown in Figure 5.4. The proposed mechanisms of NDA-4N and PDA-4N are in accordance with the previous investigations on NDA and PDA based cathode materials,^[36, 41-45] suggesting that maximum four carbonyl groups of NDA-4N and PDA-4N could be effectively utilized during the redox reactions. Therefore, referring to the proposed mechanisms, NDA-4N and PDA-4N can achieve a high utilization of 79.7% and 92.3% of their theoretical specific capacities (178.0 mAh g⁻¹ and 126.0 mAh g⁻¹, respectively), revealing that small-molecule based organic cathodes also have the ability to provide practical capacity values.

100, 166 and 333 mA g⁻¹ are 139.5, 113.6, 98.6 and 87.9 mAh g⁻¹, respectively. To the author's surprise, NDA-4N could still work at a high current density of 1000 mA g⁻¹ (approximately 15 times of the initial current density), delivering a discharge specific capacity of 70.5 mAh g⁻¹. Such an excellent rate performance of NDA-4N is better than that of almost all the reported organic small molecules, indicating the possibility of small molecules to be applied for fast charging and discharging purpose. As for PDA-4N (Figure 5.5B), it delivers a moderate rate performance with discharge specific capacities of 105.5, 86.6, 67.2 and 43.9 mAh g⁻¹ at 66, 100, 166 and 333 mA g⁻¹. PDA-4N was also examined at 1000 mA g⁻¹, however, the specific capacity rapidly declines to almost zero. The result possibly indicates a larger polarization and a poorer kinetic reaction at high current densities of PDA-4N as compared with NDA-4N. Nevertheless, when the current density was reset back to the initial value of 66 mA g⁻¹ (dashed dark blue lines in Figure 5.5A & B), both NDA-4N and PDA-4N could immediately revert back with reasonable capacity retentions, as 65.6% (91.5 mAh g⁻¹) and 66.5% (70.1 mAh g⁻¹) of their initial specific capacities could be achieved, respectively.

To further figure out the factors that could possibly result in the different rate performance between NDA-4N and PDA-4N, electrochemical impedance spectroscopy (EIS) measurement was carried out. Apparently, NDA-4N and PDA-4N show similar features that each profile consists of a semi-circle in the high frequency range and a tail in the low frequency range. As shown in the enlarged EIS profiles (inset of Figure 5.5C), PDA-4N and NDA-4N possess the same electrolyte resistance (ohmic resistance) of a small value approximate to 7 Ω. From the Nyquist plots (Figure 5.5C), it could be clearly noticed that NDA-4N electrode exhibits a much lower charge-transfer resistance (159 Ω) as compared with PDA-4N electrode (626 Ω), revealing a better kinetic reaction between NDA-4N electrode and the electrolyte. In addition, the tail (oblique line) observed at low frequencies, which represents the Warburg resistance, suggests a better lithium-ion diffusion capability within NDA-4N electrode. Therefore, the superior rate behavior of NDA-4N could be confirmed by its fast charge-transfer capability and good electric response when deployed as an active material.

Figure 5.5 Rate stability in terms of of charge-discharge curves of (A) NDA-4N and (B) PDA-4N at different current densities. (C) EIS comparison between NDA-4N (black dot line) and PDA-4N (pink dot line), the frequency ranges from 100 kHz to 10mHz. (D) Long-term cycling (solid dots for charge capacity, hollow dots for discharge capacity) and Coulombic efficiency (CE) (hollow dots) of both NDA-4N and PDA-4N at a current density of 66 mA g⁻¹.

Figure 5.5D shows the long-term cycling of NDA-4N and PDA-4N. Due to the higher theoretical capacity, NDA-4N is expected to show a higher inherent lithium-ion storage compared to PDA-4N, at the initial cycles. However, even though the initial reversible specific capacity of NDA-4N could achieve a high value of 141.8 mAh g⁻¹, it decays continuously during cycling. After 99 cycles, NDA-4N shows a specific capacity of 48.8 mAh g⁻¹, retaining only 34.4% of its initial capacity. Nevertheless, the average Coulombic efficiency of NDA-4N is still as high as 99.09%. Benefiting from organic chemistry, the organic structure of NDA-4N could be furthered tailored to present a better cycling capability. After replacing the naphthalene aromatic core structure with perylene, the larger multi-aromatic ladder-structured small molecule, PDA-4N, delivers an initial

reversible specific capacity of 116.3 mAh g^{-1} with a high value of 82.4 mAh g^{-1} after 99 cycles. The result shows an enhanced stability of PDA-4N with an improved capacity retention of 70.9%, which indicates a 36.5% increase of the capacity retention through the adoption of a larger multi-ring aromatic organic structure. Moreover, PDA-4N reaches an even higher average Coulombic efficiency of 99.71%, revealing a more excellent reversibility of PDA-4N during the cycling. Thus, the author's hypothesis to improve the cycling stability of small molecules by adopting large aromatic backbones has been well supported by these results.

5.3.2 Results and Discussion of PPTO and PEPTO

Synthetic routes to obtain redox-active PPTO and PEPTO were shown in Figure 5.6A. Benefiting from the four redox-active carbonyl groups on pyrene cores,^[46] PPTO and PEPTO are expected to reversibly lithiate and delithiate four lithium-ions during the discharge-charge process (Figure 5.6B&C). Additionally, the formation of Li_4PPTO and Li_4PEPTO during the reduction can stabilize the reduced carbonyl groups.^[46-48]

Figure 5.6 (A) Design and synthesis of redox-active PPTO and PEPTO cathodes. (B) and (C) Proposed reaction mechanisms for PPTO and PEPTO cathodes.

The molecular structures of PPTO and PEPTO were also examined by density functional theory (DFT) (B3LYP/6-31G*^{30, 31}). To simplify the calculation, PEPTO and PPTO trimers were selected and optimized as shown in Figure 5.7A&B. Subsequent frequency analysis was performed to assure that the optimized structures were in stable states. Consistent with the author's assumption, the planarity of PEPTO is greatly enhanced after the introduction of triple bonds (C≡C). As depicted from the side view of the trimers, the dihedral angle between the adjacent PTO unit is ca. 34° (Figure 5.7C), while that for PEPTO is zero (Figure 5.7D). For this reason, PEPTO with an enhanced conjugation is anticipated to deliver better electrochemical stability.

The chemical structure of precursor **2** was confirmed by ¹HNMR, ¹³CNMR and HRMS (Figure AB1-AB3). Due to their poor solubility, the structures of PPTO and PEPTO can only be confirmed by FTIR and elemental analysis (EA). As shown in Figure 5.7E, compound **2** displays apparent multiple peaks at ~2947 cm⁻¹, which can be attributed to the -CH₂ group. No typical carbonyl (C=O) peaks can be observed at ~1700 cm⁻¹, indicating the successful protection of carbonyl groups. In contrast, the -CH₂ peaks at ~2900 cm⁻¹ disappear for both as-prepared PPTO and PEPTO. Moreover, two strong peaks at 1683 cm⁻¹ and 1678 cm⁻¹ for both PPTO and PEPTO reappear, suggesting the recovery of C=O functional groups after deprotection. EA was also conducted to further confirm the elemental composition of PPTO and PEPTO. PPTO and PEPTO show good thermal stabilities as examined by thermal gravimetric analysis (TGA) (Figure 5.7F). Both compounds are thermally stable up to 400 °C and 360 °C, respectively (indicated by the 10% weight loss). As shown in Figure AB4, the morphologies of as-prepared PPTO and PEPTO were characterized by high resolution scanning electron microscopy (HRSEM). They show irregular nanostructured particles with average diameters in the ranges of 50-200 and 100-300 nm, respectively.

Figure 5.7 The optimized molecular structure of PPTO trimer, top view (A) and side view (C). The optimized molecular structure of PEPTO trimer, top view (B) and side view (D). (E) FTIR spectra of compound 2, PPTO and PEPTO. (F) TGA profiles of PPTO and PEPTO under a nitrogen atmosphere.

Electrochemical performances of PPTO and PEPTO were investigated by coin-type half-cell fabrications. As shown in the galvanostatic charge-discharge profiles (Figure 5.8A&B), PPTO and PEPTO deliver a large reversible capacity of 234 mAh g⁻¹ and 244 mAh g⁻¹ at the 1st charge, respectively. Specific capacities in the 2nd and 3rd cycles display insignificant deteriorations, indicating a good reversibility of PPTO and PEPTO. Both cathodes exhibit two pairs of sloping discharge plateaus at about 3.1-2.4 V, 2.4-1.7 V and 3.1-2.4 V, 2.5-1.9 V (vs. Li/Li⁺), generating an average operating voltage (discharge) of around 2.44 V for PPTO and 2.47 V for PEPTO (Table 5.1). Both plateaus indicate a two-stage redox behavior of each material.⁴⁶⁻⁴⁹ Figure 5.8C&D show that after 100 cycles, the reversible capacity of two materials could still be maintained at a high capacity of 161 mA h g⁻¹ for PPTO and 155 mAh g⁻¹ for PEPTO. Importantly, the Coulombic efficiency (CE) values of both polymers are as high as ~100%. To investigate the reaction mechanisms of both polymer-based electrodes, cyclic voltammetry (CV) analyses were conducted. In well accordance with the charge-discharge profiles, both PPTO and PEPTO encounter a two-step redox process between 3.5 and 1.5 V as revealed

by two pairs of distinct enolation redox peaks at the carbonyl groups (Figure 5.8E&F):⁴⁶⁻⁴⁹ 2.8/3.2 V, 2.1/2.6 V for PPTO, and 2.9/3.0 V, 2.2/2.5 V for PEPTO. The CV profiles of both compounds in the following 2nd and 3rd cycles almost overlap, confirming the good reversibility of two polymer electrodes.

Figure 5.8 Electrochemical properties of PPTO and PEPTO cathodes between 3.5 and 1.5 V. Charge-discharge profiles of (A) PPTO and (B) PEPTO at 20 mA g⁻¹ (the initial three cycles). Cycling performance of (C) PPTO and (D) PEPTO at 20 mA g⁻¹. CV measurements of (E) PPTO and (F) PEPTO (the initial three cycles) at a scan rate of 0.2

mV s⁻¹. (G) Rate and long-cycling stability of PPTO and PEPTO at various current densities.

Table 5.1. Average operating voltage calculations of PPTO and PEPTO cathodes between 3.5 and 1.5 V. The energy density values are obtained from the galvanostatic charge-discharge profiles of PPTO and PEPTO at 20 mA g⁻¹. The average operating voltages are calculated by energy density/specific capacity.

Compound	Energy Density (Wh kg ⁻¹)	Specific Capacity (the 2 nd discharge) (mAh g ⁻¹)	Average Operating Voltage (V)
PPTO	530	217	2.44
PEPTO	507	205	2.47

The rate and long-term cycling stability of PPTO and PEPTO were further studied. As shown in Figure 5.8G, PPTO delivers the reversible capacities of 230, 201, 161 and 22 mAh g⁻¹ at the current densities of 20, 50, 100 and 300 mA g⁻¹, respectively. Unfortunately, at relatively higher current densities of 500, 800 & 1500 mA g⁻¹ (the shadow pink zone), the capacities of PPTO suddenly drop to infinitesimal values, revealing an extremely poor rate stability of PPTO under harsh conditions.^{50, 51} Nevertheless, when the current density was reset back to a small value (20 mA g⁻¹), PPTO could immediately recover a high value (96%) of its initial capacity (with respect to the average capacity at 20 mA g⁻¹). Due to the low rate stability, long-term cycling of PPTO was therefore conducted at only 100 mA g⁻¹, a high capacity of 97 mAh g⁻¹, corresponding to a retention of 74% with regard to the 47th cycle (the 1st cycle when the current density was reset back), could still be obtained after 1000 cycles. As for PEPTO, the capacities of 249 and 200 mAh g⁻¹ delivered at low current densities of 20 and 50 mA g⁻¹ are very close to that of PPTO. In sharp contrast, at higher current densities from 100 mA g⁻¹ onward (the shadow pink zone), PEPTO shows a significantly-improved rate stability compared with PPTO. In detail, PEPTO delivers much higher capacities of 189, 176, 167 and 152 mAh g⁻¹ at 100, 300, 500 and 800 mA g⁻¹, respectively. Even at an extremely high current density of 1500 mA g⁻¹, PEPTO still delivers a capacity of 98

mAh g^{-1} . The capacity of PEPTO could recover 95% of its initial capacity (with respect to the average capacity at 20 mA g^{-1}). After 1000 cycles of continuous testing at a high current density of 800 mA g^{-1} , PEPTO could still achieve an excellent capacity of 110 mAh g^{-1} , corresponding to a high retention of 79% with respect to its 47th cycle. Moreover, PEPTO maintained a high CE of 99.80% at the 1000th cycle.

The superior rate stability of PEPTO (compared to PPTO) could also be observed from the specific capacity versus current density plots (Figure 5.9A). Especially, from 100 mA g^{-1} onward (the shadow pink zone), PEPTO provides significantly-higher capacities comparing to PPTO. The energy density values delivered by PEPTO can therefore be expected to show great improvement as compared to those delivered by PPTO. As shown in Figure 5.9B, PEPTO provides energy density and power density up to 507 Wh kg^{-1} and 2961 W kg^{-1} , respectively. More importantly, the energy densities show insignificant deterioration at higher current densities (the shadow pink zone). In contrast, PPTO presents a much lower power density of 1622 W kg^{-1} . Although the energy density could reach to a high value of 530 Wh kg^{-1} , the values show significant deterioration at higher current densities.

Figure 5.9 (A) Specific capacity versus current density plots of PPTO and PEPTO cathodes. (B) Energy density versus power density plots of PPTO and PEPTO cathodes. (C) Calculation of the energy levels (HOMO and LUMO) and optimized structures of

PPTO and PEPTO trimers. (D) EIS comparison between PPTO and PEPTO, the frequency ranges from 100 kHz to 10 mHz.

To gain deeper insight into the relationship between the difference of rate stability of PPTO and PEPTO, the energy levels of the HOMO and LUMO for the two compounds (their optimized trimer structures as models) were further investigated (Figure 5.9C). The LUMOs of PPTO (-3.94 eV) and PEPTO (-3.95 eV) trimers are very close, confirming the similar discharge behaviors of PPTO and PEPTO.^[46] Owing to the more effective conjugation of the planar PEPTO, the calculated bandgap (ΔE) for PEPTO trimer (2.65 eV) is much smaller than that of PPTO trimer (3.03 eV). A smaller ΔE can facilitate the electron and Li^+ transfer in organic batteries and therefore enhance the rate stability of PEPTO cathode.^{52, 53} Experimental electrochemical impedance spectroscopy (EIS) was also conducted. As shown in Figure 5.9D, the Nyquist plots of PPTO and PEPTO are presented by the well-defined semicircles and straight lines. The charge transfer resistance (R_{ct}) of PEPTO is 210 Ω , which is much lower than that of PPTO (391 Ω). Evidently, a smaller R_{ct} resistance indicates a faster charge transfer capability.^[54] This demonstration further confirmed that PEPTO is better than PPTO in terms of electronic conductivity and lithiation kinetics. All results suggested that the introduction of $\text{C}\equiv\text{C}$ bonds has effectively promoted the rate stability of PTO-based polyquinones. Thus, the author's hypothesis to improve the performance of organic cathodes from the perspective of structural designing and tailoring has been well supported by this approach.

5.4 Conclusions

In conclusion, two innovative strategies to obtain better organic cathodes have been proposed by designing four novel redox-active carbonyl organic cathodes. The results successfully reveal the feasibility of large aromatic dianhydride and quinone based organic compounds to be used as promising positive materials. A comparison table including the works involved in this chapter and the previously reported literature works is provided in APPENDIX C. Our novel structural tailoring strategies provide alternative solutions to develop organic cathodes toward next-generation of high stability and energy

density batteries. Other than Li-organic batteries, carbonyl compounds are believed to be universal materials for future multivalent-ion batteries. Because they could allow fast multivalent-ion insertion and de-insertion through unique ion-coordination charge storage mechanism, which is totally different as compared with inorganic materials. Therefore, carbonyl compounds are believed to be future candidates to resolve the kinetic issues that frequently encountered by multivalent-ion batteries using inorganic cathode materials.

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Chapter 6*

Toward a High-Performance All-Plastic Full Battery with a Single Organic Polymer as Both Positive and Negative Electrode

The design and fabrication of high-performance all-plastic batteries is essentially important to achieve future flexible electronics. A major challenge in this field is the lack of stable and reliable soft organic electrodes with satisfactory performance. In this chapter, a novel all-plastic-electrode based Li-ion battery with a single flexible bi-functional ladderized heterocyclic poly(quinone) poly(2,3-dithiino-1,4-benzoquinone) (PDB) was demonstrated. The superior performance of PDB-based electrode rivals most of the demonstrations on organic-based Li-ion shuttling batteries. This study provides an effective strategy to develop stable bi-functional electrode materials toward the next-generation of high performance all-plastic batteries.

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6.1 Introduction

To pursue next generation of lightweight, flexible and wearable electronic devices, organic soft batteries have been receiving numerous attentions.^[1-9] Designing and fabricating all-plastic rechargeable batteries is very promising.^[10] The concept of all-plastic batteries, where both the positive and negative electrodes are made from electroactive polymers, was proposed about 30 years ago.^[11, 12] However, such preliminary demonstrations showed very poor rechargeable capability and low Coulombic efficiency. Only recently, efforts start to be devoted to searching stable anion or cation host polymer reservoirs for plastic-electrode based batteries. For example, polymers including hydrocarbons,^[13] redox p-type molecules,^[14, 15] nitroxide radicals^[16, 17] and imides^[18, 19] have been widely investigated and fabricated into all-organic-electrode batteries. Unfortunately, most of them delivered limited specific capacity, low operating voltage, and thus poor energy density. In addition, these batteries were often constructed with two different organic materials with asymmetric properties, making them very difficult to be employed as potential flexible batteries. Therefore, designing and fabricating innovative all-plastic-electrode batteries with better electrochemical performance and flexibility is necessary. Moreover, the solubility, stability, and redox ability of suitable electrode materials should be carefully optimized when considering the storage capacity, cycle life, and operating voltage of plastic batteries.^[20]

Among various polymer materials, poly(quinones) and their derivatives are outstanding candidates as redox-active electrodes for organic batteries due to their fast-redox ability, high storage capacity and structural diversity.^[21-25] Nevertheless, poly(quinones) as bi-functional electrodes for all-plastic-electrode batteries are rarely explored. Attractive attempts of poly(quinones) on metal-ion (e.g. Li^+ , Na^+ , K^+ & Mg^{2+})^[26-28] and proton (H^+)^[29] batteries have been performed, indicating their good compatibility with different types of shuttling-ions. More importantly, poly(quinones) have been demonstrated to show bi-functional properties as they can be reversibly reduced and oxidized at either high or low potentials (vs. Li^+).^[30, 31] To further improve the redox potential and electronic conductivity of quinones, the introduction of sulfur atoms presents an effective

strategy.^[32] It was found that polymers with the thioether bonds (C–S–C) do not undergo bond cleavage during the redox reactions. Moreover, the thioether groups formed in redox polymers could provide strong intermolecular reactions, particularly at the charged states, enabling excellent cycling and rate stability of the electrodes.^[33-34] Since the superiorities of quinones and thioether-containing polymers ideally complement each other, the weakness of both compounds, for example, relatively short cycle life for quinones and low storage capacity for thioether-containing polymers,^[21, 33, 35] can be addressed by a rational design that integrates the advantages of both two characteristics into one. Despite the early few investigations on doped polyacetylene and bi-polar polyparaphenylene, little study on bi-functional all-plastic symmetric batteries has been achieved.^[11-13]

In this chapter, a novel dithioether-containing polyquinone, poly(2,3-dithiino-1,4-benzoquinone) (PDB) was designed and synthesized. It has been the first time that such a unique ladder-structured polymer was developed and used as the anode, cathode and bifunctional electrode with high-performance. Prior to fabricating all-PDB based symmetric full-batteries, free-standing electrodes by mixing of as-prepared PDB and carbon nanotubes (CNTs) were prepared and exhibited good flexibility. As a proof-of-concept, the heterocyclic poly(quinone) was first used as a bi-functional electrode, enabling the construction of an all-plastic-electrode based symmetric full-battery. This study presents a rational design to develop flexible, stable and high-storage bi-functional electrodes toward future high performance all-plastic batteries.

6.2 Synthesis, Characterization and Measurement

6.2.1 Synthesis of PDB

2,3,5,6-tetrafluorocyclohexa-2,5-diene-1,4-dione (0.9 g, 0.005 mol) and Na₂S·9H₂O (4.8 g, 0.02 mol) were dissolved into a mixture solvent of ethanol (40 mL) and water (50 mL). This solution was stirred at 80 °C for 3 hrs, then a DMF (30 mL) solution of 2,3,5,6-tetrafluorocyclohexa-2,5-diene-1,4-dione (0.9 g, 0.005 mol) was added. After refluxing

for 10 hrs, the mixture was allowed to cool down to room temperature, and the pH value was adjusted to 3~4 by 5% hydrochloric acid. Then the precipitate was collected by filtration and washed by DMF, water and ethanol. After washing the precipitate by ethanol with soxhlet extractor, pure PDB was obtained as black powder (0.5 g, 30%).

6.2.2 PDB Anode, Cathode and Bi-functional Electrodes fabrication

PDB electrodes fabrication: The as-prepared PDB samples were mixed with carbon additives (multi-wall CNTs) and polymer binders (polyvinylidene fluoride (PVDF)) with a weight ratio of 3:5:2 in NMP solvent. The mixture powders were ground with a pestle for 20 mins and then transferred into a small glass bottle. Stir and sonication were performed for 30 mins to well disperse the mixtures. Homogeneous PDB electrode slurries were obtained and further ground with a pestle for another 20 mins at room temperature. The slurries were uniformly pasted onto the battery grade aluminum foils through a slow roll-press. The as-prepared smooth cathode films were dried at 60 °C overnight in a vacuum atmosphere. Flexible and free-standing cathodes were easily obtained by peeling-off the films from the aluminum foil substrates. Flexible and free-standing circular disk PDB cathodes with diameters of 12 mm were punched to be used. The cathode loading is between 1.1-2.1 mg (corresponding to an active PDB cathode of around 0.33-0.63 mg). The PDB anodes were fabricated by mixing of 80 wt% active material (PDB), 10 wt% carbon nanotubes (CNTs) and 10 wt% polyvinylidene fluoride (PVDF) in n-methyl-2-pyrrolidone (NMP) solvent, and then pasted onto the copper foil current collector. For anode pre-lithiation process, PDB anodes were obtained by mixing of as-prepared PDB, CNTs and PVDFs with a weight ratio of 7:2:1 in NMP. The same preparation procedures were applied on all PDB anodes. The anode loading is between 0.4-1.3 mg (corresponding to an active PDB anode of around 0.28-0.91 mg). SEM on electrode thickness of the electrode films gives a thickness of between 9 to 11 μm for cathode PDB and denser between 8 to 11 μm for anode PDB.

Half-Battery Fabrication: To investigate the electrochemical performance of PDB as a cathode-active material, lithium foils were used as the counter electrodes and aluminum

foils were used as the current collectors for PDB cathodes. The optimized ether-based electrolyte system consists of 1 mol/L (M) LiTFSI in DOL/DME solvent (1/1, v/v). As a reference experiment, 1 M LiPF₆ in EC/DMC solvent (1/1, v/v) were used as the traditional carbonate-based electrolyte system. To investigate the electrochemical performance of PDB as an anode-active material, the electrolyte used was 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, v/v). For all battery fabrications, Celgard 2400 membranes were applied as the separators and CR2032 coin-type electrochemical cell construction was applied. The cells were prepared in a glovebox filled with pure inert gas (argon gas) wherein the oxygen and moisture levels were both maintained below 1 ppm. The cells were finally assembled and placed for an equilibration time of 12 hrs (to thoroughly rinse the electrodes) to be tested. For anode pre-lithiation process, half-cells containing PDB anodes, lithium foils, copper foils and ether-based electrolyte (1 M LiTFSI in DOL/DME) were fabricated. After 12 hrs of equilibration, deep discharging of PDB anodes to 0.005 V at 100 mA g⁻¹ was conducted at the first discharge. The half-cells were then dis-assembled in the argon-filled glovebox. Finally, pre-lithiated PDB anodes were taken out from the cells to be used for all-plastic-electrode full-battery fabrication.

All-Plastic-Electrode Full-Battery Fabrication: All-PDB full-cells were constructed by pre-lithiated PDB (as the active anode) and pristine PDB electrode (as the active cathode). The full-cells consisting of PDB anode (with copper foils), Celgard 2400 separator, PDB cathode (with aluminum foils), and ether-based electrolyte (1 M LiTFSI in DOL/DME) were constructed in the argon-filled glove box. The full-cells were placed for an equilibration time of 8-10 hrs to be tested. As a cathode-limited design, the reversible charge and discharge capacity of the cell was calculated based on the weight of the cathode-active PDB. The optimized loading mass for anode-active PDB is in the range of 0.48-0.63 mg and cathode-active PDB is in the range of 0.27-0.33 mg, keeping a mass ratio of around 1.8-1.9.

6.2.3 Characterization and Measurement of PDB

Materials characterization: EA was conducted on a PerkinElmer 2400Series II CHNS/O elemental analyzer. FTIR spectra were recorded on a PerkinElmer Spectrum Frontier FTIR spectrometer. TGA profile was obtained from a TA Instruments TGA Q500 at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. EDS elemental mapping was collected by a Field Emission SEM (FESEM) JEOL/JSM-7600F at an accelerating voltage of 15 kV. SEM images were obtained by a JEOL/JSM-6340F at 5 kV.

Electrochemical Cell Fabrication and Measurements: The cells were tested on a NEWARE multichannel battery test system (at room temperature) with the galvanostatic charge and discharge in the ranges of 3.4-1.5, 3.6-1.5, 3.9-2.0 and 4.4-1.5 V for cathode investigations, 3.0-0.005 V for anode, anode pre-lithiation and CNT additives investigations, 2.9-0.005 and 3.2-0.005 V for all-PDB based full-cell demonstrations. C-rate here was calculated based on fully charging PDB at a current density of 248 mA g^{-1} (the maximum specific capacity at the 1st cycle), thus the current density applied (e.g. at 20 mA g^{-1}) was approximately corresponding to a C-rate of 0.08 C. All the cells for galvanostatic charge and discharge processes were pre-activated for one cycle. The cell for all-plastic-electrode battery tested at 500 mA g^{-1} was pre-activated for 15 cycles. CV was performed on an electrochemical analyzer (CH Instrument CHI604e) at a scan rate of 0.1 mV s^{-1} . EIS analysis was conducted by the same instrument between 100 kHz and 10 mHz. For ex-situ FTIR analysis, half-cells were cycled and terminated at certain charge and discharge states. The electrodes were disassembled and rinsed by DOL/DME solvent in argon-filled glove box. The dried electrodes were then collected for measurement.

6.3 Results and Discussion

Derived from the characteristics of both quinone- and thioether-containing redox polymeric structures, the stable ladderized heterocyclic poly(quinone) PDB, $(\text{C}_6\text{O}_2\text{S}_2)_n$ was synthesized. The polymer sample was synthesized through a simple two-step

polymerization between 2,3,5,6-tetrafluorocyclohexa-2,5-diene-1,4-dione and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ at 80°C ^[36] (Figure 6.1).

Figure 6.1 Synthesis of ladder-structured quinone and dithioether-containing PDB.

The morphology of PDB was characterized by scanning electron microscopy (SEM). Figure 6.2A shows that the as-prepared PDB samples are typically large micro-sized blocks ($\sim 5\text{--}10\ \mu\text{m}$) with irregular shapes. By further dispersing them into N-methyl-2-pyrrolidone (NMP) solvent via stirring and sonication, PDB microparticles with average diameters of 500 nm to 1 μm could be obtained (Figure 6.2B&C).

Figure 6.2 SEM images of (A) as-prepared PDB large blocks and (B & C) PDB microparticles obtained after dispersing as-prepared PDB in NMP via stirring and sonication.

The chemical structure of PDB (Figure 6.3A) was confirmed by a variety of characterizations. Figure 6.3B shows the Fourier transform infrared spectroscopy (FTIR) spectrum of as-prepared PDB. The strong peak at $1632\ \text{cm}^{-1}$ corresponds to the stretching vibration of the $\text{C}=\text{O}$ groups.^[37] The peaks at 1423, 1380, 1149 and 1088 are attributed to the C-S bonds, revealing the successful formation of the thioether bond (C-S-C) during the reaction.^[32, 37, 38] Figure 6.3C shows the thermogravimetric analysis (TGA) of as-prepared PDB. As depicted by the onset of decomposition temperature, PDB is thermally stable up to 290°C (under nitrogen atmosphere) and still keeps 55% of its weight at a high temperature of 700°C .

Figure 6.3 (A) Design strategy and chemical structure of the ladder-structured heterocyclic PDB. (B) FTIR spectrum and (C) TGA profile of the as-prepared PDB.

To further confirm the chemical structure of PDB, elemental analysis (EA) was employed. The measured carbon/sulfur (C/S) molar ratio of PDB is close to its theoretical ratio, indicating a good purity of the as-prepared PDB polymer (Table 6.1). The detailed chemical structure and polymerization degree of PDB is also proposed. The EA result gives an information that the as-prepared PDB is mainly composed of oligomers with an average polymerization degree of $n=8$, and the ending groups are dominantly --SNa (Table 6.2). Moreover, as shown in Figure 6.4, the C, S and O elements in PDB skeleton are homogenously distributed as detected by energy dispersive X-ray spectrometry (EDS) elemental mapping, and negligible amounts of F and Na elements could be observed from PDB, further confirming the successful polymerization of PDB between the monomer reactants. Therefore, all these results clearly suggest the successful synthesis of PDB and confirm its desired ladderized structure $(\text{C}_6\text{O}_2\text{S}_2)_n$.

Table 6.1 Elemental Analysis (EA) of as-prepared PDB $(\text{C}_6\text{O}_2\text{S}_2)_n$.

Element	Carbon (C)%	Sulfur (S)%	C/S Ratio
Calculated	42.85	38.13	1.12
Measured	39.33	37.85	1.04

The slightly lower carbon content suggests that the terminal groups of as-prepare PDB are dominantly -SNa groups (refer to Figure 6.1). According to above measured EA result, the proposed exact structure of as-prepared PDB can be predicted as shown in below Table 6.2.

Table 6.2 Proposed structures, degree of polymerization and calculated elemental analysis of as-prepared PDB.

Structure	General Formula	Polymerization Degree (<i>n</i>)	C%	S%
Ending groups are dominantly -SNa	$C_{6n}O_{2n}S_{2n+2}Na_4$	8	38.39	38.44
Ending groups are -SNa and -F	$C_{6n}O_{2n}S_{2n+1}Na_3F$	8	39.34	37.19
Average			38.87	37.82

Figure 6.4 (A) FESEM image of as-prepared PDB. EDS elemental mapping of as-prepared PDB: (B) Carbon (C); (C) Sulfur (S); (D) Oxygen (O); (E) Fluorine (F) and (F) Sodium (Na) elements. (To minimize the noise signal that would disturb the elemental mapping result, the duration for elemental mapping analysis is therefore shortened).

It is noted that CNTs have been widely used as both the conductive additives and supporting frameworks for flexible electrode materials because of the excellent electronic conductivity, large surface area, and good flexibility.^[3, 39-41] Before fabricating all-PDB based full-batteries, free-standing electrodes consist of as-prepared PDB and CNTs were prepared by a simple solution process, which involves dispersing PDB and CNTs into NMP, followed by drying and peeling-off the film from the substrate (Figure 6.5A) (see the synthesis section for detailed experimental process). Figure 6.5B shows the SEM image and photograph (inset image) of the as-prepared free-standing PDB electrode. A good microporous distribution of PDB microparticles surrounded by CNT networks could be achieved. Such a free-standing electrode exhibits good flexibility as it can be reversibly bended (Figure 6.5C), revealing an exciting potential to develop future all-organic based thin-film or paper-like energy-storages devices with bendable or wearable properties.

Figure 6.5 (A) Schematic procedures for preparing a free-standing PDB electrode film. (B) SEM image and photograph (inset, scale bar: 6 mm) of a free-standing PDB electrode. (C) Photographs exhibiting the reversible bendable property of the free-standing PDB electrode.

Electrochemical properties of PDB including redox ability, rate capability and cycling stability were characterized through the fabrication of electrochemical half-cells. PDB was first investigated as an active cathode material between 3.4 and 1.5 V (vs. Li/Li⁺). On the basis of the two redox-active carbonyl groups, PDB possesses a high theoretical specific capacity of 319 mAh g⁻¹. However, limited capacity with a poor cycle life of PDB was obtained in traditional carbonate-based electrolyte (Figure 6.6A). Although the capacity could be improved by increasing the upper cut-off potential to 4.4 V (Figure

6.6B), significant cycling deterioration could still be observed (Figure 6.6C). Moreover, electrochemical impedance spectroscopy (EIS) analysis was investigated (Figure 6.6D). The cell containing carbonate-based electrolyte shows a significant higher intrinsic resistance ($149\ \Omega$) as compared with the cell containing ether-based electrolyte ($28\ \Omega$) (a 5.3 times higher resistance). Inset image shows the enlarged EIS plot of the cell with ether-based electrolyte. The resistance values were extracted from the semi-circles in the high-frequency range. Obviously, a smaller resistance indicates a faster electron transfer rate. The result suggests the better compatibility of ether-based electrolyte compared with traditional carbonate-based electrolyte with respect to PDB electrode.

Figure 6.6 (A) Cycling stability and corresponding CE of PDB electrode in traditional carbonate-based electrolyte (LiPF_6 in EC/DMC), between 3.4 and 1.5 V at $20\ \text{mA g}^{-1}$. (B) Typical charge-discharge profiles of PDB electrode in carbonate-based electrolyte at $20\ \text{mA g}^{-1}$ in the ranges of 3.6-1.5 V and 4.4-1.5 V. (C) Electrochemical performance of PDB electrode in carbonate-based electrolyte, tested between 4.4 and 1.5 V at $20\ \text{mA g}^{-1}$. (D) EIS analysis of fresh cells added with ether-based electrolyte (LITFSI in DOL/DME) (red dots) and carbonate-based electrolyte (LiPF_6 in EC/DMC) (black dots).

The solubility tests further reveal that PDB is more stable in ether-based solvent (Figure 6.7). Solubility tests of PDB before and after cycling were conducted. As can be seen from Figure 6.7A, almost no dissolution can be observed from both tests, indicating the

poor intrinsic solubility of PDB. Separators were taken out from the disassembled cells (after cycling) with traditional carbonate-based (LiPF_6 in EC/DMC) and ether-based (LITFSI in DOL/DME) electrolyte (Figure 6.7B). The separator with carbonate-based electrolyte shows obvious color change (from transparent to brown) after cycling. In contrast, almost no color change can be observed from the separator with ether-based electrolyte, indicating the insignificant deterioration of PDB electrode in ether-based electrolyte. These results are in accordance with the reported investigations on different electrolytes.^[42, 43] Hence, ether-based electrolyte is selected as the optimized electrolyte for the subsequent studies.

Figure 6.7 Solubility tests of PDB before and after cycling. (A) Photographs of as-prepared PDB in EC/DMC and DOL/DME solvents. (B) Separators taken out from the disassembled cells (after cycling) with traditional carbonate-based and ether-based electrolyte.

Based on the two-electron redox reaction, PDB possess a high theoretical capacity of 319 mAh g^{-1} (Figure 6.8A). During the initial galvanostatic charge-discharge process (Figure 6.8B), PDB gives an operating potential of around 2.7 V, with a notably improved charge capacity of 248 mAh g^{-1} , corresponding to a utilization of 78% of its theoretical capacity (319 mAh g^{-1}). Although the capacity utilization could be improved to around 100% by tuning the potential window to 3.9-2.0 V, the cycling stability is extremely poor (Figure 6.8C). As a result, 3.4-1.5 V is selected as the optimum voltage window for PDB cathode. Between 3.4 and 1.5 V, the initial high capacity could be maintained, and more importantly, a reversible high storage of $>200 \text{ mAh g}^{-1}$ was still achieved after 100 cycles with an excellent Coulombic efficiency (CE) close to 100% (Figure 6.8D). To assess the rate stability of PDB, different current densities were applied. The capacities of PDB at the current densities of 20, 40, 100, 300, 800 and 1000 mA g^{-1} are as high as 255, 249,

234, 223, 204 and 190 mAh g^{-1} , respectively, with no significant deterioration (Figure 6.8E). Remarkably, PDB delivers a large capacity of 161 mAh g^{-1} at an ultra-high current density of 1500 mA g^{-1} . Moreover, after cycling, the capacity of PDB (242 mAh g^{-1}) could immediately revert back to 95% of its initial capacity (255 mAh g^{-1}) at 20 mA g^{-1} , indicating an excellent rate performance of PDB. Rate discharge and charge profiles of PDB are presented (Figure 6.8F), the profiles are well-maintained at different current densities.

Figure 6.8 Electrochemical performance of redox-active PDB deployed as an active cathode material. (A) Reaction mechanism and theoretical specific capacity of PDB. (B) Representative charge and discharge profiles of PDB between 3.4 and 1.5 V at a current density of 20 mA g^{-1} . Cycling performance of PDB and corresponding Coulombic efficiency (CE) of PDB between (C) 3.9 & 2.0 V and (D) 3.4 & 1.5 V at 20 mA g^{-1} . (E) Rate stability at different current densities between 3.4 and 1.5 V. (F) Corresponding charge and discharge profiles between 3.4 and 1.5 V.

The energy and power density of PDB (versus lithium anode) can reach extraordinary high values of 624 Wh kg^{-1} and 3346 W kg^{-1} , respectively (Figure 6.9A). Due to such an excellent battery performance, cyclic voltammetry (CV) profiles were performed to investigate the electrochemical reactions occurred on PDB (Figure 6.9B). Between 3.4 and 1.5 V, three pairs of redox peaks can be obtained. In detail, the first two pairs of redox peaks at 2.30/2.43 and 2.90/2.92 V are well known as the lithium enolization

process,^[26] indicating that the two active carbonyl groups of PDB can be successfully involved into the reversible redox reactions.

Figure 6.9 (A) Energy density versus power density plot for PDB cathode (relative to lithium anode). Inset table shows the detailed values. (B) Cyclic voltammetry measurement of PDB (the initial 3 cycles) at a scan rate of 0.1 mV S⁻¹. Ex-situ FTIR analysis of PDB electrode between 3.4 and 1.5 V. (C) Galvanostatic charge and discharge profiles with marked points at different discharge and recharge points. Corresponding FTIR spectra of (D) C=O and (E) =C-O groups obtained from the disassembled cells.

This enolization process was also confirmed by ex-situ FTIR analysis of PDB electrode at different discharge and recharge states (Figure 6.9C). As shown in Figure 6.9D, the intensity of the absorption peak (highlighted in pink) from the C=O stretching at around 1632 cm⁻¹ decreases during the discharging process (3.4 to 1.5 V, from point a to c), indicating the disappearance of the C=O groups upon lithiation or reduction. On recharging to 2.5 V (point d), the revival of the C=O signal indicates the formation of C=O groups during the delithiation or oxidation. Additionally, the peak at around 1059 cm⁻¹ (highlighted in deep yellow) is attributed to the =C-O stretching (Figure 6.9E).^[44] Initially (at point a), the =C-O signal can hardly be observed. On discharging from 3.4 to 1.5 V (from point a to c), the intensity of the =C-O peak increases, revealing the formation of =C-O groups during the lithiation. However, on recharging to 2.5 V (point d), the intensity of =C-O groups decreases indicates the reoxidation of =C-O groups to form

C=O groups. These results confirm the reversibility and reactivity of the redox C=O groups in PDB during lithiation and delithiation.

Note from the CV profiles that another pair of weak redox peaks at a relatively higher potential of 3.14/3.23 V was observed. This pair of peak is attributed to the oxidation of sulfur atoms to form thioether cations during the electrochemical process.^[33, 34, 45] Therefore, after oxidizing, the electrolyte anions would delocalize along the PDB polymer backbone and the thioether units might interact each other in an intermolecular way, resulting in a stabilized interaction between PDB units.^[33, 34] This observation is in agreement with the author's hypothesis that the incorporation of such a dithioether ring structure could benefit the cycling stability of organic electrode materials.

To further confirm the stability of PDB, ultra-long term cycling performance of PDB was explored in details. To the author's surprise, under the high current densities of 1000 (Figure 6.10A) and 1500 mA g⁻¹ (Figure 6.10B), PDB can sustain for 500 and 1000 cycles respectively, retaining 85.9% and 80.5% of its capacity (with regard to the initial cycle, respectively). Such a long cycle life (1000 cycles, >80% capacity retention) of PDB is amongst one of the best performed quinone materials.^[21]

Figure 6.10 Long-term cycling and corresponding CE of PDB at the current densities of (A) 1000 mA g⁻¹ for 500 cycles and (B) 1500 mA g⁻¹ for 1000 cycles, with high capacity retentions.

Apart from the cathode performance, PDB was also investigated as an anode-active material. The galvanostatic charge-discharge process was performed between the potential of 0.01 and 3.0 V at a current density of 100 mAh g^{-1} . The charge-discharge profiles of the 1st, 2nd, 3rd, 10th and 100th cycles are displayed in Figure 6.11A. It can be observed that PDB delivered an initial discharge capacity of 1614 mAh g^{-1} and a high reversible capacity of 1050 mAh g^{-1} in the subsequent charge process, corresponding to a Coulombic efficiency of 65.1%. The loss of 564 mAh g^{-1} is attributed to the irreversible capacities from the formation of the SEI film, which is widely known as a very common phenomenon for the anode materials during the initial discharge process. As shown in Figure 6.11B, the rate capability of the sample was further examined at different current densities including 0.1, 0.2, 0.5, 1.0 and 4.2 A g^{-1} . Each current density corresponds to five cycles of charge and discharge processes. The results indicated that PDB could deliver reversible capacities of 887, 692, 500, 357 and 107 mAh g^{-1} , respectively, at different current densities mentioned above. It is worthy to note that, a high reversible capacity of 748 mAh g^{-1} could still be achieved when the current density returned back to 0.1 A g^{-1} . This reversible capacity of 748 mAh g^{-1} was quite consistent with the reversible capacity of 793 mAh g^{-1} at the same cycle during the charge and discharge process at 100 mA g^{-1} , indicating a good repeatability and an excellent structure stability of the PDB electrode material.

To investigate the cycling stability of PDB, specific capacity vs. cycle number was plotted as shown in Figure 6.11C. It can be seen that, even after 100 cycles, PDB could still display a high specific capacity of 681 mAh g^{-1} , retaining 71% of its specific capacity as compared with its 5th cycle. This good specific capacity belongs to one of the best performances of pure organic electrode materials that have been reported so far. Moreover, apart from the first cycle, the average Coulombic efficiency of each cycle (excluding the 1st cycle) is as high as 99.1%, further confirming the good stability of PDB. Figure 6.11D shows the ultra-long cycling capability of the sample. The reversible specific capacity of PDB was maintained at 161 mAh g^{-1} after 1000 cycles at a high current density of 2 A g^{-1} . Although the result suggests a moderate specific capacity of

PDB at high current density, the performance is still better than those of majority of the reported lithium salt anode materials for LIBs.

Figure 6.11 (A) Galvanostatic charge-discharge profiles of PDB at a current density of 100 mA g⁻¹. (B) Rate performance of PDB at different current densities. (C) Cycling performance and Coulombic efficiency of PDB at a current density of 100 mA g⁻¹. (D) Ultra-long cycling performance of PDB at a high current density of 2 A g⁻¹. The inset image shows the charge-discharge curves accordingly.

Due to the good electrochemical performance of PDB, the author is encouraged to fabricate an all-PDB full-battery. Nevertheless, before fabricating such a full-battery, the maximum capacity of PDB needs to be explored. Thus, pre-lithiation was carried out by fully reducing PDB to a low potential of 0.005 V (Figure 6.12A). The pre-lithiation capacity (~1600 mAh g⁻¹) is very close to the initial discharge capacity obtained from the investigation of PDB as an anode material (Figure 6.11A).^[36] Cycling stability of this prelithiated PDB electrode using the ether-based electrolyte (LITFSI in DOL/DME) was also presented to show the high reversible capability of this material (Figure 6.12B). To be noted that, the small amount of capacity contribution (~45 mAh g⁻¹) (Figure 6.12C) originated from the CNT additive (between 3.0 and 0.005 V) is deducted from the anode performance of PDB electrode.

Figure 6.12 (A) Pre-lithiation discharge curve of PDB electrode by deep discharging it to a low potential of 0.005 V at a current density of 100 mA g⁻¹. Exploration of PDB as an anode-active material. (B) Cycling performance of PDB anode between 3.0 and 0.005 V (excluding the 1st pre-lithiation process) at a current density of 100 mA g⁻¹, after deducting (C) the capacity contribution from the CNT additives (between 3.0 and 0.005 V) is around 45 mAh g⁻¹.

From the reversible charge capacity calculation, each lithium-ion transfer process of PDB anode corresponds to a specific capacity of 159.5 mAh g⁻¹. Since PDB anode delivers a reversible capacity of 1075 mAh g⁻¹ at the initial cycle (the 1st charge capacity, refer to Figure 6.12B), such a high capacity value equals to the lithiation of a high amount of ~6.8 lithium-ions. Therefore, besides the lithiation of 2 lithium-ions at the two active carbonyl groups, another maximum of 4.8 lithium-ions might be inserted onto the unsaturated carbon atoms when deep discharging PDB to 0.005 V.^[30, 46-50] Thus, a superlithiation process could be inferred to take place on the unsaturated carbon atoms of PDB during the deep discharging.^[30, 46-50] Therefore, PDB has the ability to show bi-functional properties that it can either undergo a two-electron reaction (on the carbonyl groups) at a relatively high potential or a six electron reaction (on the unsaturated carbons) at a relatively low potential. However, restricted by the two-electron capability

at the cathode side, an overall reversible two-electron reaction can be predicted when a PDB full-cell is developed. As proposed in Figure 6.13A, upon discharging, pristine PDB accepts two Li-ions at the cathode, while simultaneously pre-lithiated PDB releases two Li-ions at the anode. To confirm this proposed mechanism, an all-PDB polymer based full-battery was developed as illustrated in Figure 6.13B. Note that current demonstrations on full-batteries require a balance between the utilization of the active anode and cathode materials, especially in a coin cell configuration.^[51] Optimization of the active material loading and thickness is thus a necessary process to obtain a full-battery with satisfactory performance. For the case of the all-PDB symmetric full-battery, smooth surfaces of the anode (before pre-lithiation) and cathode were obtained, and their thicknesses were kept almost the same ($\sim 10\ \mu\text{m}$) (Figure 6.13C).

Figure 6.13 All-plastic-electrode symmetric full-battery demonstration. (A) Proposed redox mechanism of PDB used as active bi-functional electrodes (pristine PDB as the cathode and pre-lithiated PDB as the anode). (B) Configuration of the fabricated all-PDB based full-battery. (C) Cross-sectional SEM images of the PDB cathode and PDB anode (scale bar: $5\ \mu\text{m}$).

Figure 6.14A shows the prototype of the all-plastic-electrode full-battery using pristine PDB as the cathode and pre-lithiated PDB as the anode. Typical charge and discharge profiles of the full-battery are shown in Figure 6.14B. The reversible charge capacity of such a novel all-plastic battery reaches a high value of $249\ \text{mAh g}^{-1}$ (equivalent to 1.6 electrons) between 2.9 and 0.005 V, confirming that it underwent a two-electron transfer process as proposed. The battery exhibits an average charge output potential of $\sim 2.0\ \text{V}$. To be highlighted that, the energy and power density of this symmetric battery can reach values as high as $276\ \text{Wh kg}^{-1}$ and $948\ \text{W kg}^{-1}$ (considering only the active electrode

materials), respectively (Figure 6.14C). To evaluate its cycling and rate stability, different current densities were applied. As shown in Figure 6.14D, the all-plastic battery delivers the capacities of 249, 219, 193, 135, 55 mAh g⁻¹ at the current densities of 20, 40, 100, 300, 1000 mA g⁻¹, respectively. After 125 cycles of charging and discharging, the capacity is still as high as 195 mAh g⁻¹, retaining 78.3% of its initial capacity. To fully explore the storage capacity and cycling stability of this all-PDB full-battery, the upper cut-off potential was increased to a higher value of 3.2 V. Under an even harsh condition of a consistent high current density of 500 mA g⁻¹ for 250 cycles, the battery still survive a high reversible capacity of 119 mAh g⁻¹ with an approximately 100% CE (Figure 6.14E). These results show significant improvements with respect to the previous investigations on all-plastic symmetric batteries,^[11-13] even better than state-of-the-art inorganic metal-containing symmetric batteries in terms of storage capacity, energy density and cycling stability.^[52-54]

Figure 6.14 Prototype and electrochemical performance of the all-plastic-electrode symmetric full-battery. (A) Prototype of the all-PDB-electrode battery. (B) Representative charge and discharge profiles between 2.9 and 0.005 V at 20 mA g⁻¹. (C) Energy density versus power density plot for the all-PDB battery (inset table shows the detailed values). The values are obtained based on the weight of the cathode-active PDB loading. Energy density values are calculated by the integration area under the charge-discharge profile. Correspondingly, power density values are calculated by energy density/discharge time (in hour). (D) Cycling and rate stability at different current

densities. (E) Long-term cycling and corresponding CE for 250 cycles at 500 mA g⁻¹ between 3.2 and 0.005 V.

6.4 Conclusion

In this chapter, a ladder-structured heterocyclic poly(quinone), (C₆O₂S₂)_n, has been developed for the first time as a electrochemical stable anode, cathode and bi-functional electrode. Such a superior electrode material PDB shows an insoluble behavior, therefore delivering outstanding energy density and ultra-long cycling stability as both the anode and cathode materials. Furthermore, an innovative all-plastic-electrode symmetric full-battery was fabricated with excellent electrochemical performance. A comparison table including the all-plastic-electrode battery mentioned in this chapter and the previously reported all-plastic-electrode batteries is provided in APPENDIX D. This study provides an effective strategy to develop flexible and stable organic electrodes toward next-generation of high performance all-plastic batteries. With further incorporation of novel quasi-solid or solid polymer electrolytes as well as plastic battery components into the author's battery system, it is believed that flexible, light and safe all-solid state plastic batteries with high-performance can be produced for future applications in electronic devices. Since all-solid-state plastic batteries do not contain any active metal materials like lithium and sodium, they could potentially suppress metal dendrites and enable direct stacking of individual cells. Moreover, considering their non-flammable properties, the development of next-generation of safer and greener batteries could be achieved.

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Chapter 7

Discussion and Future Work

In this chapter, a general summary of the whole project is presented by discussing the hypothesis and results achieved in this thesis. Overall, this thesis has been focused on the design, synthesis and characterization of several novel redox-active organic compounds, which have been applied as active positive, negative and bi-functional electrode materials for rechargeable lithium batteries. The recommended future works, including objectives, current situation and effective strategies to obtain advanced flexible battery systems (on the basis of multivalent Mg and Al-ions) are also discussed. Since the major challenge in this field is the lack of stable and reliable soft organic electrodes with satisfactory performance. In our future works, we plan to fabricate flexible electrodes based on our existing polymer materials first, and a large amount of optimization works regarding the electrolyte systems (associated with Mg and Al-ion species) are also needed to be performed. Once we have accumulated enough experience, we will design and develop new redox polymers for the application of future multivalent flexible batteries. Here, we present the current demonstrations and design strategies related to our goals.

7.1 General Discussion

This thesis focuses on the design, synthesis, characterization and electrochemical performance of several novel redox-active polymers and large aromatic molecules for lithium related rechargeable batteries. The strategies, methods and approaches to achieve the objectives are discussed in each chapter. The conclusions are separately summarized in the following sub-sections.

7.1.1 Novel Nanostructured Conjugated Polymers as High-Performance Negative Electrodes for Li-Organic Batteries

In chapter 4, two novel ladder conjugated polymers were designed and obtained through a simple one-step polymerization process, respectively (Figure 7.1). Benefiting from nanoengineering, the nanostructures of both samples were obtained. Taking over the merits of heteroatoms doping (e.g. N and O) and utilizing ladder polymers' rigid backbone structure, the two polymers in terms of their 1D and 2D structures with a rich number of heteroatoms were proved to be promising negative materials for lithium-organic batteries. In detail, nanostructured 1D PPCQ and 2D NG-COF were developed to deliver remarkable high initial capacity values (1678 and 1021 mAh g⁻¹, respectively at 100 mA g⁻¹), good rate performances (up to 10 and 2.5 A g⁻¹) and ultra-long cycle lives (1000 and 600 cycles) with excellent Coulombic efficiencies (99.8% and 99.6%), respectively. These superior results bring the battery performance of organic materials to a new level. The investigations present an efficient method to develop multi-electron redox-active polymers with high and stable electrochemical performance. Conjugated ladder polymers, especially their heterocyclic nanostructures are superior negative materials for rechargeable batteries. Considering their easy synthesis, low temperature reactions and non-metal containing structures, they are potential green resources for future eco-friendly and sustainable energy storage devices.

Figure 7.1 Schematic illustration of the two conjugated polymers discussed in chapter 4.

7.1.2 Novel Carbonyl-Containing Large Aromatic Molecules and Polymers as High-Performance Positive Electrodes for Li-Organic Batteries

In chapter 5, four novel carbonyl-containing compounds were obtained and demonstrated as positive electrodes for lithium-organic batteries (Figure 7.2). In detail, two organic compounds, NDA-4N and PDA-4N with large aromatic multi-ring ladder-structured architectures were developed. They have been investigated between 2.0 and 3.9 V (vs. Li^+/Li) to show high initial specific capacity values (141.8 mAh g^{-1} and 116.3 mAh g^{-1} , respectively), reasonable rate performance (up to 1000 mA g^{-1}) and stable cycling capability (~ 100 cycles) with considerable efficiencies (99.09% and 99.71%). The results successfully reveal the feasibility of large aromatic multi-ring based organic compounds with good reversibility to be used as promising positive electrode materials. In addition, two polymers, PPTO and PEPTO based on pyrene-4,5,9,10-tetraone building blocks are investigated. The two positive electrodes show high specific capacities and energy densities. Benefiting from the enhanced conjugation and planarity, PEPTO with $\text{C}\equiv\text{C}$ bonds as bridges shows effectively-improved rate and long-term stability, therefore delivering better performance at harsh conditions. Moreover, a reversible capacity (110 mAh g^{-1}) of PEPTO could still be retained after 1000 cycles with an excellent CE of 99.80%. These structure-designing strategies provide alternative solutions to develop organic cathodes toward next-generation of high stability batteries.

Figure 7.2 Schematic illustration of the four carbonyl compounds discussed in chapter 5.

7.1.3 Toward a High-Performance All-Plastic Full Battery with a Single Organic Polymer as Both Positive and Negative Electrode

In chapter 6, a novel ladder-structured poly(quinone), poly(2,3-dithiino-1,4-benzoquinone) (PDB), was obtained through a simple two-step polymerization process. Prior to fabricating PDB based half and full batteries, free-standing electrodes by mixing of as-prepared PDB and carbon nanotubes (CNTs) were prepared and exhibited good flexibility. Benefiting from the unique ladder-like quinone and dithioether structure, the as-prepared polymer PDB shows a high output potential of 2.7 V, a large specific capacity of 248 mAh g⁻¹ and an ultra-stable cycling performance of 1000 cycles (with a high capacity retention of 80.5%) as a positive electrode. In addition, the electrochemical performance of PDB as a negative electrode was also investigated and showed a high initial reversible capacity of 1050 mAh g⁻¹ with a reversible capacity of 681 mAh g⁻¹ after 100 cycles. As a proof-of-concept, such a stable heterocyclic poly(quinone) was deployed as a bi-functional electrode, enabling the construction of an innovative all-plastic-electrode based symmetric full-battery (Figure 7.3). The as-fabricated symmetric full-

battery delivers an outstanding redox ability with an impressive capacity of 249 mAh g^{-1} (at 20 mA g^{-1}) and a good capacity retention of 119 mAh g^{-1} after 250 cycles (at 500 mA g^{-1}). This study provides an effective strategy to develop flexible and stable redox-active electrodes toward the next-generation of all-plastic batteries with high performance.

Figure 7.3 Schematic illustration of the all-plastic-electrode cell discussed in chapter 6.

7.2 Future Work

7.2.1 Specific Aims of the Future Work

The design and fabrication of high-performance all-organic or all-plastic batteries is essentially important to achieve future flexible electronics. A major challenge in this field is the lack of stable and reliable soft organic electrodes with satisfactory performance. Therefore, the author's future work is to design, synthesize and develop redox-active organic electrode based flexible rechargeable batteries. We aim at developing flexible batteries and investigating the electrochemical performance of novel organic compounds, including their nanostructured one-dimensional (1D) and two-dimensional (2D) structures versus metal-ions (e.g. Li^+ , Mg^{2+} & Al^{3+}) for all-organic flexible batteries with high energy and power density, good rate stability and long cycle life.

The detailed objectives are listed below:

- Developing novel redox-active organic compounds with different heteroatoms or functional groups (especially carbonyl groups).

- b) Tuning the activation energy of Li, Mg or Al intercalation into organic compounds by adjusting the redox-active molecular structures.
- c) Comparing different electrolyte & solvent systems with a variety of concentrations and additives, selecting an optimized electrolyte system to perform battery fabrication.
- d) Fabricating well-performed free-standing electrodes (both anodes and cathodes) and assembling all-organic-electrode based half and full-batteries.
- e) Studying the high-current-density metal-ion (Li^+ , Mg^{2+} & Al^{3+}) storage properties of the as-prepared organic and their nanomaterial-based electrodes.
- f) Investigating the structural and morphological properties, and performing bending tests of the flexible electrodes before and after the charge/discharge cycling process.

7.2.2 Current Situation

As mentioned in Chapter 6, from life-cycle evaluation on the extraction, processing and recycling of metal-containing inorganic electrode materials in rechargeable batteries, a huge negative impact will be caused on the environment. Thus, the usage of sustainable and environmentally-friendly organic battery materials to replace their inorganic counterparts is highly desirable.^[1-2] Particularly, in the arena to pursue next generation of lightweight, flexible and wearable electronic devices, organic soft batteries have been receiving more and more attentions.^[3-9] Therefore, designing and fabricating all-plastic rechargeable batteries is very promising.^[10] The concept of all-plastic batteries, where both the positive and negative electrodes are made from electroactive polymer materials, was proposed about 30 years ago.^[11-12] However, such preliminary demonstrations showed very poor rechargeable capability and low Coulombic efficiency.

The design and development of high-performance, light-weight, flexible and environmental-friendly all-organic rechargeable batteries have recently attracted tremendous attentions.^[13] Strong efforts have been conducted to develop promising organic-based electrode materials.^[14] Earlier approaches on organic electrodes have been focused on organosulfide, thioether and nitroxyl radical compounds.^[15] Although some of them were demonstrated to show noteworthy electrochemical performances, there are

still many challenges to develop high energy-density and long cycle life organic electrodes. Conjugated heterocyclic and carbonyl compounds including their small molecules and polymers are promising types of redox-active materials due to their extended π -conjugation and tunable property.^[16] More importantly, they can allow a simple and fast redox process, thus the serious structural alterations that often encountered with inorganic materials can be successfully avoided.^[17] Due to these superiorities, remarkable rate performance and ultra-long cycle life rechargeable batteries can be potentially achieved on the basis of redox-active organic compounds.

Among the battery designs beyond Li-ion configuration, magnesium-ion (Mg-ion) rechargeable batteries and aluminium-ion (Al-ion) rechargeable batteries are quite promising for future large-scale energy storage applications, due to the abundance of Mg and Al metals. In addition, they are not only abundant but also safe to be handled in ambient atmosphere. Most importantly, they are energetically conferred by their multi-electron redox behaviours.^[18-24] Nowadays, the most popular rechargeable battery systems are relied on above mentioned metal-ion technology (Li, Mg or Al-ion) for their high energy & power density.^[14-28] Therefore, the author's future work will mainly focus on these battery systems. By designing and synthesizing flexible organic electrode materials, in addition with novel methods to demonstrate battery electrode materials, the author aims at developing all-organic based flexible electrodes for the application of Li, Mg or Al-ion batteries. We also plan to strengthen the development of energy systems by modifying and tailoring organic materials, including their composite structures. Through the adoption of renewable organic electrode materials, to replace the current toxic metal-containing inorganic electrode materials. And also, by developing high-performance all-organic electrode based flexible rechargeable batteries, to reduce the dependence on fossil fuels and thus lowering the carbon emissions.

7.2.3 Significance and Innovation

The development of flexible or bendable portable electronics, for example, rollup and wearable devices requires the batteries to be soft and flexible.^[29] Achieving a flexible

rechargeable battery requires the development of flexible active electrode materials, such as inorganic metal or metal oxide-based nanoparticles.^[30] However, the development of multivalent-ion rechargeable batteries has met a bottleneck due to the small practical capacity (e.g. LiCoO_2 , LiFePO_4) and low stability (e.g. NCM & NCA) (Figure 7.4, top) of inorganic materials. Moreover, the large production of the transition metal based materials (e.g. Co, Ni & Mn) causes numerous concerns for resources and environmental issues (Figure 7.4, bottom). Therefore, more and more researchers are looking for potential eco-friendly organic electrode materials that can be applied for rechargeable batteries due to their redox stability and high theoretical gravimetric capacity.^[31]

Figure 7.4 Limitations and disadvantages of inorganic electrode materials. Reproduced from Ref 30b. Copyright Royal Society of Chemistry.

Organic redox-active conjugated compounds and carbonyl compounds are promising candidates for multivalent-ion batteries. Organic synthesis could simply allow chemists to control the structures and functional groups in a large amount,^[15] and organic compounds usually consist of low atomic weight elements (e.g. H, C, N, O and S). In addition, they are potentially sustainable and greener materials as many of them can be obtained from natural products and biomass.^[32-33] In fact, a lot of organic conjugated

compounds (and their building blocks to obtain conjugated polymers) with electrochemically active heteroatoms or carbonyl groups have been successfully reported as the electrode materials.^[18-24, 34] More recently, two-dimensional (2D) organic materials including covalent organic frameworks (COFs) and conjugated microporous materials were demonstrated with high charge storage.^[34-35] All these compounds are potential organic materials for all-organic flexible multivalent-ion electrodes.

Although some recent works have shown that organic materials can be used as battery electrodes with good performance, the all-organic-based nanostructured flexible electrodes still keep unexplored. The obtained knowledge from literature is still rare and limits our ability to design high-efficiency all-organic flexible batteries. Thus, in order to improve the competence of rechargeable batteries (versus Li^+ , Mg^{2+} or Al^{3+}) for future practical applications, the stability of the electrochemical performance at high current densities is a key. Low-cost multivalent battery chemistries (Mg^{2+} , Al^{3+}) have been recently investigated separately for large-scale energy storage applications. However, their commercialization is plagued by the poor power density and cycle life of cathodes. Recently, Wang *et al.* developed an industrial redox-active polyimide (PI) as a universal material for Li^+ , Mg^{2+} and Al^{3+} -ion batteries^[36] (Figure 7.5). This approach resolves the serious kinetics and cost concerns of the previous multivalent battery chemistries using inorganic crystalline cathode materials. It provides a new opportunity to design the high power and long cycle life multivalent rechargeable batteries.

Figure 7.5 Left figure: a) Illustration of PI@CNT synthesis. b) FTIR spectra PI@CNT. TEM images (c, d, e) and HRTEM image (f) of the PI/CNT composite. Right figure: a) Galvanostatic charge-discharge voltage profiles of PI@CNT as Mg-ion cathode; b) Galvanostatic charge-discharge voltage profiles of PI@CNT as Al-ion cathode; c) Cycling performance of PI@CNT as Mg-ion cathode; d) Cycling performance of PI@CNT as Al-ion cathode; e) Voltage profiles of PI@CNT composite as Mg-ion cathode at different current densities; f) Comparison of rate performance of PI@CNT composite as Li, Mg, and Al ion cathodes. (g) Cycling performance of PI@CNT as Li ion cathode at a current of 10 C. Reproduced from Ref 36. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

7.2.4 Approach

Below process illustrates the overall procedures to approach the target of our future work.

Here, the proposed future work can be dissected into four linked parts:

a) *Design strategy and approach toward an all-organic flexible battery*

Achieving a flexible or bendable rechargeable battery requires the electrode materials to be soft enough.^[10] Most of the organic materials (especially polymers) are inherently soft and flexible. Moreover, both of their mechanical and electrochemical properties can be modified through chemical synthesis. Hiroyuki Nishide and Kenichi Oyaizu proposed an easy design of all-organic based flexible battery (Figure 7.6).^[10] The flexible battery deploys thin layers of polymers with electrolyte layer sandwiched between them. The polymers are redox-active polymers with a repeatable number of redox-active groups. Therefore, the polymer backbones serve as a matrix to connect the redox-active sites for the hopping of electrons, resulting in the storage of charge.

The R groups (usually, carbonyl C=O or heteroatom-containing functional groups like C=N, C=S and N=N) in the anode and cathode possess different redox potentials, providing output voltage of the battery. The curve matrix polymer chains connecting the R groups offer flexibility, and the R groups attached to the polymer chains are the host for electrons hopping between the neighboring R groups to provide output current. By using this strategy, we plan to develop all-organic based flexible batteries on the basis of novel conjugated small molecules or polymers. In details, the anode materials can use heterocyclic conjugated polymers with a rich number of heteroatoms, such as nitrogen and sulfur, for their relatively low redox potentials. The cathode material can use carbonyl compounds along with their flexible composite forms with CNT & graphene due to the relatively high redox potential of carbonyl groups. Therefore, combining the strategies to obtain flexible all-organic batteries, we are confident to develop next-generation of all-organic electrode based flexible batteries. Not only limited to the investigations on Li-ions, but also Mg^{2+} and Al^{3+} -ions.

Figure 7.6 Proposed design strategy of an all-organic based flexible battery configuration. The R groups (functional groups) in the anode and cathode materials should have different redox potentials. Reproduced from Ref 10. Copyright Nature Publishing Group.

b) Design and development of novel redox-active organic compounds.

Organic anode materials: High energy density rechargeable battery requires anode materials to possess relatively low working potentials versus Li/Li^+ (as low as possible). Heterocyclic conjugated polymers and carbonaceous materials including their nanostructures are suitable anode materials due to their relatively low redox potential during charging and discharging process.^[37] However, pure organic-based anode materials, especially high-performance organic materials, are still rare and yet to be discovered.

From the past experience on organic materials, our preliminary investigations revealed that heterocyclic conjugated ladder polymers could be good substitutes for high performance and fast storage anode materials.^[38-40] Our group designed and synthesized several similar structured ladder-like conjugated polymers (Figure 7.7, left) with their nanostructures and investigated the electrochemical properties of different structures with the involvement of six-membered or five-membered rings.^[38-40] Due to the relatively low working potential of the conjugated polymers during charging and discharging, they are

promising anode materials for rechargeable Li-ion batteries. Their battery performances were tested through the fabrication of Li-half cells, which displayed extraordinary cycling stability compared with the state-of-the-art organic anode materials (Figure 7.7, right). The overall electrochemical performance of above mentioned conjugated ladder polymer nanostructures is very attractive. They possess both large reversible capacity ($>1000 \text{ mAh g}^{-1}$) and superior cycle life when tested between 3-0 V. Importantly, high Coulombic efficiencies could also be observed during cycling. The excellent electrochemical performance could be attributed to the nanosized polymer structures, extended π conjugations as well as large number of heteroatoms. With further developments, these conjugated polymers could also be applied to Mg or Al-ion batteries with the involvement of different Mg^{2+} or Al^{3+} containing electrolyte systems.

Figure 7.7 Chemical structures and electrochemical performance of several novel conjugated polymers that have been developed by our group. Left, organic structures. Right, corresponding cycling performance of (a) BBL. (b) SBBL. (c) PQL. (d) PPCQ. Reproduced from Ref 38, 39 & 40. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Copyright American Chemical Society.

Organic cathode materials: In contrast to anode materials, the intention for high energy density rechargeable batteries requires the cathode materials to have relatively high average potentials versus metal ions, for example Li/Li^+ (as high as possible if the electrolyte solution can support). To explore high capacity and good reversibility cathode materials, organic compounds with carbonyl groups ($\text{C}=\text{O}$) are quite popular as they are easy to be designed and modified, and their redox actions are usually occur above 1.5 V (vs. Li/Li^+).^[17] Moreover, the mechanism of the lithiation and delithiation process on the

carbonyl groups has been thoroughly investigated and explained.^[17, 41] Compared with the traditional inorganic cathodes that usually based on the first-row transition metals (e.g. LiCoO_2 , LiMn_2O_4 and LiFePO_4), the specific capacity, operating voltage and cycling stability of organic materials can be further improved by the introduction of different heteroatoms (e.g. sulfur S and nitrogen N) and electron withdrawing groups (e.g. $-\text{F}$, $-\text{CN}$ & $-\text{SO}_3\text{Na}$) into the organic structures.^[42-43] To further solve the dissolution issue for organic materials, the solubility of organic compounds can be reduced by the introduction of large and extended heterocyclic organic structures. Therefore, novel organic structures with effective redox-active groups are highly desirable to be synthesized for metal-ion rechargeable batteries.

As mentioned in Chapter 5, the author reported the developments of several new redox-active carbonyl organic cathodes with high performance.^[44-45] Based on the highly redox-active carbonyl groups, two organic compounds, NDA-4N and PDA-4N with large aromatic multi-ring ladder-structured architectures were first developed and investigated. In addition, to investigate the relationship between the planarity and electrochemical performance of organic materials, we designed and synthesized two novel organic cathodes: poly(pyrene-4,5,9,10-tetraone) (PPTO) and poly(2,7-ethynylpyrene-4,5,9,10-tetraone) (PEPTO), based on the highly redox-active pyrene-4,5,9,10-tetraone. Benefiting from the enhanced conjugation and planarity, PEPTO with the addition of a carbon-carbon triple bond ($\text{C}\equiv\text{C}$) delivers significantly-improved rate stability.

Other than Li-organic batteries, carbonyl compounds are believed to be universal materials for future multivalent-ion batteries. Because they could allow fast multivalent-ion insertion and de-insertion through unique ion-coordination charge storage mechanism, which is totally different as compared with inorganic materials. Therefore, carbonyl compounds are believed to be future candidates to resolve the kinetic issues that frequently encountered by multivalent-ion batteries using inorganic cathode materials. Recently, PTO has been reported to be able to store Zn^{2+} (Figure 7.8),^[46] this strategy provides an effective route toward the next-generation of multivalent batteries.

Figure 7.8 Chemical structures and redox mechanism of PTO as an effective organic cathode to store Zn^{2+} through unique ion-coordination charge storage mechanism. Reproduced from Ref 46. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

As mentioned in Chapter 6, among various redox polymers, poly(quinones) and their derivatives are outstanding candidates as redox-active electrodes for organic batteries due to their fast-redox ability, high storage capacity and structural diversity.^[47-51] Nevertheless, poly(quinones) as bi-functional electrodes for all-plastic-electrode batteries are rarely explored. Attractive attempts of poly(quinones) on metal-ion (e.g. Li^+ , Na^+ , K^+ & Mg^{2+})^[52-54] and proton (H^+)^[55] batteries have been performed, indicating their good compatibility with different types of shuttling-ions. More importantly, poly(quinones) have been demonstrated to show bi-functional properties as they can be reversibly reduced and oxidized at either high or low potentials (vs. Li^+).^[56-57] All these approaches show promising results toward next generation of multivalent-ion batteries.

Another possible effective approach is to confine the organic molecules into the CNT or graphene matrix through heat treatment to obtain composite or hybrid materials.^[31, 58] As shown in Figure 7.5, this universal strategy can restrain the dissolution problem which often encounter on small organic molecules, therefore endowing organic materials with excellent performances as active Li^+ , Mg^{2+} and Al^{3+} -ion batteries. In our future work, other than designing novel organic compounds, various promising small carbonyls and

conjugated compounds could also be involved into CNT and graphene structures to form flexible composite electrode materials for Li^+ , Mg^{2+} and Al^{3+} -ion batteries. Once we have obtained enough organic molecules that can be effectively applied, we will carry out all-organic flexible battery investigations based on their composite forms.

c) *Fabrication of flexible organic electrodes toward all-organic batteries*

Flexible all-organic electrode based batteries can be generally developed through two approaches.^[31] The first is through the use of pure redox-active polymers with inherent flexibility. Another method is through the use of composite electrodes with flexible supporting networks. Recent investigations show preliminary studies toward flexible electronic devices.^[59-65] Regarding the flexible battery designs, conjugated and conductive polymers are reported to be promising electrode materials with good performance and high flexibility. For example, a highly stretchable pure organic electrode based on polypyrrole (PPy) was developed by a simple electrochemical deposition method (Figure 7.9).^[59] Such a 2D buckled films could retain its electrochemical performance in a Mg battery configuration even after 2000 cycles of stretching with 30% strain applied.

Figure 7.9 Schematic procedures used to prepare buckled PPy films on a poly(styrene-block-isobutylene-block-styrene) (SIBS) substrate. Reproduced from Ref 59. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

As for flexible composite polymer electrodes, carbon nanotubes (CNTs) are quite popular supporting materials for their high surface area, excellent electronic conductivity and

good flexibility. A free-standing and highly conductive PEDOT-CNT film was prepared by spin coating and chemical vapor polymerization (Figure 7.10a).^[60] Such a stretchable film was investigated as an anode and delivered good performance for Li-ion batteries. PEDOT:PSS is known as a polymer mixture and possesses a high electronic conductivity.^[61] As a water soluble material, PSS has the ability to improve the dispersion of CNTs through the non-covalent stabilization.^[62] A PEDOT:PSS-CNT film in terms of its nanocomposite can be obtained with a high electronic conductivity of 950 S cm^{-1} .^[63] After incorporating inorganic nanoparticles (e.g. TiO_2 & Si) into the interpenetrating network of PEDOT:PSS-CNT, highly flexible nanocomposite anode materials can be obtained (Figure 7.10b & c). Wei *et al.* demonstrated that flexible and binder-free polymer composite electrodes could be developed by in-situ polymerization of imide on single-wall CNTs.^[64] A flexible polyimide-CNTs (PI-SWCNT) electrode was obtained and showed stable cycling and rate performance as cathode materials. This PI-SECNT film could still retain a high capacity of 206 mAh g^{-1} after 200 cycles with a high coulombic efficiency of 99.6%. Following the similar method, they also developed a large-area flexible composite film based on pyromellitic dianhydride-tris(2-aminoethyl)amine (PMTA) (Figure 7.10d).^[65] This PMTA-SWCNT film also showed good mechanical properties confirmed by the bending test.

Figure 7.10 (a) Schematic procedures to prepare a flexible PEDOT-CNT film. (b) A flexible TiO_2 -PEDOT:PSS-CNT flexible electrode under bending. (c) SEM image of a flexible Si-PEDOT:PSS-CNT electrode. (d) Preparation of a PMTA-SWCNT electrode. Reproduced from reference [60], [63] and [65]. Copyright American Chemical Society. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

Small organic carbonyl molecules can also be confined into the CNT networks, providing flexible and stable electrode materials.^[58] A recent study reported a sodium 1,4-dioxonaphthalene-2-sulfonate and multiwalled carbon nanotubes (NQS/MWNTs) hybrid film as a high-performance cathode for rechargeable Li-ion batteries (Figure 7.11a & c).^[58] The process to prepare such a highly flexible film is illustrated in Figure 7.11c, and the optical photographs of this NQS/MWNT film is shown in Figure 7.11d. Based on the two active carbonyl groups, such a cathode material showed a stable capacity almost without declination after 25 cycles of bending test between 1.6 and 3.5 V at 0.2 C. Cho *et al.* demonstrated an interesting study on organic-catholyte-containing flexible Li-ion

battery using the small molecule 1,2-benzanthraquinone (BAQ) (Figure 7.11b).^[66] A tube-type architecture based flexible battery (Figure 7.11e-f) using BAQ catholyte was developed and delivered superior battery performance under bending and stretching. This study provides an effective method to produce next-generation flexible tube-type batteries. With all these successful demonstrations of flexible batteries, more composite or nanocomposite based electrodes with high performance can be obtained to overcome the challenges (e.g. volume expansion, short cycle life and low capacity retention) of the traditional metal or metal oxide based flexible electrode materials.

Figure 7.11 Molecular structure of (a) NQS and (b) BAQ. (c) Schematic illustration to develop a NQS/MWNTs hybrid film. (d) Photographs of the flexible NQS/MWNTs hybrid electrode. (e) Preparation of a flexible tube-type catholyte-containing battery. (f) Photographs of the BAQ catholyte and principle components of the flexible tube-type battery. Reproduced from Ref 58 & 66. Copyright American Chemical Society. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

7.3 Perspective and Recommendations

Numerous studies have been conducted to achieve promising conjugated and carbonyl polymer based redox-active electrodes, and many of them have already met the competitive requirements of specific capacity, cycling stability and Coulombic efficiency. With novel design strategies and in-depth investigations, we believe that conjugated and carbonyl based redox-active polymers might not only be good candidates for rechargeable metal-ion and multivalent-ion batteries, but also be potential organic materials for hydronium and proton batteries.

However, there is one major challenge for currently developed redox-active polymers. The highly sloping voltage behavior becomes a severe disadvantage for them to be effectively used in real application. This characteristic becomes more distinct at higher current densities. Curves with flat plateaus indicate a stable electrochemical activity without disturbing side reactions and kinetic limitations. For the cases of nanostructured redox-active polymers, factors contributing to this behavior could involve the intrinsic insulation property, amorphous state of polymers, morphology & size and charge repulsion between the repeating units in the polymer chains during the electrochemical reactions. To achieve practical polymer electrodes, it is therefore highly recommended to carry out further investigations on the polarization losses as well as the hysteresis effect of redox-active polymers. With novel design strategies and molecular modifications, we believe that redox-active polymers will open a window for future development of practical polymer-based rechargeable batteries, not only limited to Li^+ and Na^+ ions but also multivalent-ions like Mg^{2+} , Al^{3+} and Zn^{2+} ions.

The doping availability of conventional p-type conductive polymers is usually low, leading to a low specific capacity of the batteries. Much less studies have been performed on the electrochemistry of the n-doped states of conductive polymers. Through n-doping of small-sized cations (usually metal ions), the energy storage of conductive polymers could be increased compared with that of bulky-sized anions. Very recently, a n-doped (Li^+ doped) PANi with a high electronic conductivity of 3 S cm^{-1} was obtained,

delivering a high specific capacity of 230 mAh g⁻¹ with a stable capacity for 400 cycles.^[67] The results are much superior to the conventional p-doped conductive polymers. Considering the high operating voltage of conductive polymers, it is of critical importance to conduct more investigations to increase the capacity of conductive polymers through the investigation of their n-doping capability. To achieve this, the exploration of novel synthesis routes, different pre-doping or doping species and a variety of morphology controls should be taken into account.

Since conjugated and carbonyl based polymers have low intrinsic electronic conductivities, a large amount of carbon additives (e.g. Super P, graphene, CNT) are usually added to improve the electron transportation within the cells. Sometimes, the weight percentage of carbon additives could reach a high value of >80%. This will decrease the utilization of active polymers and reduce the energy density of the cells accordingly. Therefore, studies on high-loading redox-active polymer materials are welcomed to achieve practical rechargeable batteries.

Last but not least, the consideration of a suitable electrolyte system is also important to achieve high-performance polymer electrodes. It is highly encouraged to select a compatible electrolyte system with a favorable ionic mobility and a good ion-solvent interaction with the electrode materials during the electrochemical reactions.^[68] This requires a lot of prior studies regarding the testing and modification of different electrolyte systems (e.g. ester or ether based solvents, etc.). In addition, electrolyte solutions with different concentrations and additives could affect the behavior of electrode materials dramatically.⁶⁹⁻⁷⁰ More recently, advanced electrolyte (quasi-solid or solid state, aqueous, etc.) systems were believed to show better performance.⁷¹⁻⁷³ Therefore, through further exploration and optimization of the electrolyte systems, improved electrochemical performance of redox-active polymers can be obtained in near future. With deeper investigations on advanced electrode and electrolyte materials, it is promising to design all organic-based full batteries on the basis of redox-active polymers. By adopting this concept, future high density flexible or wearable batteries can be obtained with extensive application prospects.

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APPENDIX A

Detailed Material Synthesis

Compound **1** was obtained with a high yield (93%) referring to the reported literature.^[A1] Compared with the synthesis of mono-anhydride **4**, it was more difficult for reactant **1** to form mono-anhydride **2** under the same condition. Even after 24 hrs of reaction, only 37% of compound **1** was successfully transformed to **2**, whereas, a large amount of reactant **1** still left unreacted.

Compound 1

To a suspension of 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA, 536 mg, 2.0 mmol) in 30 ml of acetonitrile (CH_3CN) was added 2-ethyl-1-hexanol (1.56 g, 12.0 mmol), 2-ethylhexyl bromide (2.30 g, 12.0 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.4 g, 16.0 mmol). The mixture was heated under refluxing overnight and then cooled down to ambient temperature. After removing the CH_3CN under reduced pressure, the residual was dissolved in 200 mL CH_2Cl_2 again, washed with H_2O and saturated NaCl solution subsequently. Then, the CH_2Cl_2 phase was dried by anhydrous Na_2SO_4 , filtrated and concentrated to obtain the rough product, which could be further purified by column chromatography first using hexane and then hexane: dichloromethane (1:1 V/V) as the eluent to obtain 1.4 g of colorless sticky liquid. Yield: 93%. ^1H NMR (300 MHz, CDCl_3): δ 8.00 (s, 4H), 4.28–4.18 (m, 8H), 1.78–1.70 (m, 4H), 1.47–1.32 (m, 32H), 0.97–0.87 (m, 24H). ^{13}C NMR (75 MHz, CDCl_3): δ 168.0, 133.6, 129.1, 128.6, 68.1, 38.7, 30.4, 28.9, 23.8, 23.0, 14.0, 10.9; MALDI-TOF MS: calculated for $\text{C}_{46}\text{H}_{72}\text{O}_8 + \text{H}^+$, 753.5305; found: 753.5303 (M^+).

Compound 2

A 10 mL round-bottomed flask was charged with 4.8 g (6.4 mmol) compound **1**, 0.5 ml toluene and 2.5 ml heptane before being heated to 110 °C. 1.21 g (6.4 mmol) *p*-toluenesulfonic acid monohydrate (TsOH·H₂O) was added into the solution, which was stirred at 110 °C for 24 hrs. After removing the solvent under reduced pressure, the residual was dissolved in 200 mL CH₂Cl₂ again, washed with H₂O and saturated NaCl solution subsequently. Then, the CH₂Cl₂ phase was dried by anhydrous Na₂SO₄, filtrated and concentrated to obtain the rough product, which was further purified by column chromatography using hexane: dichloromethane (1:2 to 1:3 V/V) as the eluent to obtain 1.2 g of colorless sticky liquid as the target molecule (recycling 2.1 g of compound **1**). Yield: 37%. ¹H NMR (300 MHz, CDCl₃): δ 8.69 (d, *J* = 7.5 Hz, 2H), 8.19 (d, *J* = 7.5 Hz, 2H), 4.32–4.24 (m, 4H), 1.80–1.74 (m, 2H), 1.50–1.32 (m, 16H), 0.99–0.88 (m, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 167.1, 159.4, 137.2, 132.8, 131.1, 129.8, 126.5, 121.1, 68.8, 38.7, 30.4, 28.9, 23.8, 22.9, 14.0, 10.9; MALDI-TOF MS: calculated for C₃₀H₃₈O₇ + H⁺, 511.2696; found: 511.2678 (M⁺).

Compound 3

To a solution of pyridine (5ml) was added with 270 mg (0.53 mmol) M2 and 68 mg (0.24 mmol) 1,2,4,5-Tetraaminobenzene tetrahydrochloride and the solution was refluxed under argon protection overnight. After the reaction cooled down to room temperature, the pyridine solvent was removed under reduced pressure to obtain the residual solid, which could be further purified, firstly, by silica gel column chromatography, and secondly, by neutralized Al₂O₃ column chromatography using dichloromethane:

methanol (100: 1 V/V) as the eluent to obtain 150 mg orange solid as the target molecule. Yield: 58%. The target molecule was a mixture of *cis* and *trans* isomer. ^1H NMR (300 MHz, CDCl_3 , taking $-\text{OCH}_2$ as 8H): δ 9.49 (s, 0.6H), 8.88–8.76 (m, 4.5H), 8.24–8.17 (m, 4.6H), (note: for aromatic H, totally 10H), 4.35–4.25 (m, 8H), 1.83–1.80 (m, 4H), 1.52–1.38 (m, 32H), 1.02–0.90 (m, 24H); MALDI-TOF MS: calculated for $\text{C}_{66}\text{H}_{78}\text{N}_4\text{O}_{10} + \text{H}^+$, 1087.5796; found: 1087.5780 (M^+); FTIR: 2927, 2863 cm^{-1} (CH_3- , CH_2-), 1711 cm^{-1} ($-\text{COOCH}_2$).

Compound NDA-4N

In a 50 mL schlenk flask was charged with 108.6 mg (0.1 mmol) compound **3**, 5 mL toluene and heated to 110 $^{\circ}\text{C}$. After the solid was all dissolved, 190 mg (1.0 mmol, 10 eq.) *p*-toluenesulfonic acid monohydrate ($\text{TsOH}\cdot\text{H}_2\text{O}$) was added into the solution and the solution was stirred at 110 $^{\circ}\text{C}$ for 5 hour. Afterwards, another 190 mg (1.0 mmol, 10 eq.) $\text{TsOH}\cdot\text{H}_2\text{O}$ was added again and the solution reacted for 24 hrs until a large amount of solid precipitated from the solution and there was no compound **3** existed in the solution (the solution almost had no color). Then, the solution was cooled down to room temperature and the precipitate was filtrated, washed with H_2O and methanol respectively, dried to obtain deep red solid of 58 mg. Yield: 96%. FTIR: 1781, 1700 cm^{-1} (anhydride, $-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$). Elemental Analysis calculated: C 67.78%, H 1.67%, N 9.30%; measured: C 66.91%, H 2.29%, N 8.66%.

Compound 5

To a solution of pyridine (70 ml) was added with 1.0 g (1.6 mmol) compound **4** and 197.4 mg (0.7 mmol) 1,2,4,5-Tetraaminobenzene tetrahydrochloride and the solution was refluxed under argon protection overnight. After the reaction cooled down to room temperature, the pyridine solvent was removed under reduced pressure to obtain the residual solid, which could be further purified, firstly, by silica gel column chromatography, and secondly, by neutralized Al_2O_3 column chromatography using dichloromethane: methanol (100: 3 V/V) as the eluent to obtain 551 mg purple blue solid as the target molecule. Yield: 41%. The target molecule was a mixture of cis and trans isomer. Due to the low solubility of compound **5**, ^1H NMR could not be obtained. MALDI-TOF MS: calculated for $\text{C}_{86}\text{H}_{86}\text{N}_4\text{O}_{10} + \text{H}^+$, 1335.6422; found: 1335.6400 (M^+); FTIR: $2926, 2862\text{ cm}^{-1}$ (CH_3- , CH_2-), 1706 cm^{-1} ($-\text{COOCH}_2$).

Compound PDA-4N

In a 50 mL schlenk flask was charged with 100 mg (0.075 mmol) compound **5**, 10 ml toluene and heated to $110\text{ }^\circ\text{C}$. Afterward, 190 mg (1.0 mmol) *p*-toluenesulfonic acid monohydrate ($\text{TsOH}\cdot\text{H}_2\text{O}$) was added into the solution, which was stirred at $110\text{ }^\circ\text{C}$ for 24 hrs until a large amount of black solid precipitated from the solution and there was no compound **5** existed in the solution (the solution almost had no color). Then, the solution was cooled down to room temperature and the precipitate was filtrated, washed with methanol, dried to obtain black blue solid 60.5 mg. Yield: 95%. FTIR: $1760, 1680\text{ cm}^{-1}$ (anhydride, $\text{—}\overset{\text{O}}{\parallel}\text{C—O—}\overset{\text{O}}{\parallel}\text{C—}$). Elemental Analysis calculated: C 76.24%, H 2.13%, N 6.59%; measured: C 73.45%, H 2.23%, N, 6.49%.

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APPENDIX B

Detailed Materials Synthesis

Synthesis of compound 2

2,7-dibromo-pyrene-4,5,9,10-tetraone (compound **1**, 630 mg, 1.5 mmol) and TsOH.H₂O (570 mg, 3.0 mmol) were added into a flask with a mixed solution of ethylene glycol (15 mL) and toluene (15 mL). The resulted mixture was refluxed at 140 °C under argon protection for 36 hrs. After the solution cooled down to room temperature, the precipitate was filtrated, washed in success of H₂O and small amount of MeOH, dried to obtain light yellow solid (compound **2**, 560 mg, 63%). ¹H NMR (CDCl₃, 300 MHz): δ 7.89 (s, 4H), 4.19 (s, 8H), 3.66 (s, 8H); ¹³C NMR (CDCl₃, 75 MHz): δ 135.0, 130.3, 127.4, 123.8, 91.9; HRMS: Calculated for C₂₄H₂₀Br₂O₈ + H⁺: 598.9562; Found: 598.9551 (M+ H⁺); Elemental Analysis for C₂₄H₂₀Br₂O₈: Calculated: C, 48.35%; H, 3.38%. Found: C, 48.11%; H, 1.91%.

Synthesis of PPTO

In a dried 50 mL Schlenk tube was added subsequently of bis(1,5-cyclooctadiene) nickel(0) (390 mg, 1.42 mmol), 1,5-cyclooctadiene (154 mg, 1.42 mmol) and 2,2'-bipyridine (220 mg, 1.42 mmol) and anhydrous DMF (4 mL). The solution was heated at 85 °C for 30 mins under argon protection. Compound **1** (480 mg, 0.8 mmol) in 8 mL toluene was added into the tube and the mixture solution was heated at 85 °C for 36 hrs and cooled down to room temperature. The precipitated solid was filtrated, washed in success with H₂O, MeOH and THF, dried to obtain the white solid, which was used directly in next step. The obtained solid was dissolved in a mixture of TFA-H₂O (9:1, 20 mL) and refluxed in a sealed tube under argon protection for 24 hrs. After the solution cooled down to room temperature, the mixture solution was dropped on the ice slowly. The precipitate was filtrated, washed with H₂O and methanol, dried to give the rough deep red product PPTO. The PPTO was further purified through soxhlet extraction

installation using acetone, THF and CHCl_3 respectively to obtain the PPTO (80 mg, 38%). FTIR: 1678 cm^{-1} , 1602 cm^{-1} ; Elemental Analysis: Calculated for $\text{Br(PPTO)}_3\text{H}$ (considering that Br atom could hardly be completely eradicated): C, 66.92%; H, 1.52%. Found: C, 66.42%; H, 2.65%.

Synthesis of PEPTO

In a dried 100 mL two-neck flask was added subsequently of compound **2** (480 mg, 0.8 mmol), bis(trimethylstannyl)acetylene (282 mg, 0.8 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (56 mg, 0.08 mmol) and finally anhydrous toluene (50 ml). Then the solution was refluxed at $120\text{ }^\circ\text{C}$ under argon protection for 24 hrs and cooled down to room temperature. The precipitated solid was filtrated, washed in success of H_2O , MeOH and THF, dried to obtain the green solid, which was used directly in next step. The obtained solid was dissolved in a mixture of TFA- H_2O (9:1, 20 ml) and refluxed in a sealed tube under argon protection for 24 hrs. After the solution cooled down to room temperature, the mixture solution was dropped on the ice slowly. The precipitate was filtrated, washed with H_2O and MeOH, dried to give the rough black product PEPTO. The PEPTO was further purified through soxhlet extraction installation using acetone, THF and CHCl_3 respectively to obtain the PEPTO (142 mg, 67%). FTIR: 1683 cm^{-1} ; Elemental Analysis: Calculated for $\text{Br(EPTO)}_3\text{Sn}(\text{CH}_3)_3$ (considering that Br and $\text{Sn}(\text{CH}_3)_3$ groups could hardly be completely eradicated): C, 62.44%; H, 1.93%. Found: C, 61.42%; H: 2.01%.

Figure AB1. ^1H NMR of compound 2.

Figure AB2. ^{13}C NMR of compound 2.

Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

53 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 20-24 H: 18-21 O: 0-8 79Br: 0-2 81Br: 0-2

C₂₄H₂₀Br₂O₈

cwq-2B 51 (1.134)

1: TOF MS ES+
1.01e+000

Minimum:								
Maximum:	5.0	20.0		-1.5				
				50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
598.9551	598.9562	-1.1	-1.8	13.5	12.6	0.0	C ₂₄ H ₂₁ O ₈ 81Br ₂	

Figure AB3. HRMS of compound 2.

Figure AB4. HRSEM of as-prepared (A) PPTO and (B) PEPTO.

APPENDIX C

Table AC A comparison table includes several polymer electrodes for rechargeable batteries.

Polymer electrode materials ^[reference]	Shuttling ions	Initial, final reversible capacity (mAh g ⁻¹) (at the current density or C rate)	Cycle numbers (at the current density or C rate)	Average output potential (V)
NDA-4N	Li⁺	141.8, 48.8 (at 66 mA g⁻¹)	100 cycles	2.40
PDA-4N	Li⁺	116.3, 82.4 (at 66 mA g⁻¹)	100 cycles	2.40
PEPTO	Li⁺	244, 155 (at 20 mA g⁻¹); 139, 110 (at 800 mA g⁻¹)	100 cycles (at 20 mA g⁻¹); 953 cycles (at 800 mA g⁻¹)	2.47
PPTO	Li⁺	234, 161 (at 20 mA g⁻¹); 131, 97 (at 800 mA g⁻¹)	100 cycles (at 20 mA g⁻¹); 953 cycles (at 100 mA g⁻¹)	2.44
3D-RGO/PI composite ^[A1]	Li ⁺	123, 101 (at 0.5 C)	150 cycles	2.07
EDP ^[A2]	Li ⁺	85, 75 (at 50 mA g ⁻¹)	50 cycles	~2.50
HP ^[A2]	Li ⁺	130, 110 (at 50 mA g ⁻¹)	50 cycles	~2.50
UP ^[A2]	Li ⁺	65, 130 (at 50 mA g ⁻¹)	50 cycles	~2.50
PAQI ^[A3]	Na ⁺	213, 190 (at 50 mA g ⁻¹)	150 cycles	~1.90
PI-1 ^[A4]	Li ⁺	~61, ~10 (at 25 mA g ⁻¹)	65 cycles	~2.30
PI-2 ^[A4]	Li ⁺	104, 68.5 (at 25 mA g ⁻¹)	65 cycles	~2.40
PI-3 ^[A4]	Li ⁺	~78, ~57.9 (at 25 mA g ⁻¹)	65 cycles	~2.40

PI/CNT nanocomposi te ^[A5]	Li ⁺	~102, 95 (at 100 mA g ⁻¹)	300 cycles	~2.50
PENDI ^[A6]	Li ⁺	113, ~50 (at 20.2 mA g ⁻¹)	100 cycles	~2.25

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APPENDIX D

Table AD Comparison table including a summary of the reported all-plastic-electrode based full-battery configurations and their key electrochemical parameters.

Cell configuration (cathode/anode) ^[reference]	Shuttling -ion species	Initial, final reversible capacity (mAh g ⁻¹), retention	Cycling performance (at the current density or C rate)	Energy density (Wh kg ⁻¹); Potential window) (V)	Discharg e output potential (V)	Electrode show flexibility
PDB/PDB	Li⁺	249, 195, 78.3%; 170, 119, 70%	125 cycles at 20 mA g⁻¹; 250 cycles at 500 mA g⁻¹	276; 0.005-3.0	~1.11	Yes
Polyacetylene/Polyacetylene ^[A1]	Na ⁺	- ^{a)}	20 cycles at -	20; -	-	No
Polyacetylene/Polyacetylene ^[A2]	ClO ₄ ⁻	-	-	47; 0.4- 2.5	~3.2	No
Polyparaphenylene/Polyparaphenylene ^[A3]	Li ⁺ & PF ₆ ⁻	~125, ~85, 68%	60 cycles at 40 mA g ⁻¹	~312; 1.0- 4.0	~2.5	No
Poly(TEMPO-substituted norbornene)/Poly(galvinoxystyrene) ^[A4]	Li ⁺ & ClO ₄ ⁻	~28, ~20, 71.4%	250 cycles at 360 C	~19; 0-1.2	~0.66	Yes
Polytriphenylamine/Polyy(anthraquinonyl sulphide) ^[A5]	Na ⁺ & PF ₆ ⁻	~180, ~150, 83.3%	500 cycles at 8 C	-; 0-2.7	~1.2	No
Poly(2-vinylthianthrene)/Poly(2-methacrylamide-TCAQ) ^[A6]	ClO ₄ ⁻	105, 71, 67.6%	250 cycles at 1 C	~142; 1.0- 1.6	~1.35	No

Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide)/poly(N-4,4'-bipyridinium-N-decamethylene dibromide) ^[A7]	BF ₄ ⁻	~110, ~80, ~73%	2000 cycles at 60 C	~132; 1.0-1.4	~1.2	No
PEDOT-benzonquinone/PEDOT-anthraquinone ^{[A8]b)}	H ⁺	~100, 70, 70%	150 cycles at 400 mA g ⁻¹	~50; 0-0.8	~0.5	No

^{a)}Not applicable. The values are not able to be estimated or obtained from the mentioned reference studies.

^{b)}The values are obtained based on PEDOT-anthraquinone as the limiting material.

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