Organic Electrode Materials for Energy Storage Devices

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
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Abstract

This thesis describes the design of organic electrode materials for energy storage devices and the investigation into the underlying structure-property relationships governing the performance of these materials.

Chapter 1 serves as a general introduction to energy storage devices, the use of organic electrodes in these devices, the factors governing the performance, and the quantification thereof. The characteristics and fundamentals of different types of energy storage devices and the electrochemical properties of suitable materials for each are discussed.

Chapter 2 examines the use of a polyfullerene material for supercapacitor applications. I find that the polyfullerene has a favourable redox potential and a high capacity that affords a high power supercapacitor, although, its cycling stability is limited. Examining the performance of the polyfullerene under different conditions, a key degradation mechanism is elucidated that can be used as a guideline to develop stable supercapacitor materials.

In Chapter 3, I describe the development of a biologically-derived pendant polymer cathode material for lithium-ion batteries. The polymer is derived from riboflavin (Vitamin B2) and uses a polynorbornene backbone. The polyflavin material affords a high capacity, but the cycling stability is limited. Using a combined theoretical and experimental approach, a new degradation
mechanism is uncovered that can be applied to organic electrode materials in general and the design criteria to develop highly stable materials is further refined.

Chapters 4 and 5 investigate triptycene-based frameworks for lithium-ion batteries. A cathode material is studied in Chapter 4, and an anode material in Chapter 5. Here, I draw conclusions on the utility of triptycene frameworks for electrode materials in lithium-ion batteries based on the material properties. Specifically, I find that the nature of the linker units is important for the performance of these materials. Choosing the correct linker to form a material with high crystallinity and small aggregate size yields an electrode with excellent stability and high usage of active material.

Chapter 6 serves as a summary of this thesis, provides an outlook on the future of organic electrode materials for energy storage, and suggests future directions that the field should take to develop high performance materials.
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Abbreviations

\(^{13}\text{C}\) carbon-13

Å Angstrom

\(\text{Ag}^+\) silver ion

\(\text{AgCl}\) silver chloride

Ar aromatic group

BBL polybenzimidazobenzoisoquinoline

B3LYP Becke-3 parameter, Lee, Yang, Parr

C C-rate

\(\text{C}_6\text{O}\) Buckminsterfullerene \(\text{C}_{60}\)

CB carbon black

cc cubic centimeter

cm centimeter

\(\text{CO}_2\) carbon dioxide

COF covalent organic framework

CP-MAS cross-polarization magic angle spinning

CPE constant phase element

\(C_{\text{theor}}\) theoretical capacity

CV cyclic voltammetry

DFT density functional theory
<table>
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<th>Abbreviation</th>
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<tr>
<td>DMAP</td>
<td>dimethylaminopyridine</td>
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<td>DMC</td>
<td>dimethyl carbonate</td>
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<tr>
<td>DMF</td>
<td>dimethylformamide</td>
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<td>DSC</td>
<td>differential scanning calorimetry</td>
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<tr>
<td>dV(d)</td>
<td>differential pore size distribution</td>
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<tr>
<td>dV/dt</td>
<td>derivative of voltage over time of discharge</td>
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<td>e^-</td>
<td>electron</td>
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<td>EC</td>
<td>ethylene carbonate</td>
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<tr>
<td>EDG</td>
<td>electron donating groups</td>
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<tr>
<td>EESS</td>
<td>electrochemical energy storage system</td>
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<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
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<td>electron paramagnetic resonance</td>
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<td>EWG</td>
<td>electron withdrawing groups</td>
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<td>fused naphthalene-triptycene framework</td>
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<td>fused perylene-triptycene framework</td>
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<tr>
<td>F-pyro-Tc</td>
<td>fused pyromellitic-triptycene framework</td>
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<td>Fe/Fe^+</td>
<td>ferrocene/ferrocenium</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<td>--------------</td>
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<tr>
<td>FTIR</td>
<td>Fourier-transform infrared</td>
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<td>g</td>
<td>gram</td>
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<td>HCl</td>
<td>hydrogen chloride</td>
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<td>Hertz</td>
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<td>i</td>
<td>current</td>
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<td>lithium tetrafluoroborate</td>
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<tr>
<td>LiPF_6</td>
<td>lithium hexafluorophosphate</td>
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<td>m</td>
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<td>molarity</td>
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<td>mA</td>
<td>milliampere</td>
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<td>milliampere hour</td>
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<td>Definition</td>
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<tr>
<td>MeI</td>
<td>methyl iodide</td>
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<tr>
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<td>milligram</td>
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<td>millivolt</td>
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<td>milliWatt</td>
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<td>number of charges</td>
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<td>number of repeating units</td>
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<td>NaBF₄</td>
<td>sodium tetrafluoroborate</td>
</tr>
<tr>
<td>NDI</td>
<td>naphthalene diimide</td>
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<tr>
<td>NDI-Tc</td>
<td>naphthalene diimide-triptycene framework</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
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<tr>
<td>P</td>
<td>pressure</td>
</tr>
<tr>
<td>PC₆₀</td>
<td>polyfullerene material</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
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<tr>
<td>Pd</td>
<td>palladium</td>
</tr>
<tr>
<td>PDI</td>
<td>perylene diimide</td>
</tr>
<tr>
<td>PDI-Tc</td>
<td>perylene diimide-triptycene framework</td>
</tr>
<tr>
<td>PEDOT</td>
<td>poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>$P_{\text{max}}$</td>
<td>maximum power</td>
</tr>
<tr>
<td>$P_0$</td>
<td>initial pressure</td>
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<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PVDF</td>
<td>polyvinylidene fluoride</td>
</tr>
<tr>
<td>$Q$</td>
<td>total charge</td>
</tr>
<tr>
<td>R</td>
<td>resistor/resistance</td>
</tr>
<tr>
<td>RC</td>
<td>resistor-capacitor</td>
</tr>
<tr>
<td>ROMP</td>
<td>ring opening metathesis polymerization</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Equivalent series resistance</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>SC</td>
<td>supercapacitor</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>STP</td>
<td>standard temperature and pressure</td>
</tr>
<tr>
<td>TBABF$_4$</td>
<td>tetrabutylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>TBASbF$_6$</td>
<td>tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>TEABF$_4$</td>
<td>tetraethylammonium tetrafluoroborate</td>
</tr>
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TEDGME  tetraethylene glycol dimethylether

TEM  transmission electron microscopy

TGA  thermogravimetric analysis

$V$  volt

$V$  voltage

$V_i$  initial voltage

Wh  Watt-hour

Wo  Warburg element

XPS  X-ray photoelectron spectroscopy

XRD  X-ray diffraction

$Z'$  real impedance

$Z''$  imaginary impedance

$\text{Zn(OAc)}_2$  zinc (II) acetate

$\mu$g  microgram

$\mu$m  micrometer

$\Omega$  Ohm

$\Delta t$  time of discharge or charge

$\mu$L  microliter
Chapter 1
Introductory Chapter

1 Statement of contributions

Portions of this chapter have been published. Bryony McAllister, Dr. Pengfei Li, and myself drafted the manuscript, which was edited by Prof. Dwight Seferos.

2 Introduction to Energy Storage Systems

2.1 Overview of the Field

Energy storage is imperative for the integration of intermittent renewable power sources (solar, wind, tidal) into the grid, the widespread adoption of electric vehicles, and the continued development of portable electronics, including emerging flexible and wearable applications. Electrochemical energy storage system (EESS) applications are growing enormously on multiple scales, from smart card microbatteries, to large-scale battery packs for electric vehicles, and warehouse-sized redox flow batteries. While much progress has been made, it is clear that higher performing, more versatile, smaller, lighter, and, importantly, economically viable energy storage solutions will be required in the future.

The materials used for EESSs are traditionally metal-based inorganic compounds, such as cobalt, lead, iron, nickel, or manganese-based materials for batteries and conductive carbon materials for supercapacitors (SCs). Inorganic materials rely on changes in metal oxidation state for charge storage and a concomitant balancing of the charged structure with specific counter-ions. In the case of intercalation compounds for metal-ion batteries, the counter-ion is specific to the crystal structure of the inorganic compound due to size restrictions in the crystal lattice, ionic conductivity, and reversibility of the redox reaction. This inherently restricts the versatility of inorganic compounds, where the same cathode material cannot be used for different series of alkali metal batteries such as lithium and sodium-ion. One of the biggest pitfalls of inorganic complexes is that they typically require extraction and synthetic methods that are harmful to the environment. Extraction can release toxic materials that are otherwise trapped underground. Synthesis can create large amounts of heavy metal waste and often requires energy intensive processing. Additionally, the inherent mechanical properties of these metal oxides make it
difficult for them to be used in batteries requiring mechanical flexibility unless nanostructuring is used. In order to realize the predicted widespread use of EESSs, these challenges must be overcome.

Organic materials provide an excellent opportunity to further improve existing energy storage technologies, and are a versatile platform to develop novel EESSs. Organic materials are abundant, relatively inexpensive, and their synthesis can be designed so that it is not energy intensive and produces minimal waste. Organic compounds are also structurally diverse, able to be functionalized with relative ease through many synthetic methods. This allows one to tune oxidation and reduction potentials to optimize the operating voltages of EESSs. Modifying the chemical structure is an ideal way to suit the needs of specific applications by changing capacity, solubility, crystal structure, electron transfer rates, ionic conductivity, and mechanical properties. Also, organic materials are typically not restricted by choice of counter-ion. This means that, to a certain extent, the same organic material can be useful for a wide variety of different energy storage devices such as lithium-ion, sodium-ion, multivalent-ion, and dual-ion batteries.

Organic materials have been studied as electrodes for EESSs since 1969, with the first report of an organic cathode material using dichloroisocyanuric acid. After this, multiple research groups tested a variety of organic small molecules such as quinones, di-anhydrides, and phthalocyanines. Poly(acetylene) were initially tested as a cathode material, followed by many other conjugated polymers such as polypyrrole, polythiophene, polyaniline, and derivatives thereof. Research on organic electrode materials for energy storage faded when inorganic transition metal complexes were developed that reversibly intercalate lithium ions at high potentials with high capacity. In the past decade, however, research on organic electrode materials has been reignited due to the increased demand for energy storage that is high performing, inexpensive, and able to accommodate the mechanical property and form factor needs in emerging devices such as flexible and wearable electronics.

2.2 General Working Principles of Energy Storage Systems

The working mechanism of any EESS relies on an inherent potential difference between two electrodes known as the operating voltage. The operating voltage of the device is dictated by the differences in redox potential of the positive and negative electrode. The potential difference is used to drive electrochemical reactions on either electrode when they are connected through an
external circuit. This creates a flow of electrons from the negative electrode to the positive electrode. The flow of electrons induces oxidation reactions on the negative electrode (anode) and reduction reactions on the positive electrode (cathode) when discharging. The charged electrodes are balanced by a concomitant flow of counter-ions. EESSs are grouped into a number of different categories depending on the composition of the electrodes, the counter-ions, and the nature of the redox reactions (Figure 1.1). This thesis will focus on two types of these devices: SCs and solid-electrode batteries.

Figure 1.1 Schematic depicting the working principle of (a) SCs, (b) metal-ion batteries, (c) dual-ion batteries, and (d) redox flow batteries. The insets show the ideal electrochemical behaviour of each type of device when measured using cyclic voltammetry and galvanostatic charging/discharging. Here, $V$ is voltage and $i$ is current. Adapted from reference 1. Published by the Royal Society of Chemistry.
3 Supercapacitors

3.1 Supercapacitor Working Principle

SCs are EESSs that are composed of a positive electrode, a negative electrode, an electrolyte, and a separator between them that prevents short-circuiting (Figure 1.1a). Their ability to store charge is described by their capacitance. In capacitors and SCs, capacitance is constant over a defined voltage window. In a galvanostatic charge/discharge experiment, an equal rise/fall in potential as a function of charge is observed. In a cyclic voltammetry (CV) experiment, this is observed as a constant current as a function of potential (inset Figure 1.1a).

SCs have power densities orders of magnitude higher than batteries and can store a significant amount of energy, although typically less than batteries. SCs are intermediate in terms of their power and energy densities compared to conventional capacitors and batteries (Figure 1.2). As such, they are ideal for complementing or replacing batteries in applications that require rapid charge/discharge, such as load-leveling, storage of energy generated from intermittent renewable power sources, and for acceleration and braking in electric vehicles. SCs are classified into two categories based on their mechanism of charge storage: electric double layer capacitors; and pseudocapacitors (Figure 1.3). Electric double layer capacitors are the more traditional type of SCs, and store charge electrostatically between the electrode and electrolyte interface. This type of capacitance relies on a surface charging of conductive materials, usually high surface area carbons, therefore capacitance is limited by surface area. Pseudocapacitors store charge through fast, reversible surface (or near surface) formal redox reactions. As Conway describes it, “pseudocapacitance arises when the extent of reaction, is some continuous function of potential so that a derivative arises that has properties of capacitance”. Pseudocapacitance arises from many different mechanisms and the work of Conway describes it in much greater detail.

3.2 Performance Metrics of Supercapacitors

The performance of SC materials is evaluated based on a series of important parameters. These include specific capacitance, operating potential, cycling stability, and coulombic efficiency. The capacitance, or amount of charge stored, can be calculated using cyclic voltammetry, galvanostatic-charge discharge experiments or electrochemical impedance spectroscopy, and is
reported either in terms of gravimetric (F g\(^{-1}\)), volumetric (F L\(^{-1}\)), or areal (F cm\(^{2}\)) capacitance. The general equation to calculate specific capacitance is described in equation (1):

\[
Specific\ capacitance = \frac{i}{m(dV/dt)}
\]  

(1)

**Figure 1.2** Ragone plot comparing the performance of various EESSs. Reprinted from reference 1. Published by the Royal Society of Chemistry.
Figure 1.3 Schematic representing the charge storage mechanism of electric double layer capacitors and pseudocapacitors. Adapted with permission from reference 17. Copyright 2013 American Chemical Society.

Here, $i$ is the current in amperes, $m$ is the mass of active material in grams, and $dV/dt$ is the change in voltage over the change in time in volts per second. The potential at which SC materials operate is important for the overall energy and power density of the devices. This is because the overall operating voltage of the SC device is proportional to the maximum power ($P_{\text{max}}$) and the energy density according to equations (2) and (3):

$$P_{\text{max}} = \frac{V_i^2}{4mR_s}$$

$$\text{energy density} = \frac{\text{specific capacitance} \times V^2}{2}$$

Here, $V_i$ is the initial voltage of the device in volts, $V$ is the device voltage, and $R_s$ is the equivalent series resistance in ohms.

The coulombic efficiency is measured by dividing the capacitance for discharging by the capacity for charging. This measures the ratio of charge put into the system compared to the charge coming out and is an indicator of whether the system has parasitic redox reactions occurring.
Importantly, SC electrode materials must have high cycling stability. Materials suitable for commercial devices must experience little capacity fade over thousands of cycles.

### 3.3 Electrode Materials for Supercapacitors

Due to their redox activity, organic materials used in SCs typically store charge by pseudocapacitance. Important pseudocapacitive materials include metal oxides and conjugated polymers. Metal oxides, such as RuO$_2$, have some of the highest specific capacitances, however they typically have low flexibility and conductivity (leading to limited rate capability), contain rare metals, and can be expensive. Conjugated polymers are promising alternatives to metal oxides to store energy in SCs because they can be synthesized from abundant materials, their properties can be tuned through synthetic modification, they are flexible, and are potentially inexpensive. Conjugated polymers are promising in different roles for SC electrodes other than to store energy, such as transparent current collectors.

Most research on organic SC materials has focused on p-dopable conjugated polymers such as polyaniline, polythiophene, and polypyrrole (Figure 1.4). However, the key to improvement and widespread implementation of pseudocapacitive SC technologies is innovation at the materials level. This hinges on uncovering the fundamental relationship between polymer structure and device performance. From an organic materials design standpoint, it is difficult to predict pseudocapacitive behaviour in organic compounds because, to the best of our knowledge, there are no quantitative guidelines or certain electronic properties of organic materials that can be modeled computationally to distinguish between battery-like or SC-like behaviour. Qualitatively, however, highly conductive organic materials seem to possess pseudocapacitive electrochemical profiles and this could be used as a guideline for designing new materials. This is supported by the fact that the majority of organic SC publications have focused on highly conductive conjugated polymers such as polythiophene, polyaniline, polypyrrole, and derivatives of these materials. In fact, most new SC organic materials are conjugated polymers, compared to the relatively small amount studied for battery applications. Current research in supercapacitors focuses on increasing cycling stability, energy density, power density, and decreasing the cost of the device.
Figure 1.4 Structures of common conjugated polymers studied for SC electrodes.

4 Solid-Electrode Batteries

Solid-electrode batteries are energy storage systems that store energy in solid materials that act as the negative electrode, the anode, and the positive electrode, the cathode (Figure 1.1b,c). This is in contrast to devices, such as redox flow batteries (Figure 1.1d), that store energy by a potential difference between an anolyte and catholyte where the redox species is dissolved in an electrolytic solution and is able to diffuse to a current collector for a redox event to occur and charge to flow. The focus of this discussion will be on metal-ion batteries and dual-ion batteries.

4.1 Metal-Ion Battery Working Principle

Batteries operate with a constant voltage defined, approximately, by the potential difference between the anode and cathode. Because of this, in a galvanostatic charge/discharge experiment the potential of the electrode or device ideally remains constant until the active material has been fully reduced (oxidized). In a CV experiment, one observes a reversible, sharp redox peak when a redox event occurs (inset Figure 1.1b, c, d).

Metal-ion batteries are the one of the most commonly researched EESSs. They are typically composed of an anode (negative electrode), a cathode (positive electrode), electrolyte (either aqueous, organic, solid-state\textsuperscript{20}, or polymeric\textsuperscript{21,22}), a separator (to prevent short circuiting), current collectors (to collect charge at each electrode), and a cell casing (to keep the components together and prevent exposure to the external environment). Metal-ion batteries are used for a wide variety of both portable and stationary applications for either primary or back-up power. In metal-ion batteries, the charged anodes and cathodes are balanced by the metal ion in a ‘rocking-chair’ type mechanism (Figure 1.1b). This is a strict requirement imposed by the definition of metal-ion batteries that should be clearly distinct from dual-ion batteries described below. Metal-ion batteries can be constructed with relatively small amounts of electrolyte because the ions balancing the charge at one electrode are constantly being replenished. Additionally, metal-ion...
batteries are very attractive candidates for use with solid-state electrolytes because the mobility of only one ion needs to be considered.

Metal-sulfur batteries are a relatively new subset of metal-ion batteries that use (organo)sulfur as an electrode. This is advantageous because sulfur is both inexpensive and has a high theoretical capacity \( (C_{\text{theor}}) \) of 1672 mAh g\(^{-1}\). Metal-sulfur batteries operate by the same mechanism as metal-ion batteries where both electrodes are balanced by metal-ions upon charging (discharging). The electrode that is not composed of sulfur can be composed of a variety of materials, as long as it is balanced by metal-ions in its charged or discharged state. This technology is still in development, but typically the cathode is composed of sulfur impregnated into conductive carbon in order to prevent polysulfide dissolution, which can eventually deplete the capacity of the device.\(^{23}\)

Metal-air batteries are the newest type of metal-ion battery. Here, the anode can be a number of different materials but the cathode is typically composed of a conductive carbon support with a high surface area that is impregnated with an oxygen reduction/oxidation catalyst. The cathode is exposed to either pure oxygen or ambient air. Oxygen diffuses to the cathode and is reduced to either its alkali metal superoxide or peroxide, the exact species being highly dependent on the metal-ion used.\(^{24}\) The \( C_{\text{theor}} \) of reducing oxygen to peroxide provides a maximum capacity of 1168 mAh g\(^{-1}\) (Li\(_2\)O\(_2\)) with a higher voltage than metal-sulfur batteries (2.15 vs 2.96 V vs Li/Li\(^+\)) allowing metal-air batteries to have a much greater energy density (up to \( \sim 3500 \) Wh kg\(^{-1}\)) based on the mass of lithium and oxygen alone.\(^{25}\)

### 4.2 Dual-Ion Battery Working Principle

In a dual-ion battery the charged anodes and cathodes are balanced by cations and anions respectively (Figure 1.1c). Dual-ion batteries encompass a wide variety of electrolytes and electrodes. The anodes range from negative charge-accepting compounds to reduced metals and inorganic materials. The cathodes can also be a wide variety of materials as long as they are balanced by anions when charged. Others have referred to these systems as organic batteries, metal organic batteries, and radical polymer batteries.\(^{26,27}\) Although these terms may be used to describe the electrodes, the convention of naming solid electrode batteries based on the mobile counter-ions is upheld with this nomenclature.
Dual-ion batteries rely on the diffusion of both anions and cations in the electrolyte to balance charge at the cathode and anode respectively. This requires a relatively large amount of electrolyte compared to metal-ion batteries because the ions are not replenished by a ‘rocking-chair’ type mechanism. Overall, this increases the mass of the device, decreasing the capacity of a full cell. However, the use of a positive charge-accepting cathode does have advantages. Dual-ion batteries do not require one electrode to contain metal ions. The electrodes can both be assembled in the uncharged state and without pre-treatment steps, such as electrochemical doping. They also can be paired with a diverse set of electrode materials. Much work has been carried out on radical-type polymers as an electrode, especially the use of 2,2,6,6-tetramethylpiperidinyloxyl as the redox-active unit. 28-31

4.3 Performance Metrics of Solid Electrode Batteries

A number of performance metrics need to be considered for the development of electrode materials for solid electrode batteries. These performance metrics can be used to estimate the overall performance of the device. The $C_{\text{theor}}$ of a material is the maximum amount of charge a material can hold with respect to its mass. It is typically reported in mAh g$^{-1}$ and is calculated using equation (4):

$$C_{\text{theor}} = \frac{nF}{3.6 \times M}$$

(4)

Here, $n$ is the maximum number of charges the compound can accept (or give up), $F$ is Faraday’s constant, and $M$ is the molecular weight of the compound in g mol$^{-1}$. Typically, the $C_{\text{theor}}$ is used to assess how well the material could perform under optimized conditions. If the $C_{\text{theor}}$ is reached, then it is expected that the electrode cannot accept any more charge.

The specific capacity is the measured capacity of the electrode at a specific current density for either charging or discharging. The capacity is reported in mAh g$^{-1}$ and by measuring capacity at different rates (usually reported as a C-rate, where 1 C is the amount of current it would take to collect the total charge of the $C_{\text{theor}}$ in 1 hour) the rate capabilities of the electrode can be determined. The capacity is typically calculated from galvanostatic charge/discharge curves using equation (5):

$$...$$
Here, $\Delta t$ is the time of discharging (charging) in seconds. If the capacity at low and high rates are similar, it can be said that the electrode has high rate capabilities. This typically depends on the electron transfer kinetics of the compound, and the electronic and ionic conductivity of the electrode and electrolyte.

The coulombic efficiency of batteries is measured by dividing the capacity for discharging by the capacity for charging. This provides insight into the reversibility of the redox reactions and indicates whether any side reactions occur with the electrode and electrolyte. The coulombic efficiency is a good indicator of whether a stable solid electrolyte interface is formed in the charging cycles and if the material itself will be stable upon extended cycling. If the coulombic efficiency is low in the first charging cycles but increases to $\sim$100% afterwards, it is typically attributed to the formation of a solid electrolyte interface.

The cycling stability is an important parameter that quantifies the retention of capacity upon charging and discharging the electrode multiple times. Usually this measurement is performed under galvanostatic conditions and is reported as a percentage of the initial capacity after a specified number of cycles. The current density (or C-rate) must be specified for these measurements because the rate can have a significant effect on the cycling stability. This effect is especially pronounced if capacity fading is due to electrode dissolution, which is a common problem with organic electrode materials.

The potential at which the redox process(es) occur(s) is also a very important parameter. Combined with the capacity, the redox potential can be used to predict the energy density of the device when paired with an anode/cathode of known redox potential. To have a high energy density, the potential of cathode material should be as high as possible while that of anode material should be as low as possible within the electrochemical window of the electrolyte, or within the electrolytes’ ability to form a stable solid electrolyte interface. Although an ideal battery maintains a constant voltage while it discharges, real batteries tend to have a decreased voltage with decreasing state-of-charge. This creates a sloping voltage plateau that is especially apparent in polymeric electrodes or in electrodes with multiple redox events. The reduction and oxidation
peak splitting, or hysteresis, is also important to provide insight into electron transfer kinetics, and to predict the energy efficiency of the device.

The energy density of a fully assembled device is also an important parameter that quantifies how much energy the EESS can store. The energy density is calculated using equation (6):

$$energy\ density = \frac{QV}{m}$$ (6)

Here, $Q$ is the total charge of the battery in either coulombs or mAh. The energy density is usually reported in Wh kg$^{-1}$ or Wh L$^{-1}$ if volume is used instead of mass, although the standard units are J kg$^{-1}$ or J L$^{-1}$.

Power density is also an important parameter that is used to quantify how fast energy can be released from the EESS. Power density can be calculated using equation (7):

$$power\ density = \frac{energy\ density}{\Delta t}$$ (7)

The power density is typically reported in W kg$^{-1}$ or W L$^{-1}$.

While energy and power density are important parameters to gauge the performance of EESSs, these pertain to fully assembled devices and relate to the combined performance of all aspects of the device including both the anode and cathode, the electrolyte, membrane, and resistances associated with various aspects of the device. Therefore, when designing single electrode materials for EESSs, it is more important to report redox potentials, resistances, and capacities since the energy and power densities can be approximated for a fully assembled device using any counter electrode. Additionally, it is important to report the electrode formulations and procedure for electrode manufacturing, electrode morphologies, electrode thicknesses, electrolyte, and the conditions under which the experiments are being performed. All of these factors can have an enormous effect on device performance. For example, in our lab we have observed that changes in the electrolyte solvent can influence the electrochemical properties, such as the capacity, by as much as an order of magnitude. Therefore, reporting the details of electrode preparation and testing in full is very important.
The relevant chapters on solid electrode batteries in this thesis focus solely on metal-ion batteries and, therefore, the rest of this discussion will be on them.

4.4 Electrode Materials for Metal-Ion Batteries

Organic materials can be used as the anode and/or cathode in metal-ion batteries. Typically, organic materials are synthesized in the neutral state without charge-balancing ions incorporated into their structure. For metal-ion batteries to function, the opposite electrode must contain the charge-balancing metal ions. For example, if a cathode material does not contain metal ions in its structure, the anode must contain metal ions and vice versa. The consequence is that to satisfy this requirement, the counter electrode is usually a reduced metal (e.g. magnesium, sodium, lithium) regardless of whether the organic electrode is the anode or cathode material.

Recent work on organic electrodes for metal-ion batteries has focussed on a number of aspects in order to improve performance and the overall cost of the entire device. The relatively low potential at which organic electrodes operate limits the overall energy and power density when incorporated into a full device. By adding electron withdrawing groups (EWGs), the potential at which the organic cathode accepts an electron is increased. Conversely, adding electron-donating groups (EDGs) to anode materials lowers the reduction potential and also increases the operating potential of the device. These increase the overall operating voltage of the device, but also has the effect of decreasing the $C_{\text{theor}}$ since the EWG/EDGs typically add mass to the compound without affecting the number of electrons it can accept. Other popular strategies to tune the redox potential include substituting heteroatoms into the aromatic core, and developing different isomers without significantly changing the mass:charge ratio of the compound.

Another popular strategy to overcome the low voltages of organic compounds is to use compounds that inherently have a high mass:charge ratio. These have high a $C_{\text{theor}}$ and can have high energy densities in a full device without necessarily having a high voltage. Obviously, the best solution would be to combine the two strategies of increasing voltage and $C_{\text{theor}}$, however more work is needed to find an optimal trade-off between $C_{\text{theor}}$ and voltage.

Decreasing the cost of the electrode, especially the cathode, is a major motivation for the investigation of organic electrode materials. This is because the cathode in lithium-ion batteries can account for ~30% of the cost of the device. Although the investigation of organic electrode
materials with high performance is important, it is equally important to develop low cost materials for applications that do not necessarily require a high energy or power density. The use of electrolytes other than lithium can also greatly decrease the cost of the device. Although lithium has the lowest reduction potential and highest \( C_{\text{theor}} \) out of all the alkali metals, it is also the most expensive. It is expected that the cost of lithium will continue to increase due to depletion of resources.\(^4\)

Pure organic materials typically used for solid-electrode batteries can be grouped into four different classes: 1) small molecules including arylene diimides,\(^{34-36}\) organic carbonyl compounds,\(^{37-39}\) imine-containing compounds,\(^{40,41}\) and other more exotic compounds such as fullerenes\(^{42}\); 2) conjugated polymers\(^{43,44}\); 3) non-conjugated polymers including pendant polymers\(^{28,45,46}\) and polymers that have aromatic segments in the backbone linked through non-conjugated segments,\(^{47,48}\) and; 4) covalent organic frameworks and other cross-linked polymers (Figure 1.5).\(^{49-52}\) There is also a wealth of research devoted to electrodes containing organic compounds covalently attached to carbon nanostructures,\(^{53,54}\) and hybridized with inorganic components.\(^{55}\)

**Figure 1.5** Representative structures from (a) small molecule, (b) conjugated polymer, (c) non-conjugated polymer, and (d) covalent organic framework and cross-linked polymer organic electrodes.
5 Scope of Thesis

In this work, I describe my efforts in developing organic materials for energy storage devices and my investigation into the fundamentals of their performance. I design, model, synthesize, and characterize the electrode materials as well as assemble, test, and interpret the data from full devices. From materials design to device construction, I draw conclusions about the fundamental properties of organic electrode materials and create general design rules that will help in the effort to create high performance materials. Each chapter focuses on a specific problem of organic electrode materials, the design of novel materials with predicted properties to address these issues, and the investigation into the fundamental electrochemical properties of the materials and why they behave that way. Determining why materials have the properties that they do, for both high- and low-performing systems, is important for developing predictive methods for materials performance.

Chapter 2 examines a polyfullerene material for SC applications. A similar negative charge accepting material was previously reported to possess electrochemical properties well-suited for SCs, however its application was never pursued. Negative charge accepting materials for SC applications are rare in the literature and in order to achieve high power, high energy organic SCs, negative charge accepting materials that reduce at low voltages are required to pair with the relatively well-developed positive charge accepting materials. The polyfullerene material has a favourable redox potential and high capacity that affords high power SCs when paired with a positive charge accepting polymer. However, its limited cycling stability proved to be problematic and through empirical investigation a key degradation mechanism is uncovered.

Chapter 3 was originally designed to build upon the lessons from Chapter 2. By using a biologically-derived material to address the cost issues for fullerene-based materials, I attempted to design a SC material to resolve the stability issues of the polyfullerene material. (Un)fortunately, this idea did not work out as expected and it was found that the material has electrochemical properties that are more suitable for battery applications. Testing this material as a lithium-ion battery cathode, a high capacity is achieved. However, the cycling stability of the material is surprisingly poor. Using a combination of computational chemistry, materials characterization, and chemical intuition, a new degradation mechanism is uncovered and
important design criteria for the development of stable organic electrodes for EESSs are developed.

The last half of this thesis focuses on triptycene-based frameworks for lithium-ion batteries. This work was inspired by the large amount of work on triptycene frameworks for gas storage and by the work of a post-doc in our group who performed initial calculations on these types of materials. Additionally, triptycene-based frameworks are rigid, permanently porous structures that address the issues of cycling stability in Chapters 2 and 3. I designed and tested this new type of framework for electrode materials using well-known redox motifs. Design criteria are elucidated that can be implemented into the design of electrodes with high capacity, stability, and voltage. This work is split into two chapters, investigating a cathode material in Chapter 4, and an anode material in Chapter 5. Here, I draw conclusions on the utility of triptycene frameworks for electrode materials in lithium-ion batteries based on the materials’ properties. Specifically, I find that the linker units for these materials are critically important for the performance of these materials. Choosing the correct linker leads to a material with high crystallinity and small aggregate size, and an electrode with excellent stability and high usage of active material.

My hope is that readers will be able to use this work to aid in the rational design of high performance organic electrode materials.

6 References

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Chapter 2
Polyfullerene Electrodes for High Power Supercapacitors

1 Contributing Statement

Portions of this chapter have been published. Dr. Paul DiCarmine provided guidance throughout this project and insight into the design of the supercapacitor. I performed all the synthesis, characterization, and testing presented in this chapter. I wrote the manuscript, which was edited by Dr. Paul DiCarmine and Prof. Dwight Seferos.

2 Introduction

SCs are important for energy storage solutions because they store a significant amount of energy and deliver high power. Additionally, integrating SCs with batteries in electronic devices can help reduce the size of the EESS, the time needed for charging, and extend the life of the battery. Pseudocapacitive materials, such as organic conjugated polymers and inorganic metal oxides, are highly attractive for SCs because they store charge both Faradaically and non-Faradaically, providing a much higher capacitance than traditional carbon-based electrodes. Conjugated polymers, due to their low cost, are becoming widely recognized as a cheap and highly capacitive replacement for activated carbon SC electrodes. Unfortunately, they are mainly limited to positive charge-accepting materials that are only stable in the neutral or positively charged state. Using only positive charge-accepting polymers limits the operating potential, energy, and power of the device.

The design of new electrode materials, electrolytes, the modification of electrode surfaces, and the optimization of electrode architecture are critically important for SC research, as all device components have a large effect on performance. For SCs using pseudocapacitive materials, the operating potential is the potential difference between the extremes of each electrode’s Faradaic potential window. Using only positive charge-accepting materials for both electrodes restricts the potential; when the device is charged, one electrode is charged and the other is discharged and when the device is fully discharged, each electrode is at an intermediately charged state. The consequence is that the full charge in each electrode is never fully harnessed and the operating potential is limited. A highly attractive configuration is an asymmetric device where both positive and negative charge-accepting pseudocapacitive materials...
are used as the positive and negative electrodes respectively. This way, the device operating voltage is extended and the full charge on each electrode is utilized.

Fullerene C\textsubscript{60} has become an important material in organic electronics due to its high electron affinity, three-fold degenerate LUMO, and three-dimensional electron transporting abilities\textsuperscript{25,26}. Each C\textsubscript{60} molecule can reversibly accept up to five electrons at room temperature making it an excellent candidate as a highly capacitive negative electrode for SCs\textsuperscript{27,28}. Unfortunately, the well-defined localized reductions of pristine C\textsubscript{60} give rise to large variations in current as a function of potential, prohibiting its use as a negative pseudocapacitive material. The use of fullerene derivatives that have delocalized charges and broadened reduction waves still remains relatively unexplored in SCs. Egashira et al. reported the use of toluene-insoluble fullerene-soot prepared by pyrolyzing C\textsubscript{60} in a symmetric SC with a 2.5 V operating potential. The authors, however, attribute the capacitance to a double-layer charge storage mechanism\textsuperscript{29}. Winkler et al. prepared a C\textsubscript{60}-Pd polymer that exhibited either a dominant pseudocapacitive behavior or double-layer capacitive behavior depending on the amount of Pd that was incorporated\textsuperscript{30}. This material exhibits high capacitance (200 F g\textsuperscript{-1}) for a single electrode material, however the use of a stoichiometric amount of Pd makes this material impractical for commercial devices.

Herein, I describe a C\textsubscript{60} fullerene polymer (PC\textsubscript{60}) that is a highly pseudocapacitive negative charge-accepting material for SCs. A device using PC\textsubscript{60} as a negative electrode and PEDOT as a positive electrode has a large operating potential (2.2 V), and high maximum power (4300 kW L\textsuperscript{-1}) and energy density (5.3 ± 0.7 Wh L\textsuperscript{-1} at 3.8 A cm\textsuperscript{-3}). The asymmetric device architecture affords high \textit{P}\textsubscript{max} relative to that of the symmetric capacitors constructed using PEDOT only. These results highlight the utility of using negative charge-accepting organics for electrochemical energy storage.

3 Results and Discussion

3.1 Synthesis and Characterization

C\textsubscript{60} was electropolymerized on gold-coated Kapton\textsuperscript{TM} by cycling the potential from 1.86 V to -1.84 V (versus Fe/Fe\textsuperscript{3+}) in dichloromethane containing 0.15 mM C\textsubscript{60}/0.05 M TBASbF\textsubscript{6}, adapted from literature procedures\textsuperscript{31}. The non-nucleophilic antimony salt was used instead of the arsenic salt used by Bruno et al., as it has a reduced toxicity\textsuperscript{32,33}. Electrochemical oxidation of C\textsubscript{60} avoids
the need for binders and deposits the film directly on the current collector. Cycling two hundred times at 400 mV s\(^{-1}\) produces an increase in the current with increasing cycle numbers, indicative of electropolymerization (Figure 2.1a).

![Graph showing current vs. potential](image)

**Figure 2.1** (a) Representative oxidative polymerization of C\(_{60}\). (b) Proposed structure of PC\(_{60}\).

As there is a large variation in morphology and structure of reported C\(_{60}\) polymers, I chose to begin this study by carefully examining the film with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The morphology of the film is similar to some of the reported electropolymerized C\(_{60}\) polymers.\(^{31,34}\) The film has a rough surface due to the presence of small polymer particles (Figure 2.2a). The SEM cross-section shows that the film is approximately 170 nm thick (Figure 2.2b). The film is also porous, as observed by TEM, which is favorable because electrolyte must easily penetrate the entire film during the charging and discharging processes (Figure 2.2c).

Attempts to characterize the film by XRD yield only a small diffraction peak corresponding to a d-spacing of 0.93 nm, consistent with C\(_{60}\) polymers joined together by cyclobutane rings (Figure 2.1b),\(^{35-37}\) and a large amorphous halo demonstrating that an amorphous polymer was formed (Figure 2.3). When compared with pristine C\(_{60}\), the Raman spectrum of PC\(_{60}\) contains a number of features that are in agreement with C\(_{60}\) polymers such as a downshift in Raman frequency and lower intensity (Figure 2.4a). The A\(_{g}(2)\) mode shifts from 1467 cm\(^{-1}\) to 1454 cm\(^{-1}\) suggesting that the polymer is branched.\(^{38}\) The bonds connecting the C\(_{60}\) molecules are likely caused by [2+2] cycloaddition reactions between the six-member rings in the C\(_{60}\) monomer, creating the cyclobutane-like linkages.\(^{39}\)
Figure 2.2 (a) Top-view and (b) cross-sectional SEM image of the electropolymerized PC$_{60}$ polymer. (c) TEM image of the PC$_{60}$ polymer deposited from an ethanol suspension. (d) Photograph of the assembled SC with electrical connections and (e) schematic of the assembled SC. The PEDOT electrode is partially cut away for clarity.

The FTIR spectrum of PC$_{60}$ is complex compared to C$_{60}$ or the electrolyte TBASbF$_6$ (Figure 2.4b). The bands attributed to PC$_{60}$ are located at 1634 and 1065 cm$^{-1}$ and are likely caused by vibrations associated with the cyclobutane linkages between the C$_{60}$ cages. The bands at 3403 and 1713 cm$^{-1}$ are due to adsorbed water$^{31}$ and the C-H stretches at 2938 and 2869 cm$^{-1}$ and peaks located at 1458, 1376, and 733 cm$^{-1}$ are all attributed to various absorption processes of the supporting electrolyte. Large peaks in the secondary-ion mass spectrum corresponding to C$_{60}^-$ (720 m/z) and C$_{60-n}^-$ are observed (Figure 2.4c,d). Importantly, higher order C$_{60+n}^-$ species as well as the C$_{120}^-$ cluster (1440 m/z) are also observed and demonstrate that an addition reaction between the monomers has occurred. The lower intensity of the 1200–1800 mass range is due to the instability of the higher order C$_n$ species.$^{31}$ The mass limit of the instrument prohibits examining larger species (>1800 m/z).
Figure 2.3 XRD of PC$_{60}$ film electropolymerized onto gold-covered silicon wafer.

The film contains fluorine, antimony, oxygen, carbon, and gold from the substrate (Figure 2.5a) as confirmed by XPS. The carbon peak is asymmetric (Figure 2.5b) due to the presence of carbon atoms in different covalent environments, as well as the presence of ‘shake-up’ features from the highly conjugated C$_{60}$ cages. The dominant peak (C1s A) is assigned to carbon atoms that are in the C$_{60}$ cage. The third peak (C1s C) is assigned to the sp$^3$ hybridized carbon atoms that form the cyclobutane rings. The remaining carbon peaks (C1s B, and C1s D) are assigned to the tetrabutyl groups on the ammonium counterion.

3.2 Electrochemical Performance of the Polyfullerene Electrode

Having fully characterized the composition of the PC$_{60}$ film, I next determined the electrochemical properties. The PC$_{60}$ electrode exhibits a nearly ideal triangular charge-discharge behaviour at high current densities when cycled in the carefully purified TBASbF$_6$ electrolyte with a coulombic efficiency of 60% at 12 A cm$^{-2}$ (Figure 2.6a). When the electrochemistry was examined in a 0.1 M TEABF$_4$/acetonitrile electrolyte, the electrode exhibited close to ideal behaviour at high current densities but became asymmetric at lower current densities with coulombic efficiencies of 39% and 25% at 100 A cm$^{-2}$ and 10 A cm$^{-2}$ respectively. This lower coulombic efficiency is likely due to charge leakage occurring at the most negative potentials caused by impurities such as small amounts of water or oxygen in the electrolyte. Although a decrease in coulombic efficiency was observed for the TEABF$_4$ electrolyte it was used throughout the rest of the study instead of the TBASbF$_6$ electrolyte used for the synthesis, due to increased electrode stability with smaller cations. This phenomenon is discussed later.
Figure 2.4 (a) Raman spectra of $C_{60}$ and PC$_{60}$. (b) FTIR spectra of $C_{60}$, TBASbF$_6$ and PC$_{60}$. (c and d) TOF-SIMS spectrum of PC$_{60}$ (c) from 600 m/z to 800 m/z and (d) 1200 m/z to 1800 m/z. Starred peaks correspond to the monomer and dimer species.

Figure 2.5 (a) Full survey of the XPS spectrum of PC$_{60}$ and (b) the deconvoluted carbon XPS.

The film exhibits a pseudo-rectangular cyclic voltammogram for scan rates up to 1 V s$^{-1}$ (Figure 2.6b). The absence of any sharp redox peaks indicates that the charges in PC$_{60}$ are significantly delocalized. A double-layer type charge storage mechanism may also play a large role in the capacitive behaviour. The capacitance (Figure 2.6c) of the PC$_{60}$ electrode ranges from 110 – 220 F cm$^{-3}$ (at current densities from 100 – 10 A cm$^{-2}$, respectively). Capacitance decreases as the
current density increases due to limitations imposed by resistance at high rates. PC₆₀ has a significantly larger volumetric capacitance than a similarly prepared PEDOT electrode (90 nm thick, 87 F cm⁻³ at 10 A cm⁻³) likely due to the ability of PC₆₀ to accept more electrons per monomer (Table 2.1).⁴²

Table 2.1 Capacitance values for individual electrodes.

<table>
<thead>
<tr>
<th>Current Density [A cm⁻³]</th>
<th>PC₆₀ capacitance [F cm⁻³]</th>
<th>PEDOT capacitance [F cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>220</td>
<td>87</td>
</tr>
<tr>
<td>20</td>
<td>190</td>
<td>86</td>
</tr>
<tr>
<td>50</td>
<td>150</td>
<td>75</td>
</tr>
<tr>
<td>100</td>
<td>110</td>
<td>62</td>
</tr>
</tbody>
</table>

Figure 2.6 (a) Galvanostatic charge-discharge curves of the PC₆₀ electrode in a 0.1 M TBASbF₆/acetonitrile electrolyte. (b) Cyclic voltammograms of the PC₆₀ electrode in a 0.1 M
TEABF₄/acetonitrile electrolyte. (c) Capacitance versus current density for PC₆₀ and PEDOT electrodes. (d) Complex plane impedance plot of PC₆₀ electrode at various potentials.

I next probed the impedance of the electrode at different potentials using EIS (Figure 2.6d). The PC₆₀ electrode exhibits a semicircle at high frequencies, typical of SCs, and an arc shape at low frequencies, deviating from the linear response of ideal SCs. The non-ideal curvature of the line can be explained by the presence of irreversible trap sites that become populated preferentially at low charging potentials. Additionally, the RC time constants were calculated from the Bode plots (Figure 2.7). The time constants for PC₆₀ and PEDOT are 473 ms and 661 ms respectively, showing the superior frequency response of the PC₆₀ film.

![Bode plot of PC₆₀ and PEDOT electrodes at their discharged states.](image)

**Figure 2.7** Bode plot of PC₆₀ and PEDOT electrodes at their discharged states.

The electrode exhibits degradation when scanned for one hundred and fifty cycles in a TBASbF₆ electrolyte (Figure 2.8a), however smaller cations can increase the stability of negative charge accepting polymers. I therefore examined the effect of four different salts: TBASbF₆, TEABF₄, NaBF₄, and LiBF₄. The shape of the voltammogram is vastly different between the alkyl ammonium and the alkali salts (Figure 2.8b). The alkyl ammonium salts allow the charging to be delocalized, broadening the reductions and giving reversible capacitive characteristics. The alkali salts on the other hand on display a strong irreversible reduction. This is attributed to trapped charges and the hard nature of the alkali cations, which “pin” and localize the charged state.

To determine whether the size of the alkyl ammonium salt has an effect on stability, CV was performed on PC₆₀ films with a 0.1 M solution of TBABF₄ and TEABF₄ (Figure 2.9). Cycling the
film using TBABF₄ degrades the electrode, losing its capacitive characteristics completely after 250 cycles, while using TEABF₄ the film maintains its capacitive characteristics until 400 cycles. This suggests that the degradation of the film is caused by mechanical stresses associated with counter-ion flow into the film upon charging. Stability could be further improved by limiting the potential range in which the electrode operates or adding carbon nanotubes, however these experiments were beyond the scope of this work.

**Figure 2.8** (a) Cyclic voltammetry curves of PC₆₀ when cycled 250 times at 100 mV s⁻¹ in 0.1 M TBASbF₆ acetonitrile electrolyte. (b) Cyclic voltammograms of the PC₆₀ electrode in various salt/acetonitrile electrolytes.

**Figure 2.9** Cycling stability of PC₆₀ electrode in 0.1 M solution of (a) TBABF₄ and (b) TEABF₄ in acetonitrile. Scan rate is 100 mV s⁻¹.
SCs with a PEDOT positive electrode (290 nm thickness) and PC\textsubscript{60} negative electrode (170 nm thickness) were constructed and used to demonstrate the utility of a PC\textsubscript{60} film in an asymmetric SC. The PEDOT electrode was thicker in order to balance the charge on each of the electrodes. This is required to prevent each electrode from becoming overcharged/discharged and to use the entire redox activity of each electrode. A symmetric PEDOT SC (290 nm thickness for each electrode) was also constructed and used for comparison purposes (Figure 2.10). The potential range with the most current (1.2 – 2.2 V) occurs when both PC\textsubscript{60} and PEDOT electrodes are operating in their Faradaic potential window (Figure 2.11, Figure 2.12a). The large Faradaic current in the high potential region is favourable since most of the charge delivered occurs at high cell voltages.\textsuperscript{2} The charge-discharge behaviour of the PC\textsubscript{60}/PEDOT SC deviates somewhat from the ideal triangular shape (Figure 2.12b). This is likely due to the mismatch of the electrodes, which is present in many other asymmetric configurations found in the literature,\textsuperscript{7,47-49} and due to the charge leakage effect as discussed previously. The symmetric PEDOT/PEDOT SC exhibits the highest capacitance out of the devices (22 ± 0 F cm\textsuperscript{-3} at 0.11 mA) followed by PC\textsubscript{60}/PEDOT (7.9 ± 1.1 F cm\textsuperscript{-3} at 0.11 mA) (Table 2.2). Although the PEDOT/PEDOT SC has about three times the capacitance of the PC\textsubscript{60}/PEDOT SC, the charging takes place over a more narrow potential window. As a result, the energy density of PC\textsubscript{60}/PEDOT (5.3 ± 0.7 Wh L\textsuperscript{-1}) is comparable to PEDOT/PEDOT (4.5 ± 0.4 Wh L\textsuperscript{-1}) due to its extended potential window. The extended potential window gives the PC\textsubscript{60}/PEDOT SC almost five times greater $P_{\text{max}}$ than the PEDOT/PEDOT SC (860 kW L\textsuperscript{-1}) achieving an impressive 4270 kW L\textsuperscript{-1} and average power values range from two to three times greater than the PEDOT/PEDOT device. The values from Table 2.2 were used to construct a Ragone plot (Figure 2.12c).

It is recognized that the PC\textsubscript{60}/PEDOT SC has superior power performance compared to the symmetric PEDOT/PEDOT device as well as compared to a commercially available 3 V activated carbon SC and a 3.6 V Li ion battery. The stability of the asymmetric SC was also examined by CV (Figure 2.12d). A significant amount of capacitance is lost after the first 50 cycles and the Faradaic contribution of the capacitance is almost completely diminished after 250 cycles. The instability may be due to charge leakage in the PC\textsubscript{60} electrode, causing the potential differences between the two electrodes to change on timescales faster than the scan rate as well as contributions from possible reactions between the poly(methylmethacrylate) and the highly reduced PC\textsubscript{60}. This stability matched or exceeded that obtained with other systems at the time
using positive and negative charge-accepting polymers for the electrodes when cycled at potentials greater than 2.0 V.5,8

Figure 2.10 (a) Cyclic voltammogram at 100 mV s\(^{-1}\) and (b) charge-discharge experiment of a PEDOT/PEDOT symmetric SC in 0.1 M TEABF\(_4\)/acetonitrile/15 wt % poly(methylnethacrylate).

Figure 2.11 Overlapping cyclic voltammogram of PC\(_{60}\) and PEDOT electrodes showing the potential window of the asymmetric SC. Scan rate is 100 mV s\(^{-1}\).

4 Conclusions

In conclusion, a C\(_{60}\) polymer was electrochemically synthesized and characterized. The C\(_{60}\) monomers are joined together by a cyclobutane ring, forming a branched polymer. The polymer exhibits negative charge-accepting pseudocapacitive behaviour, which is ideal for n-type SC
materials. Whereas the best conductive polymers have a charge density below 0.5 per monomer, \( C_{60} \) monomers are able to accept multiple electrons making the material highly capacitive. Due to a larger operating potential, asymmetric \( PC_{60}/PEDOT \) SCs exhibit comparable energy densities with symmetric PEDOT/PEDOT SCs even though the capacitance of the device is substantially lower. The \( P_{\text{max}} \) of the \( PC_{60}/PEDOT \) device, however, is greater than four times that of the symmetric PEDOT SC due to the larger operating potential. Overall, this work demonstrates the advantage of using an organic negative charge-accepting material as a negative electrode for SCs.

**Figure 2.12** (a) Cyclic voltammogram of \( PC_{60}/PEDOT \) SC in 0.1 M TEABF\(_4\)/acetonitrile/15 wt \% poly(methylmethacrylate) at 100 mV s\(^{-1}\). (b) Galvanostatic charge/discharge curve of the \( PC_{60}/PEDOT \) SC at 3.5 mA cm\(^{-3}\) and 7.0 A cm\(^{-3}\). (c) Ragone plot of constructed SC plotted with a commercially available 3 V 0.2 F activated carbon SC and a 3.6 V 110 mAh Li ion battery. The lines are shown to guide the eye. (d) Cycling stability of an asymmetric \( PC_{60}/PEDOT \) device. Scan rate is 100 mV s\(^{-1}\).
Table 2.2 Capacitance, energy density, power density at different applied currents and equivalent series resistance for assembled SCs.

<table>
<thead>
<tr>
<th>Applied Current [mA]</th>
<th>Performance Metrics</th>
<th>Symmetric PEDOT/PEDOT device(^a) ((\Omega))</th>
<th>Asymmetric PEDOT/PC(_{60}) device(^b) ((\Omega))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>Capacitance [F cm(^{-3})]</td>
<td>22 ± 0 ((1.1 ± 0.1 \times 10^{-2}))</td>
<td>7.9 ± 1.1 ((7.7 ± 1.1 \times 10^{-2}))</td>
</tr>
<tr>
<td></td>
<td>Power Density [W L(^{-1})]</td>
<td>1600 ± 0 ((2.0 ± 0.4 \times 10^{-1}))</td>
<td>3500 ± 300 ((3.4 ± 0.3 \times 10^{-1}))</td>
</tr>
<tr>
<td></td>
<td>Energy Density [Wh L(^{-1})]</td>
<td>4.5 ± 0.4 ((5.6 ± 0.5 \times 10^{-2}))</td>
<td>5.3 ± 0.7 ((5.2 ± 0.7 \times 10^{-2}))</td>
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<tr>
<td>0.22</td>
<td>Capacitance [F cm(^{-3})]</td>
<td>21 ± 0 ((1.1 ± 0.1 \times 10^{-2}))</td>
<td>6.9 ± 1.1 ((6.7 ± 1.1 \times 10^{-2}))</td>
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<tr>
<td></td>
<td>Power Density [W L(^{-1})]</td>
<td>3200 ± 100 ((4.0 ± 0.1 \times 10^{-1}))</td>
<td>7200 ± 700 ((7.1 ± 0.7 \times 10^{-1}))</td>
</tr>
<tr>
<td></td>
<td>Energy Density [Wh L(^{-1})]</td>
<td>4.5 ± 0.3 ((5.5 ± 0.4 \times 10^{-2}))</td>
<td>4.6 ± 0.7 ((4.5 ± 0.7 \times 10^{-2}))</td>
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<tr>
<td>0.55</td>
<td>Capacitance [F cm(^{-3})]</td>
<td>20 ± 0 ((10 ± 0 \times 10^{-3}))</td>
<td>5.3 ± 1.3 ((5.2 ± 1.2 \times 10^{-3}))</td>
</tr>
<tr>
<td></td>
<td>Power Density [W L(^{-1})]</td>
<td>8100 ± 300 ((9.9 ± 0.4 \times 10^{-1}))</td>
<td>19000 ± 2000 ((1.9 ± 0.2))</td>
</tr>
<tr>
<td></td>
<td>Energy Density [Wh L(^{-1})]</td>
<td>4.3 ± 0.1 ((5.3 ± 0.2 \times 10^{-2}))</td>
<td>4.0 ± 0.8 ((3.9 ± 0.8 \times 10^{-2}))</td>
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<td>1.1</td>
<td>Capacitance [F cm(^{-3})]</td>
<td>20 ± 0 ((10 ± 0 \times 10^{-3}))</td>
<td>5.3 ± 1.3 ((5.2 ± 1.2 \times 10^{-3}))</td>
</tr>
<tr>
<td></td>
<td>Power Density [W L(^{-1})]</td>
<td>16000 ± 1000 ((2.0 ± 0.1))</td>
<td>41000 ± 2000 ((4.0 ± 2.3))</td>
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<tr>
<td></td>
<td>Energy Density [Wh L(^{-1})]</td>
<td>4.1 ± 0.1 ((5.0 ± 0.1 \times 10^{-2}))</td>
<td>3.6 ± 0.9 ((3.5 ± 0.9 \times 10^{-2}))</td>
</tr>
<tr>
<td>2.2</td>
<td>Capacitance [F cm(^{-3})]</td>
<td>19 ± 1 ((9.1 ± 0.4 \times 10^{-3}))</td>
<td>4.6 ± 1.4 ((4.5 ± 1.4 \times 10^{-3}))</td>
</tr>
<tr>
<td></td>
<td>Power Density [W L(^{-1})]</td>
<td>31000 ± 1000 ((3.8 ± 0.1))</td>
<td>87000 ± 7000 ((8.5 ± 0.7))</td>
</tr>
<tr>
<td></td>
<td>Energy Density [Wh L(^{-1})]</td>
<td>3.7 ± 0.2 ((4.5 ± 0.2 \times 10^{-4}))</td>
<td>3.1 ± 1.0 ((3.0 ± 0.9 \times 10^{-4}))</td>
</tr>
<tr>
<td>2.2</td>
<td>Equivalent Series Resistance(^c) [Ohms]</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>N/A</td>
<td>Maximum Power Density [kW L(^{-1})]</td>
<td>860 ((1.1 \times 10^{-1}))</td>
<td>4300 ((4.2 \times 10^{-1}))</td>
</tr>
</tbody>
</table>

\(^a\) Calculated based on total volume of both PEDOT electrodes. \(^b\) Calculated based on the volume of the PC\(_{60}\) electrode plus the volume of the PEDOT electrode. \(^c\) Calculated based on the volume of the entire device including electrodes, casing, electrolyte, separator and current collectors. \(^d\) Determined by the average x-intercept of the impedance data obtained from the devices at different states of charge.
5 Experimental

5.1 Synthesis

5.1.1 Synthesis of TBASbF$_6$

The preparation of TBASbF$_6$ was carried out using a modified literature procedure.$^{50}$ Briefly, sodium hexafluoroantimonate (2.6 g, 10 mmol) and tetrabutylammonium bromide (3.3 g, 10 mmol) were dissolved in acetone (10 mL) and stirred at room temperature for 24 hours. The mixture was then filtered to remove the NaBr salt. The solvent was evaporated and the resulting white solid was dissolved in CH$_2$Cl$_2$, washed with distilled water three times, dried using MgSO$_4$, and filtered. The solvent was evaporated, the product was recrystallized twice from ethyl acetate/diethyl ether (1:2), and dried at 125 °C under vacuum for 72 hours.

5.1.2 Synthesis of PC$_{60}$ Films

A solution containing C$_{60}$ (0.15 mM), TBASbF$_6$ (0.05 M) and CH$_2$Cl$_2$ was placed in a custom-made Teflon electrochemical cell sealed with a Viton® O-ring$^{51,52}$ and cycled from 1.86 to -1.84 V using a three-electrode configuration. A gold-coated Kapton™ foil (Astral Technology Unlimited) or a gold-coated silicon wafer (Platypus Technologies) with a surface area of 0.636 cm$^2$ was used as the working electrode, a platinum wire was used as the counter electrode and a silver wire was used as a pseudoreference electrode. After 200 cycles the film was rinsed three times with CH$_2$Cl$_2$ and left in the glove-box for further electrochemical characterization.

5.1.3 Synthesis of PEDOT Films

A solution containing EDOT (7.5 mM), TBABF$_4$ (0.05 M) and CH$_2$Cl$_2$ was placed in a custom-made Teflon electrochemical cell sealed with a Viton® O-ring. The solution was held at 0.9 V until a charge of 18 mC was collected. The film was rinsed three times with CH$_2$Cl$_2$ and left in the glove-box for further characterization.

5.2 Characterization

5.2.1 Material Characterization

The morphology of the films was examined using SEM (Hitachi S-5200 SEM) and TEM (Hitachi H-7000 TEM). Powder X-ray diffraction was performed using a Bruker AXS SAXS NanoStar
diffractometer. Raman spectroscopy was carried out on a Thermo Scientific DXR Raman microscope with a 780 nm excitation laser. For PC$_{60}$, a fluorescence correction was applied to eliminate the fluorescent background. FT-IR was performed on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a 10-bounce diamond/ZnSe ATR accessory. XPS was carried out using a Thermo Scientific K-Alpha spectrometer with a monochromated Al K$_\alpha$ source. For low-resolution experiments the pass energy was 200 eV and for high-resolution experiments the pass energy was 25 eV. Binding energies were calibrated to place Au4f7/2 at 84.0 eV. TOF-SIMS was performed on an ION-TOF TOF-SIMS IV spectrometer using a Bi$_3$ ion source in negative polarity mode. Profilometry was performed on a KLA-Tencor P16+ profilometer using a force setting of 0.5 mg and a scanning length of 5 microns.

5.2.2 Electrochemical Characterization of Electrode Films

All electrochemistry experiments on the as synthesized films were performed in a custom made Teflon cell using a 0.1 M TEABF$_4$/acetonitrile electrolyte with a platinum wire counter electrode and a silver wire pseudoreference electrode. Each electrode was rinsed three times with the electrolyte solution in order to replace the salt from the polymerization solution. Power and energy densities calculated for the Ragone plot were based on the volume of the electroactive material for all devices. Energy densities were calculated using Equation 3 and average power densities were calculated as $P = E/\Delta t$. $P_{\text{max}}$ was calculated using Equation 2.

5.3 Supercapacitor Fabrication and Testing

To fabricate a device, each electrode was held at a specific potential (-0.19 V and -0.79 V for PEDOT and PC$_{60}$ respectively in the PC$_{60}$/PEDOT device, 0.31 V for PEDOT in the PEDOT/PEDOT device) for 45 seconds in a 0.1 M TEABF$_4$/acetonitrile electrolyte. The electrolyte was removed, the Teflon cells were disassembled and the gold-coated Kapton™ foils were trimmed to minimize the amount of bare gold in the device. Each electrode was placed on silicone adhesive tape with the polymer side facing away from the tape. A 0.1 M TEABF$_4$/acetonitrile/15 wt % poly(methyl methacrylate) electrolyte was smeared on the polymer films and a Kimwipe separator soaked in 0.1 M TEABF$_4$/acetonitrile was place on one electrode. The two electrodes were brought together (rotated 180 degrees relative to one another) with the polymer films overlapping. For each measurement, three devices were constructed and tested independently to obtain an average value and a standard deviation.
6 References


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(18) Zhang, L.; Candelaria, S. L.; Tian, J.; Li, Y.; Huang, Y.-x.; Cao, G. J. Power Sources 2013, 236 (c), 215–223.


Chapter 3
Bio-Derived Cathodes for Lithium-Ion Batteries

1 Contributing Statement

Portions of this chapter have been published previously.1 Dr. Colin Bridges helped conceive the idea for the project and performed some of the initial computational work. Dr. Andrew Tilley and Dr. Colin Bridges provided guidance on the synthetic aspects of this project. Mark Miltenburg helped in the thin-film studies. I wrote the manuscript, which was edited by Dr. Andrew Tilley, Dr. Colin Bridges, Mark Miltenburg and Prof. Dwight Seferos.

2 Introduction

Lithium-ion batteries have experienced wide-spread commercial success in portable electronics and electric vehicles,2,3 and are the current market-leading energy storage technology. As demand for portable electronics and energy conversion devices continues to grow, complimentary energy storage technologies must be developed that are light-weight, cost effective, and can be manufactured from environmentally benign materials. Current state-of-the-art lithium-ion batteries use transition metal based cathodes that require energy-intensive processing and extraction methods that are detrimental to the environment. Furthermore, ~30% of the cost of lithium-ion batteries can be attributed to the cathode material, typically a metal oxide or phosphate, which adds a significant economic cost to their production.4 Therefore, the development of sustainable and cost-efficient energy storage devices is critical to enable the continued development of portable electronics and energy conversion technologies.

Redox-active organic molecules are highly promising alternatives to transition metal based electrodes currently employed in lithium-ion batteries. Redox-active organic molecules have a high theoretical capacity, tunable electronic properties, and can be made into light-weight materials, which exhibit high mechanical strength and tunable structural properties.5-9 Despite their considerable promise, a number of challenges remain to be overcome before transition metal based electrodes are replaced by redox-active organic materials. Firstly, polar organic solvents typically dissolve the redox-active organic component, which results in rapid capacity fading upon cycling, limiting the use of organic molecules for rechargeable batteries.10-13 This can be at least partially mitigated by incorporating redox-active groups into polymers. For example, polymers
composed of redox-active pendant groups retain the attractive features of redox-active organic molecules but are much less soluble in lithium-ion battery electrolytes due to the limited solubility of the polymer backbone in polar solvents and the greatly decreased entropy of mixing. Most of the polymers used as electrodes in batteries have pendant, redox-active groups bearing stable radicals, such as nitroxyl and phenoxy. However, while these materials exhibit fast charging and discharging, they are limited in their theoretical capacity because bulky alkyl groups are required to stabilize the charged organic species and they can only accept up to one charge per radical group. Furthermore, these highly functional organic materials often require complex syntheses and extensive purification, which can diminish their large-scale production.

Biomolecules are an attractive class of materials that can be used in place of petroleum-based organic materials. Biomolecules, being derived from natural sources, greatly decrease the costs associated with complex multistep syntheses due to the built-in functionality already installed by nature. This approach is termed semi-synthesis. Semi-synthesis is already being used to make a wide variety of commercial polymers, such as poly(lactic acid)s, for other applications. Indeed, many examples of stable redox-active molecules are found in nature that could be constructed into useful materials at a fraction of the cost of a total synthesis.

Herein, I describe the semi-synthesis of a pendant flavin polymer and its use as a cathode material in a lithium-ion battery. Flavins, which can be derived from riboflavin (vitamin B₂), are highly promising electrode materials due to their ability to accept two electrons per unit, high potential (~2.5 V), and high theoretical capacity (~142 mAh g⁻¹ for riboflavin). Furthermore, their ability to accept multiple electrons provides scope for materials with high capacity. This is the first polymer that uses a pendant biologically-derived redox unit for battery applications. The polyflavin polymer provides a capacity of 125 mAh g⁻¹ with a voltage of 2.5 V in a device using lithium metal as the anode material. This is the highest capacity reported for biologically-derived polymeric cathodes. Due to the polymeric nature of this material, it has a much higher performance than the small molecule riboflavin. By examining the reduced species using computational chemistry, a new degradation mechanism is uncovered that may be applicable to organic electrodes in general and a strategy is proposed to solve this issue. This work highlights the considerable potential of biologically-derived redox-active pendant polymers for sustainable energy storage applications, and provides design guidelines for how they can be improved in the future.
3 Results and Discussion

3.1 Project Design

Initially, the goal of this work was to create an electropolymerizable monomer that could be used as a SC electrode. This idea was inspired by work using electropolymerized riboflavin as an electrocatalyst that exhibited an electrochemical profile that was suitable for SCs. The polymer design was such that it could accommodate the insertion of electrolyte upon charging and discharging due to the lack of cross-linking and the favourable interactions with the electrolyte. The motivation for this was that by having favourable interactions with the solvent, the mechanical stress associated with ion and electrolyte insertion would be mitigated, addressing the stability issues of the material discussed in the previous chapter. However, it was found that electropolymerization of the flavins led to short, oligomeric compounds that were highly soluble in the electrolyte. Additionally, the extent of charge delocalization was found to be insufficient to produce SC-like electrochemical behaviour. Instead, the compounds exhibited a sharp redox peak that was deemed appropriate for battery applications (Figure 3.1). Therefore, I decided to pivot the direction of the project and focussed on developing a flavin polymer that could build upon the synthetic work already performed and the knowledge that was gained from the previous chapter.

![Figure 3.1](image)

Figure 3.1 (a) Electropolymerized flavin polymer and (b) resultant voltammogram in a 0.1 M TBAPF$_6$ acetonitrile electrolyte at 100 mV s$^{-1}$.

3.2 Synthesis and Characterization

My new goal was based on the idea that incorporating redox-active flavin units within a pendant polymer architecture would provide the opportunity to synthesize it using scalable methods, be
stable in common electrolytes, have tunable structures, and could swell to accommodate electrolyte penetration. Knowing that post-polymerization modification can be problematic, due to incomplete functionalization and difficulties associated with purification, the monomer was designed to have a pendant flavin group. A methacrylate polymer with the flavin unit appended though an ester linkage was first targeted for this study. However, by attempting to polymerize styrene in the presence of the flavin monomer, it was found that controlled or uncontrolled radical polymerizations are not compatible with the flavin motif, presumably due to a reaction between the free radical and the flavin units. A norbornene-based monomer was then targeted in order to allow the use of ring opening metathesis polymerization (ROMP), a robust process tolerant to a variety of functional groups and conditions. The endo, exo norbornene diacid chloride was specifically chosen for this synthesis in order to minimize the expected electrostatic repulsion between charged flavin units in the pendant polymer architecture. The monomer 3 was polymerized using Grubbs’ 2nd generation catalyst to yield polymer P3 (Scheme 3.1) in 84% yield. P3 is a dark green solid that is highly fluorescent in dilute solutions (Figure 3.2). However, upon increasing the concentration the fluorescence quenches and the emission wavelength red-shifts, indicating aggregation. Due to the solubility of P3, it is solution-processable in dichloromethane and chloroform, forming smooth featureless films when spun-cast from a chloroform solution (Figure 3.3). The lack of diffraction peaks in the powder X-ray diffractogram of P3 indicates that the polymer is largely amorphous (Figure 3.4). P3 is stable until at least 170 °C, where a loss in mass could be decomposition or loss of bound water, and does not have a glass transition or melting temperature before it decomposes, as determined by TGA and DSC (Figure 3.5).

Scheme 3.1 Synthesis of P3 by ring opening metathesis polymerization.
**Figure 3.2** Fluorescence spectra of P3 dissolved in chloroform at different concentrations.

**Figure 3.3** Atomic force microscopy (a) height and (b) phase images of spuncast polymer P3 on glass slides. The lack of nanoscale morphology is indicative of the absence of ordered self-assembly and semi-crystallinity.

**Figure 3.4** Powder XRD of P3.
Figure 3.5 (a) TGA and (b) first heating DSC of P3 run under a nitrogen atmosphere.

The proton NMR spectrum of P3 (Figure 3.6) consists of broad, low intensity peaks with the expected chemical shifts for a norbornene-based polymer. Assignments were determined by chemical shifts compared to the proton NMR of other norbornene polymers and 3, however, the integrations are slightly off due to the broadness of the peaks and the low solubility of P3. Attempts to characterize molecular weight by light scattering and gel permeation chromatography were unsuccessful due to polymer chain aggregation, even in dilute solution, as indicated by the fluorescence spectra (Figure 3.2). This also hampered efforts at performing end-group analysis on the proton NMR spectrum of P3. Characterization of the molecular weight was also attempted using matrix-assisted laser desorption/ionization mass spectrometry; however, this again proved unsuccessful. Although the low solubility and propensity for aggregation led to problems with molecular weight characterization, this was expected to be advantageous for applications in lithium-ion batteries since dissolution of organic electrodes is known to significantly diminish device performance. The optical absorption spectra of P3 and monomer 3 in chloroform solution have two absorption maxima centered at 349 and 448 nm, and are strongly overlapping (Figure 3.7a). This is consistent with the incorporation of flavin moieties within the polymer structure, and shows that the optoelectronic properties of the flavin groups are largely preserved in the pendant polymer structure. The FTIR spectrum of P3 has weak signals corresponding to the aliphatic C-H stretches below 3000 cm⁻¹, numerous bands in the range of 1750 - 1500 cm⁻¹ corresponding to the various ester and diimide groups, along with bands in the fingerprint region (Figure 3.7b). The FTIR spectrum of 3 is almost identical to P3 due to their similar bonding motifs and functional groups and is, again, consistent with the presence of flavin groups in the polymer.
CV was performed to determine if the polymerization conditions affected the desirable electrochemistry of the flavin motif (Figure 3.7c). The redox wave centered at -1.50 V vs Fc/Fc$^+$ is not shifted upon polymerization indicating that polymerization does not modify the redox potential of the flavin unit. It is noted, however, that the magnitude of the current decreases. This is attributed to the slower diffusion of the polymer in solution meaning that less redox-active material encounters the electrode surface during the cycling experiment. This is an unavoidable consequence that is due to the macromolecular nature of P3.

![Figure 3.6 Proton NMR spectra of P3 in CDCl$_3$.](image)

**Figure 3.6** Proton NMR spectra of P3 in CDCl$_3$.

![Figure 3.7 (a) UV-Vis spectra in chloroform of P3 and 3. (b) FTIR spectra of P3 and 3. (c) CV of P3 and 3 in 0.1 M TBAPF$_6$ dichloromethane in solution at 100 mV s$^{-1}$. The potential is referenced to Fc/Fc$^+$.](image)

**Figure 3.7** (a) UV-Vis spectra in chloroform of P3 and 3. (b) FTIR spectra of P3 and 3. (c) CV of P3 and 3 in 0.1 M TBAPF$_6$ dichloromethane in solution at 100 mV s$^{-1}$. The potential is referenced to Fc/Fc$^+$. 
3.3 Electrode Characterization

The preparation of an electrode consisting of a composite of the active material, carbon additive, and binder is required to study the polymer as a lithium-ion battery cathode. Here, P3, CB, and PVDF were used as the active material, carbon additive, and binder respectively. The first attempt to prepare a functional electrode was to formulate P3 as nanoparticles by the flash precipitation method followed by mixing the components together in NMP (Section 5.3). This method generates polymer aggregates (Figure 3.8a,b) leading to poor performance when testing in a lithium-ion battery due to the high charge-transfer resistance (Figure 3.9). The optimal formulation was achieved by stirring a solution of CB and P3 in chloroform, evaporating the solvent and then sonicking the components in a solution of PVDF and NMP. Uniformly spreading the slurry with a 250 µm notch bar49 yields films that are 30 ± 4 µm thick (Figure 3.10). Under these conditions, P3 coats the CB surface allowing for a homogenous film (Figure 3.8c,d). This is supported by energy dispersive X-ray measurements, which reveals the homogenous distribution of carbon, oxygen, nitrogen, and fluorine in the film (Figure 3.11). The hierarchical structure of CB particles and P3, where a thin layer of P3 covers and connects adjacent CB particles, can be clearly observed in the respective TEM images (Figure 3.8e).

Figure 3.8 Examination of electrode film morphology and hierarchal nanostructure of the polymer (P3) and carbon black (CB). (a,b) SEM images of films cast with prepared P3 nanoparticles. (c,d) Films cast by first dissolving P3 in CHCl3 with CB. (e) TEM images of P3 CB hybrids. (f) TEM images of CB.
Figure 3.9 Electrochemical performance of battery with cathode prepared with P3 nanoparticles. (a) Galvanostatic charge/discharge curves at different C-rates, (b) rate capabilities of the battery, (c) cycling stability and coulombic efficiency performed at 1 C, and (d) impedance spectroscopy at different states of charge before and after degradation.

Figure 3.10 Histogram of cathode height prepared by first mixing P3 and CB in CHCl$_3$ and then mixing with PVDF in NMP measured by profilometry.
Figure 3.11 Energy dispersive X-ray spectra of a cathode prepared by first mixing P3 and CB in CHCl₃ prior to mixing with PVDF in NMP. (a) SEM image, (b) C Kα image, (c) O Kα image, (d) N Kα image, and (e) F Kα image.

3.4 Lithium-Ion Battery Testing and Characterization

The electrochemical performance of the polymer electrode was tested by assembling a coin cell (CR2032) with a lithium metal anode and a Celgard polypropylene lithium-ion separator in a 1.0 M LiPF₆ TEGDME electrolyte (Figure 3.12). Two distinct redox peaks centered at 1.84 V and 2.55 V vs Li/Li⁺ are observed in the CV (Figure 3.12a). This is in contrast to the solution CV where only one redox peak is observed. The difference between the two voltammograms results from changing the counter-cation from tetrabutylammonium to lithium, consistent with previous reports.⁵⁰,⁵¹ From the galvanostatic charge/discharge measurements (Figure 3.12b) it is observed that the device has two voltage plateaus (where a redox event occurs) centered at 2.65 V and 1.85 V at a current of 0.1 C (0.1 C = 14.4 mA g⁻¹) and this leads to an almost constant voltage as a function of time for each plateau. At 0.1 C, the capacity is 125 mAh g⁻¹ corresponding to 87% of the theoretical maximum value. This high capacity is due to the ability of the repeat unit to accept up to four electrons (two per flavin motif). At 1 C, the voltage plateaus shift slightly to 2.61 V and 1.76 V and the device has a 77 mAh g⁻¹ capacity corresponding to 53% of the theoretical maximum value. The decrease in capacity with increasing current is common for battery materials. This is because kinetic factors such as lithium-ion diffusion and electron transfer rates limit the amount of charge extracted from the electrode at higher currents.
Figure 3.12 Performance of lithium-ion battery using the polymer (P3) as the cathode. (a) CV at 1 mV s⁻¹, (b) galvanostatic charge/discharge curves at different C-rates, (c) rate capabilities of the battery, (d) and cycling stability and coulombic efficiency. Cycling stability experiments were performed at 1 C. Experiments were performed using 1.0 M LiPF₆ TEGDME and lithium as the anode.

Cycling the battery substantially decreases capacity (Figure 3.12d). This is surprising because flavins are known to have reversible electrochemistry and high stability in similar electrolytes.⁴¹,⁴³ Measuring the absorption spectrum of P3 before and after cycling provides insight into the chemical degradation of the material. The optical absorption profiles are very similar for the sample extracted from a pristine electrode and one that has been cycled in the TEGDME electrolyte (Figure 3.13). Upon cycling in an EC:DMC electrolyte, P3 dissolves and migrates out of the electrode. This means that there is no P3 left in the electrode to perform absorption measurements on. Therefore, it is unsurprising that the absorption spectrum of the EC:DMC sample does not resemble the TEGDME or the pristine sample. The kinetics of the reduction reactions, related to the charge-transfer resistance, were examined by impedance spectroscopy at...
different cycle numbers (Figure 3.14, Table 3.1). Before cycling, the charge-transfer resistance for the first reduction (2.40 V) is 207.8 Ω. This value is small compared to the second reduction (1.75 V), which has a 544.9 Ω charge-transfer resistance. The larger resistance for the second reduction indicates that the reduction kinetics for this step are slower. After 5 cycles, the charge-transfer resistances decrease to 147.5 Ω and 371.3 Ω for the first and second reduction, respectively. These more rapid reduction kinetics are accompanied by an increase in capacity. After 50 cycles, the charge-transfer resistance for the first reduction decreases to 92.28 Ω, while the charge-transfer resistance for the second reduction increases to 632.7 Ω. This is accompanied by a steep decrease in capacity. After 200 cycles the capacity has mostly faded and the charge-transfer resistances for the first and second reduction are increased to 250.6 Ω and 848.1 Ω respectively. This shows that the reduction kinetics after the battery has been cycled are much slower. Overall, this suggests that the capacity fading is related to the slower kinetics, or the larger charge-transfer resistance, of the reductions after extended cycling.

Capacity fading is the most substantial challenge for organic materials to overcome. The most common mechanism of capacity fading in organic batteries is dissolution of the active material into the electrolyte. I did not observe a colour change in the electrolyte after cycling and can therefore rule this out as a possible degradation mechanism (Figure 3.15). I have also been able to rule out delamination of the electrode from the current collector because the electrode is still intact after cycling and disassembly (Figure 3.15e). Surprisingly, the battery stability is improved when it is cycled in an electrolyte that is a better solvent for the polymer (Figure 3.16). This suggests that there is another degradation mechanism at play. No significant changes in the P3 electrode morphology are observed at different stages of cycling (Figure 3.17), and thus the morphology does not appear to contribute to capacity fading.
Figure 3.13 UV-Vis trace of P3 electrode that was cycled in 1.0 M LiPF₆ 200 times, a P3 electrode that was cycled in 1.0 M LiPF₆ 200 times, and a pristine electrode that was extracted with chloroform.

Figure 3.14 Electrochemical impedance spectroscopy of P3 lithium-ion batteries after 0, 5, 50 and 200 cycles at (a) 1.75 V and (b) 2.40 V. (c) The modified Randles circuit that was used to fit the data. Rs is the equivalent series resistance, CPE is a constant phase element, Rct is the charge-transfer resistance and Ws is the Warburg impedance. The fits according to the model equivalent circuit are depicted by the solid lines.
Table 3.1 Fitting parameters from the modified Randles circuit for the frequency response of P3 electrodes after different numbers of cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rs (Ω)</th>
<th>CPE1-T (F)</th>
<th>CPE1-P</th>
<th>R1 (Ω)</th>
<th>Ws1-R (Ω)</th>
<th>Ws1-T (s)</th>
<th>Ws1-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 cycles at 2.4 V</td>
<td>8.400</td>
<td>9.22x10⁻⁶</td>
<td>0.79331</td>
<td>207.8</td>
<td>1376</td>
<td>2.455</td>
<td>0.54302</td>
</tr>
<tr>
<td>0 cycles at 1.75 V</td>
<td>8.185</td>
<td>8.92x10⁻⁶</td>
<td>0.79249</td>
<td>544.9</td>
<td>817.7</td>
<td>3.694</td>
<td>0.37415</td>
</tr>
<tr>
<td>5 cycles at 2.4 V</td>
<td>8.462</td>
<td>9.39x10⁻⁶</td>
<td>0.79465</td>
<td>147.5</td>
<td>1129</td>
<td>2.580</td>
<td>0.55828</td>
</tr>
<tr>
<td>5 cycles at 1.75 V</td>
<td>8.234</td>
<td>8.62x10⁻⁶</td>
<td>0.79598</td>
<td>371.3</td>
<td>460.4</td>
<td>4.109</td>
<td>0.40312</td>
</tr>
<tr>
<td>50 cycles at 2.4 V</td>
<td>15.96</td>
<td>2.24x10⁻⁵</td>
<td>0.69794</td>
<td>92.28</td>
<td>2199</td>
<td>3.784</td>
<td>0.61954</td>
</tr>
<tr>
<td>50 cycles at 1.75 V</td>
<td>15.27</td>
<td>1.57x10⁻⁵</td>
<td>0.70284</td>
<td>632.7</td>
<td>514.4</td>
<td>2.704</td>
<td>0.49232</td>
</tr>
<tr>
<td>200 cycles at 2.4 V</td>
<td>20.76</td>
<td>1.64x10⁻⁵</td>
<td>0.70858</td>
<td>250.6</td>
<td>3760</td>
<td>6.189</td>
<td>0.61317</td>
</tr>
<tr>
<td>200 cycles at 1.75 V</td>
<td>20.78</td>
<td>1.51x10⁻⁵</td>
<td>0.71217</td>
<td>848.1</td>
<td>3520</td>
<td>27.71</td>
<td>0.56175</td>
</tr>
</tbody>
</table>

Figure 3.15 (a) Picture of riboflavin dissolution in 1.0 M LiPF₆. Pictures of P3 solubility in (b) 1.0 M LiPF₆ EC:DMC 1:1, (c) 1.0 M LiPF₆ TEGDME, (d) of 1.0 M LiPF₆ TEGDME after P3 electrode has been cycled and in the discharged state, and (e) the P3 cathode after cell cycling and disassembly showing that the cathode is still intact.
Figure 3.16 Performance of battery with the cathode prepared by first mixing P3 and CB in CHCl₃ prior to mixing with PVDF in NMP cycled in a 1.0 M LiPF₆ EC:DMC 1:1 electrolyte. (a) Galvanostatic charge/discharge curves at different C-rates, (b) rate capabilities of the battery, (c) cycling stability and coulombic efficiency performed at 1 C, and (d) impedance spectroscopy at different states of charge before and after degradation.

To gain molecular-scale insight into electrode degradation, I performed a series of DFT calculations on the reduced structures of a P3 repeating unit. The neutral repeating unit and the unit where each flavin has undergone a one electron reduction (each flavin balanced by one lithium ion) have almost the same molecular geometry (Figure 3.18b,c). The flavin motifs are oriented away from each other and the lithium ion is coordinating to the N5 nitrogen and the C4 carbonyl group. However, upon reducing each flavin motif once more, the geometry changes significantly, and the second lithium ion coordinates to the N1 nitrogen, C2 carbonyl, and the carbonyl group of the ester linkage (Figure 3.18d). This large change in molecular geometry led me to believe that the second reduction is responsible for the capacity fading. To provide more evidence for this, I cycled the cell in a limited potential window between 3.25 and 2.0 V (Figure 3.19). The potential window that was chosen only allows each flavin motif to be reduced once. The cell is completely stable under these conditions with a ~100% coulombic efficiency and a
110% capacity retention after 250 cycles. This provides strong evidence that capacity fading results from the second one-electron reduction of each flavin unit. The gradual increase in capacity (from 53 mAh g\(^{-1}\) to 59 mAh g\(^{-1}\)) is likely due to increased electrolyte penetration/electrode activation upon cycling. The electrolyte penetration/electrode activation is caused by a swelling and contracting of the active material in the electrode by lithium ion and electrolyte insertion upon charging and discharging.\(^\text{52,53}\) This reduces the overpotential associated with the electrochemical processes, and is further supported by the decrease in charge-transfer resistances after 5 cycles.

![Figure 3.17 TEM images of P3 electrodes after (a,b) 5 cycles, (c,d) 50 cycles, and (e,f) 200 cycles. (g,h) SEM images of cathode prepared by mixing P3 and CB in chloroform prior to mixing with PVDF in NMP after cycling.](image-url)
Figure 3.18 Calculated geometries of P3 repeating unit at different states of charge. (a) Structure of the modeled repeating unit. Optimized geometries of P3 repeating unit in the (b) neutral, (c) negative 2 state, and (d) negative 4 state. Carbon atoms are grey, nitrogen atoms are blue, oxygen atoms are red, hydrogen atoms are white and lithium atoms are pink. There is little change in geometry from the neutral to the negative 2 state but upon reducing to the negative 4 state, the lithium ions coordinate to the ester groups linking the flavin to the norbornene backbone inducing a large change in geometry. (e) Mechanism of P3 operation in a battery.

To complement our theoretical investigation of the degradation mechanism, the electrodes were examined by Raman spectroscopy before and after cycling (Figure 3.20). Raman spectroscopy is highly sensitive to local molecular environment of highly conjugated surfaces and can thus provide information about molecular-scale interactions between P3 and CB. The Raman bands that lie at 1345 and 1579 cm$^{-1}$ are the D and G bands respectively for CB. The position of the G band can be used to determine the extent of $\pi$-$\pi$ interactions between pendant flavin units of P3.
and CB. In the pristine electrode, the G band appears at 1574 cm$^{-1}$ while the G band in the cycled electrode appears at 1582 cm$^{-1}$. The increase in Raman shift upon cycling suggests a modification in the geometry of the P3 molecules on the surface of CB, and is thus consistent with the modeling and cycling experiments.

Figure 3.19 Cycling stability and coulombic efficiency of a battery using a P3 cathode cycled between 3.25 and 2.0 V. The electrolyte is 1.0 M LiPF$_6$ TEGDME and the cell was cycled at 1 C.

Figure 3.20 Raman spectra showing the G and D bands of a CB PVDF blend, cycled P3 electrode after 200 cycles between 3.25 V and 1.25 V, and pristine P3 electrode.

FTIR experiments were performed to further elucidate the mechanism of capacity fading. The FTIR spectra of the sample cycled 200 times resembles the spectra obtained for the fully reduced species (Figure 3.21). In the pristine electrode, the stretches for the C2=O4 and C4=O4 bonds are centered at 1616 cm$^{-1}$, consistent with previous work, and these shift to 1644 cm$^{-1}$ and 1642 cm$^{-1}$ in the cycled and reduced electrodes respectively. Additionally, the stretches at 1577 cm$^{-1}$ and
1534 cm\(^{-1}\) for the pristine electrode shift to 1570 cm\(^{-1}\) and 1530 cm\(^{-1}\) for the cycled electrode and 1572 cm\(^{-1}\) and 1531 cm\(^{-1}\) for the fully reduced electrode.

![FTIR spectra](image)

**Figure 3.21** FTIR of (a) P3 at different oxidation states and (b) a pristine P3 electrode, a P3 electrode that is fully reduced, and a P3 electrode that has been cycled 200 times.

XPS data further confirms that the cycled electrode is composed of a significant amount of fully reduced P3. The N1s envelope for the pristine electrode was deconvoluted into three different peaks at ~401.2 eV, ~400.3 eV, and ~398.9 eV corresponding to the diimide nitrogen, the sp\(^3\) nitrogen, and the sp\(^2\) nitrogens in the flavin unit (Figure 3.22a).\(^{42,55}\) A peak emerges at ~398.3 eV when the electrode is reduced and this corresponds to the reduced sp\(^2\) nitrogen(s). These same N1s features are present in the electrode that has been cycled 50 and 200 times (Figure 3.22b). In the reduced P3 electrodes, the O1s peak shifts from ~532.6 eV in the pristine electrode to ~531.9 eV in the reduced electrodes showing that the carbonyl groups participate in the reduction (Figure 3.22c). This shift is also observed in the cycled electrodes (Figure 3.22d). These results are consistent with the FTIR data described above showing that the reduced and cycled species are chemically similar. This suggests that P3 is unable to be recharged upon extended cycling, which accounts for the observed capacity fading.

The selective solubility of P3 makes this polymeric electrode both solution processable and insoluble in an organic electrolyte without the need for crosslinking or grafting onto insoluble materials, which is an advantage over some previously reported polymer cathodes.\(^{28,56-58}\) Mixing the polymer and the carbon additive in a solvent in which the polymer is soluble allows one to prepare a hierarchical structure where the polymer coats the carbon additive. This hierarchical
structure appears to facilitate excellent electron transfer between the polymer and the conductive carbon network without the use of exotic nanostructures, as shown by the increased performance relative to the electrode formulated with P3 nanoparticles. The ability of the polymer to accept up to four electrons per repeat unit leads to a high 125 mAh g\(^{-1}\) capacity at 0.1 C, higher than any previously reported bio-derived polymeric cathode material.\(^{34,37,38,45}\) This is 87% of the theoretical maximum value for this material. With this high capacity and high voltage (plateaus at 2.55 V and 1.85 V; at 0.1 C), the battery is able to power a red light-emitting diode for over 1 hour (Figure 3.23). The low resistance of the electrode allows the voltage plateau to remain almost constant at different C-rates, as demonstrated using galvanostatic charging and discharging.

**Figure 3.22** XPS N1s scan of P3 electrodes at (a) different charging states and (b) after different cycle numbers. XPS O1s scan of (c) electrodes at different charging states and (d) after different cycle numbers.
3.5 Investigation into the Mechanism of Capacity Fading

I have ruled out many of the possible reasons for the rapid capacity fading including dissolution. Recently, Häupler and coworkers investigated the use of a dithiophenedione-containing polymer for lithium-ion battery applications. They observed a similar capacity fade and attributed it to side-reactions that degrade the electrode material. They based their hypothesis on spectroelectrochemistry results, showing that changes occur in the absorption spectra upon cycling past the second reduction. Based on our results for the absorption spectra of P3 before and after cycling along with XPS and FTIR data, I have been able to rule out chemical degradation as a major contributor. Although I cannot rule out small amounts of degradation in the TEGDME electrolyte, this does not account for the large differences in capacity before and after cycling. The decrease in capacity upon cycling is solely due to the second reduction as shown by the limited potential window cycling.

I hypothesize that the capacity fading is due to local morphological changes in the polymer structure as suggested by the geometry optimization calculations along with Raman spectroscopy. As the polymer undergoes the second reduction, coordination of the lithium counter-ion to the ester carbonyl group induces molecular changes in the structure. I believe that this change in structure perturbs the overall morphology of the hierarchal structure between P3 and the CB particles eventually isolating the redox units, which does not allow the flavin units on P3 to be recharged. This is supported by XPS and FTIR results indicating that P3 is still in the reduced
state after extensive cycling. The structural changes and isolation of the redox units from the conductive pathways are supported by the large resistance that is associated with the second reduction and with the increased charge-transfer resistance after cycling.

I hypothesize that changing the chemical linkages between flavin units to decrease the structural change following reduction should increase the redox stability of the polymer. I have performed geometry optimizations on a norbornene-flavin repeat unit where the flavin is linked to the norbornene unit through the diimide nitrogen (Figure 3.24). I have found that in this repeat unit, there is very little geometry change going from the neutral to the fully reduced structure. This shows that by modifying the chemical structure of the repeat unit, the large geometry changes upon reduction can be prevented.

![Figure 3.24](image.png)

**Figure 3.24** Calculated geometries of a flavin-norbornene repeating unit that is linked through the diimide nitrogen at different states of charge. (a) Structure of the modeled repeating unit. Optimized geometries of the repeating unit in the (b) neutral, (c) negative 2 state, and (d) negative 4 state. Carbon atoms are grey, nitrogen atoms are blue, oxygen atoms are red, hydrogen atoms are white and lithium atoms are pink. Going from the neutral to the negative 2 and to the negative 4 state, there is very little geometry change suggesting that a polymer using this repeating unit could be more stable with respect to cycling.
4 Conclusions

A biologically-derived redox polymer with a poly(norbornene) backbone and flavin pendant groups has been developed for lithium-ion batteries. The use of a biologically-derived redox unit for the semi-synthesis of a polymeric cathode holds great promise for sustainable batteries, providing a capacity of 125 mA\(\text{h g}^{-1}\) at 0.1 C. Using a joint computational and experimental approach I have shown that the cycling stability is limited by the geometry change of the flavin units when charging and discharging. This changes the interaction of the polymer with the CB surface, and also increases the charge-transfer resistance. I therefore propose that computational modelling can be used to predict the relative stability of organic polymers for energy storage applications where a large geometry change between the different redox states would manifest into decreased stability.

The design of sustainable materials for energy storage, photovoltaic, and electronics applications is a challenge that must be overcome in order to decrease cost and the environmental footprint of emergent technologies. I believe that the use of biologically-derived pendant polymers is a cost effective and environmentally benign approach towards next-generation organic electrodes that should be applicable to other alkali metal batteries such as sodium, potassium and even aqueous protic batteries. This work thus serves as a useful template for the development of bio-derived pendant polymers for energy storage and related applications.

5 Experimental

5.1 General Considerations

All reagents and electrolytes were purchased from Sigma-Aldrich and used as received unless otherwise indicated. Solvents for synthetic procedures were purchased from Caledon Laboratories Ltd. and dried in a solvent purification system (Innovative Technology) under argon. All electrochemical measurements were recorded in an argon filled glovebox (mBraun) with oxygen and moisture levels below 1.0 ppm and at room temperature (23.5 °C). Battery capacities and C-rates were calculated for the active material in the cathode.
5.1.1 Instrumentation and Methods

The morphology of the films was examined using SEM (Hitachi S-5200 SEM equipped with an Oxford Inca EDX). Atomic force microscopy was carried out using a Bruker Dimension Icon Atomic Force Microscope in tapping mode. TEM was performed using a Hitachi H-7000 C-TEM with an accelerating voltage of 75 kV. Profilometry was performed using a KLA-Tencore P16+ profilometer with a 0.5 mg force setting and a scanning length of 2.5 microns. FTIR was carried out using a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a 10-bounce diamond/ZnSe ATR accessory. Optical absorption spectroscopy was performed using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Prior to extracting the electrodes with chloroform to measure the absorption spectrum of P3, the electrode was rinsed three times with acetonitrile in order to remove the high boiling point electrolyte, then dried under vacuum. Fluorescence spectra were collected with an excitation wavelength of 420 nm using a Photon Technology International (PTI) QuantaMaster 40-F NA spectrofluorometer with a photomultiplier detector and a xenon arc lamp source. Raman spectroscopy was performed on a Bruker SENTERRA dispersive Raman Microscope using a 532 nm laser at 20 mW with a resolution of 3 – 5 cm\(^{-1}\). Proton NMR was carried out on a Bruker Avance III 400 operating at 400 MHz. Chemical shifts are reported in ppm at room temperature using the solvent peak of CDCl\(_3\) or d\(_6\)-DMSO at 7.26 or 2.50 ppm respectively. Mass spectrometry was performed using a JOEL AccuTOF JMS-T1000LC mass spectrometer equipped with a DART ion source or an Agilent 6528 Q-TOF mass spectrometer.

TGA and DSC were performed on a SDT Q600 V8.3 Build 101 at a heating rate of 5 °C/ min under nitrogen. PXRD was performed on a Rigaku MiniFlex 600 X-ray Diffractometer. XPS was performed using a Thermo Scientific K-Alpha spectrometer with a monochromated Al K\(_\alpha\) source. Binding energies were referenced to 284.8 eV for the main C1s peak for carbon black. All electrochemistry experiments were performed using a Biologic SP-200 Potentiostat/Galvanostat/FRA. For solution electrochemistry of the polymer and monomer, experiments were performed using 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane at 100 mV s\(^{-1}\) with a 10 mM concentration of the flavin unit. Impedance spectra were measured with an excitation amplitude of 10 mV from a frequency range of 150 kHz – 0.1 Hz. Equivalent circuit modelling was performed using Zview software. Geometry optimizations were performed using the Gaussian 09 software suite\(^{59}\) at the B3LYP level of theory and the standard TZVP basis set.\(^{42}\) Prior to cycling stability experiments performed at 1 C (1 C = 144 mA
g⁻¹, or the amount of current that would be needed to extract the entire theoretical capacity (144 mAh g⁻¹) in one hour), all coin cells were cycled 4 charge and discharge cycles at 0.1 C to activate the electrode, and allow electrolyte penetration. In order to prepare samples of the P3 electrodes for FTIR, XPS, TEM, Raman, and SEM, the cycled batteries were disassembled in an argon filled glovebox, washed with acetonitrile three times to remove any residual electrolyte and then dried under vacuum overnight.

5.2 Synthesis

5.2.1 Synthesis of 1

The synthesis of 1 was carried out using a procedure described in a previous report and the NMR spectra is in agreement with what was reported.

5.2.2 Synthesis of 2

1 g (3.49 mmol) of Cs₂CO₃ (10.5 mmol) were added to a flame dried flask and suspended in 30 mL of DMF. 0.44 mL (6.99 mmol) of methyl iodide was then added to the suspension. The reaction was monitored by TLC (5:1 CH₂Cl₂:MeOH). Upon completion, the reaction was dumped into 0.1 M HCl (aq) and was washed 3 times with CH₂Cl₂. The aqueous layer was filtered and dried to yield a light yellow-brown product (0.72 g, 69%). ¹H NMR (400 MHz, d₆-DMSO, δ): 7.94 (s, 1H), 7.91 (s, 1H), 4.95 (t, J = 6.0 Hz, 1H), 4.72 (t, J = 6.1 Hz, 2H), 3.82 (q, J = 6.0 Hz, 2H), 3.28 (s, 3H), 2.51 (s, 3H), 2.41 (s, 3H). HRMS (DART) m/z: calculated for C₁₅H₁₇N₄O₃ [M+H]⁺: 301.1295; found: 301.1298.

5.2.3 Synthesis of 3

2.5 g (8.3 mmol) of 2 and 122 mg (1 mmol) of dimethylaminopyridine were added to a flame dried flask and suspended in CH₂Cl₂ (150 mL). Pyridine (2 mL, 25 mmol) was then added, followed by a dropwise addition of trans-3,6-endomethylene-1,2,3,6-tetrahydrophthaloyl chloride (ie. endo, exo norbornene diacid chloride, Sigma-Aldrich) (0.41 mL, 2.5 mmol). The reaction mixture was stirred overnight at room temperature in the dark. Upon completion, the reaction was diluted with CH₂Cl₂ and washed with 0.2 M HCl (aq) x 3, distilled water x 3, dried with MgSO₄ and the solvent was removed. The product was purified by column chromatography (5:0.2 CH₂Cl₂:MeOH) to yield a yellow-orange solid (1.9 g, 60%). ¹H NMR (400 MHz, CDCl₃, δ): 8.04 (s, 2H), 7.60 (s, 1H), 7.59 (s, 1H), 6.08 (dd, J = 5.6, 3.1 Hz, 1H), 5.78 (dd, J = 5.6, 2.8
Hz, 1H), 5.00 (t, J = 5.8 Hz, 2H), 4.91 (t, J = 6.1 Hz, 2H), 4.57 (m, 3H), 4.45 (m, 1H), 3.50 (s, 3H), 3.50 (s, 2H), 3.48 (s, 1H), 3.11 (t, J = 4.1 Hz, 1H), 2.99 (broad s, 1H), 2.83 (broad s, 1H), 2.54 (s, 6H), 2.44 (broad s, 6H), 2.42 (broad s, 1H), 1.28 (m, 2H).

$^{13}$C (100 MHz, CDCl$_3$, δ): 173.71, 172.66, 159.90, 159.89, 155.77, 148.74, 148.67, 148.06, 147.97, 137.54, 136.88, 136.81, 135.55, 135.51, 134.78, 134.76, 134.75, 132.71, 132.70, 131.28, 131.23, 115.41, 115.38, 77.22, 60.73, 60.31, 53.42, 50.84, 47.52, 47.43, 47.23, 46.84, 45.36, 43.16, 42.98, 28.73, 21.59, 21.56, 19.47, 19.46. HRMS (ESI) m/z: calculated for C$_{39}$H$_{39}$N$_8$O$_8$ [M+H]$^+$: 747.2885; found: 747.2853.

5.2.4 Synthesis of P3

3 (1.5 g, 2 mmol) and 20 mL of CHCl$_3$ were added to a flame dried flask. Afterwards, 17 mg (0.02 mmol) of Grubbs’ 2nd generation catalyst was added and the solution was stirred at room temperature in the dark for 19 hours. The reaction was quenched with 0.96 mL (10 mmol) of ethyl vinyl ether dissolved in 7 mL of CHCl$_3$ and allowed to stir for another 5 hours. The polymer was then precipitated in methanol twice, soxhlet extracted with methanol for 4 days and then dissolved in CHCl$_3$. The solvent was removed to yield a dark green solid (1.3 g, 84%). $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.76 (broad s, 4H), 4.91 – 4.37 (broad m, 9H), 3.28 – 2.82 (broad s, 8H), 2.48 – 1.74 (broad m, 17H).

5.3 Assembly of Lithium-Ion Battery Coin Cells

The P3/CB composite was prepared by dissolving 35 mg of P3 and 50 mg of CB in 17 mL of chloroform and stirring vigorously overnight. Based on TGA and elemental analysis, the percentage of P3 in the composite was determined to be between 39 and 50 weight percentage. The solvent was then removed under vacuum and 15 mg of PVDF powder was added, then the mixture was sonicated in 1.66 mL of NMP (70 mg mL$^{-1}$) for 1 hour stirring every 15 minutes to improve homogenization. The films were then cast using a procedure described by Dahn and coworkers where a 200 µm notch bar was used to cast the films. Briefly, the slurry was pipetted onto a strip of aluminum foil that was flattened on a smooth surface and the notch bar was used to spread the slurry by drawing it across the aluminum foil at a rate of ~1 cm s$^{-1}$. The films were then dried at 80 ºC in air and then transferred into a vacuum antechamber and heated at 65 ºC overnight in order to remove any residual NMP before bringing the films into the glovebox. In order to prepare the films with nanoparticles, nanoparticles were first made by precipitation of a 5 mg mL$^{-1}$ chloroform solution of P3 into a rapidly stirring beaker of methanol. The nanoparticles
of P3, CB and PVDF were then mixed together in a ratio of 35:50:15 in NMP at a concentration of 60 mg mL\(^{-1}\), sonicated for 1 hour stirring every 15 minutes to homogenize. The films were then cast and dried as described above. CR2032 type coin cells were purchased from MTI Corporation. A copper foil (McMaster-Carr) was used as the anodic current collector, a lithium foil with a diameter of 16 mm was used as the anode, and a Celgard lithium-ion battery separator film as the separator with a diameter of 19 mm. A stainless steel spacer and a stainless steel spring were placed on top of the cathode material prior to sealing. An electrode punch (Design Prove Machines (DPM) Solutions Inc.) was used to cut electrodes 16 mm in diameter and a coin cell press (BT Innovations) was used to hermetically seal the cells. Approximately 40 µL of electrolyte was used to fill the coin cells prior to sealing.

6 References


Chapter 4
Three-Dimensional Triptycene Frameworks for Highly Stable Lithium-Ion Batteries

1 Contributing Statement

Portions of this chapter have been published previously. Dr. Andrew Tilley provided guidance for this project, particularly on developing the synthetic aspects, and helped conceive the idea. Dr. Emily Kynaston helped with electron microscopy. I drafted the manuscript for publication, which was edited by Prof. Dwight Seferos, Dr. Andrew Tilley, and Dr. Emily Kynaston.

2 Introduction

Inexpensive, environmentally friendly, and high performance energy storage is important due to the widespread use of portable electronics, the advent of electric vehicles, and the implementation of grid-scale energy storage for renewable power generation. In the current state of electrochemical energy storage, lithium-ion batteries are viewed as the best technology to satisfy the energy requirements of these applications due to their high energy density compared to other battery technologies. However, the redox-active cathode materials in commercial lithium-ion batteries are made from heavy transition metals, cobalt being the most widely used. This is a significant concern for their cost, sustainability, and the environment during both the manufacturing and disposal streams of lithium-ion batteries. Additionally, the raw materials for cobalt-based cathodes are sourced primarily from politically unstable regions of the world, creating potential supply-chain issues that could further inflate the production cost of these key battery components.

Organic electrodes are a promising alternative to metal-based inorganic electrodes, where the inorganic redox-active component is replaced by a carbon-rich material. Organic electrodes can address many of the issues that their inorganic counterparts face due to the high natural abundance of organic materials, their relatively low toxicity, and ease of disposal. Organic electrodes have been shown to yield high performance in different energy storage devices including lithium-ion batteries, redox-flow batteries, and supercapacitors. However, their limited cycling stability severely impedes the further development and ultimate commercialization of these innovative materials. The instability of organics is typically attributed to dissolution of the redox
active materials,\textsuperscript{18-20} chemical reactions that degrade the electrode material,\textsuperscript{21} and conformational changes in the molecular structure upon charging and discharging.\textsuperscript{22}

One of the most studied classes of organic materials for energy storage are arylene diimides such as perylene diimide (PDI) or naphthalene diimide (NDI). These compounds are widely used in the pigment industry and have been extensively applied in a wide range of electronic applications including thin-film transistors, organic solar cells, and sensors.\textsuperscript{23} PDBs and NDBs reversibly accept up to two electrons at room temperature (at \(\sim 2.5\) V \textit{vs} Li/Li\textsuperscript{+}), making them popular candidates for energy storage. However, one of the main disadvantages of PDBs and NDBs is their severe capacity fading due to dissolution of the redox-active materials.\textsuperscript{24-26} Prevalent strategies for improving the cycling stability of these compounds include designing rigid molecular geometries that decrease solubility,\textsuperscript{26} creating nanostructures of the organic materials,\textsuperscript{10,27,28} incorporating PDI and NDI units into polymeric structures,\textsuperscript{29-34} and creating insoluble two-dimensional covalent organic frameworks (COFs).\textsuperscript{35-38} However, these approaches still have various drawbacks and yield less than optimal device stability. Alternate strategies that further increase cycling stability while taking advantage of full redox capability are desirable.

Triptycene-based frameworks and polymers are widely reported in the literature for applications in gas storage and capture.\textsuperscript{39-41} However, their use as energy storage electrodes has never been investigated. Triptycene-based materials offer advantages such as ease of derivatization,\textsuperscript{42,43} and microporosity that should be favourable to ion diffusion. Additionally, the rigid three-dimensional structure of triptycenes could provide insight into the effect of dimensionality on the performance of organic electrode materials.\textsuperscript{44}

Here, I report the first examples of lithium-ion batteries that use triptycene-based frameworks as the cathode material. Using a trans-functionalized triptycene as one building block and PDI/NDI as the linker, novel redox-active COFs are constructed that take advantage of the three-dimensional structure of the triptycene unit. With the PDI based system, a lithium-ion battery with a capacity of 75.9 mAh g\textsuperscript{-1} and a voltage of 2.5 V \textit{vs} Li/Li\textsuperscript{+} is obtained. The battery retains a near perfect coulombic efficiency, and has excellent stability retaining 88.2\% of its capacity after 200 cycles. Moreover, it only loses an additional 8\% of capacity in 300 cycles from cycle 200 to cycle 500. To the best of our knowledge, no PDI-containing material has ever been shown to be stable
for this large amount of cycling for lithium-ion batteries. This work thus describes a new class of highly stable cathode materials for battery applications.

3 Results and Discussion

3.1 Synthesis and Characterization

Three-dimensional PDI-triptycene (PDI-Tc) and NDI-triptycene (NDI-Tc) frameworks were synthesized in quantitative yields by the condensation of perylene-3,4,9,10-tetracarboxylic acid dianhydride or naphthalene-1,4,5,8-tetracarboxylic acid dianhydride, respectively, with amine-functionalized triptycene 1 (Scheme 4.1). Using a trans-functionalized triptycene as the vertex units is shown to yield three-dimensional frameworks (Figure 4.1). Characterization of the resultant materials with FTIR provides evidence of the formation of the diimide functionalities. For PDI-Tc, symmetric and asymmetric imide carbonyl stretches appear at 1771 and 1756 cm\(^{-1}\), respectively, carbon-nitrogen bond stretches appear at 1346 cm\(^{-1}\), and an imide ring deformation stretch appears at 732 cm\(^{-1}\) (Figure 4.2a). For NDI-Tc, symmetric and asymmetric imide carbonyl stretches appear at 1785 and 1714 cm\(^{-1}\), respectively, carbon-nitrogen bond stretches appear at 1337 cm\(^{-1}\), and an imide ring deformation stretch appears at 764 cm\(^{-1}\). \(^{13}\)C CP-MAS NMR provides further evidence for the formation of the frameworks. The successful formation of the PDI-Tc framework is confirmed by the presence of a carbonyl carbon peak at 163.3 ppm, various peaks corresponding the aromatic carbons from 146.6 to 124.1 ppm, and the aliphatic carbons in the triptycene linker at 53.9 ppm (Figure 4.2b). Similar peaks are observed for the NDI-Tc framework (Figure 4.2c) and they are consistent with what has been reported in the literature.\(^{32,44,40}\) The frameworks are stable with respect to heat, without any significant decomposition before 200ºC in nitrogen (Figure 4.3).

Scheme 4.1 Synthesis of PDI-Tc and NDI-Tc frameworks.
Figure 4.1 Simulated structure of the (a,c) PDI-Tc repeat unit and (b,d) the NDI-Tc repeat unit calculated using DFT. For the simulated structures, grey, red, blue and white spheres represent carbon, oxygen, nitrogen, and hydrogen atoms respectively.

Figure 4.2 (a) FTIR spectra of the NDI-Tc and PDI-Tc frameworks in green and red respectively. (b) $^{13}$C CP-MAS NMR spectrum of PDI-Tc with the assigned carbon atoms. (c) $^{13}$C CP-MAS NMR spectra of NDI-Tc with the peak assignments.
Figure 4.3 TGA of PDI-Tc and NDI-Tc performed at a ramp rate of 10°C min⁻¹ run under a flowing nitrogen atmosphere.

Figure 4.4 (a) Deconvoluted C1s XPS spectrum of PDI-Tc with the corresponding assignments. (b) Deconvoluted C1s XPS spectra of NDI-Tc with the peak assignments. (c) N1s XPS spectra of NDI-Tc (d) N1s XPS spectra of NDI-Tc.
High resolution XPS shows the successful formation of the appropriate elemental functionalities in the frameworks. The C1s region of PDI-Tc can be deconvoluted into 5 peaks corresponding to the sp$^3$ carbon at 284.08 eV, the aromatic sp$^2$ carbons at 284.96 eV, the sp$^2$ carbons bonded to the diimide nitrogens at 286.17 eV, the carbonyl carbon at 288.18 eV, and a broad shake-up feature at 290.17 eV (Figure 4.4a). Similar peaks are found for NDI-Tc in the C1s spectrum at 283.99 eV, 285.09 eV, 285.95 eV, 288.75 eV, and 290.47 eV for the sp$^3$ carbons, the aromatic sp$^2$ carbons, the sp$^2$ carbons bonded to the diimide nitrogens, the carbonyl carbons, and the shake-up feature respectively (Figure 4.4b). The high resolution N1s XPS spectra of both frameworks show a single symmetric peak located at 400.28 eV and 400.68 eV for the PDI-Tc and NDI-Tc framework respectively (Figure 4.4c, and Figure 4.4d). Elemental analysis confirms that the frameworks contain carbon, hydrogen, and nitrogen in amounts that are similar to the theoretical values (Section 5.3.3, Section 5.3.4). Deviations from the theoretical values are due to defects within the frameworks and residual solvent trapped inside the frameworks.\textsuperscript{48,49}

The XRD pattern of PDI-Tc shows sharp diffraction peaks, confirming the crystalline nature of the framework. The peaks correspond to diffractions at 9.32 Å, 7.15 Å, 3.58 Å, 3.23 Å, and 3.19 Å (Figure 4.5a). However, the XRD spectrum of NDI-Tc has only a broad amorphous halo corresponding to a d-spacing of 3.03 Å indicating that this framework lacks crystallinity (Figure 4.5b). \textsuperscript{1}CO$_2$ adsorption measurements of PDI-Tc and NDI-Tc show a typical type I isotherm with very little hysteresis, which indicates that these materials are microporous (Figure 4.6a,b). From the gas adsorption data, the frameworks are found to have surface areas of 236.9 and 335.9 m$^2$ g$^{-1}$ for PDI-Tc and NDI-Tc respectively. The pore size distribution, calculated from the adsorption isotherms by density functional theory, reveals that the pore sizes are approximately 3.5 Å, 4.6 Å, and 8.2 Å for the PDI-Tc sample, which is roughly in agreement with the XRD data (Figure 4.6c). The NDI-Tc has similar pore sizes of 3.5 Å, 4.8 Å, and 8.2 Å (Figure 4.6d).
Figure 4.5 XRD pattern of (a) PDI-Tc and (b) NDI-Tc with the labels corresponding to the spacing at the observed diffraction angle.

Figure 4.6 CO₂ gas adsorption isotherms of (a) PDI-Tc and (b) NDI-Tc. Pore size distribution calculated by DFT of (c) PDI-Tc and (d) NDI-Tc.
3.2 Electrode Characterization

The PDI-Tc framework can be cast into an electrode with a conductive carbon additive (Super P) and a polymeric binder that has an ideal morphology for battery applications. In the electrode, the PDI-Tc framework provides Faradaic redox activity that is used to store charge in the battery electrode, the conductive carbon provides an electrical conduction path throughout the electrode, and the binder prevents delamination from the current collector and acts as a ‘glue’ to hold the electrode together. To ensure the best performance in a lithium-ion battery, the materials were first dissolved in methanesulfonic acid and precipitated into methanol to decrease the particle size and remove any zinc impurities that could impact the electrochemical performance. Complete removal of the zinc impurities was confirmed by XPS (Figure 4.7). The precipitated frameworks were then mixed with Super P and PVDF at a ratio of 60:30:10 (w/w/w), mixed in NMP, and cast onto an aluminium foil current collector. By TEM, the PDI-Tc frameworks appear as irregular aggregates that are approximately 200 nm in diameter (Figure 4.8a,b). The precipitated NDI-Tc frameworks have plate-like and irregular aggregate shapes that range in size from approximately 200 nm to 500 nm in width after precipitating in methanol (Figure 4.8c,d). When examining the PDI-Tc electrode by SEM, rod-like aggregates of PDI-Tc, approximately 1 to 7 µm in length and 500 nm wide, are observed that are dispersed evenly in the Super P matrix (Figure 4.9a,b). This morphology is ideal because it provides an electronic conduction path to the PDI-Tc active material, via the carbon Super P, and a relatively short diffusion length for lithium ions within the PDI-Tc aggregate. When cast into an electrode, these aggregates amalgamate to form large, non-conductive structures, as indicated by the high degree of charging in the SEM images (Figure 4.9c,d).
Figure 4.7 XPS survey of (a) as synthesized and (c) precipitated PDI-Tc and (b) as synthesized and (d) precipitated NDI-Tc.

Figure 4.8 (a,b) TEM images of precipitated PDI-Tc and (c,d) TEM images of precipitated NDI-Tc.
Figure 4.9 (a, b) SEM image of the PDI-Tc electrode showing the PDI-Tc aggregates and the carbon Super P. (c, d) SEM image of the NDI-Tc electrode showing the large NDI-Tc aggregates and the carbon Super P. The distortion in the images in (c) and (d) is due to a charging effect on the non-conductive NDI-Tc aggregates. The PVDF homogenously coats the electrode components and therefore cannot be labelled.

3.3 Lithium-Ion Battery Testing and Characterization

The battery performance of the PDI-Tc framework exceeds that of any previous PDI-based frameworks and polymers. The performance of the battery was tested by assembling coin cells using the framework electrodes as cathodes and lithium metal as the anode. The PDI-Tc framework has one reversible redox wave, observed by cyclic voltammetry, centred at 2.5 V vs Li/Li⁺ (Figure 4.10a). The redox wave is due to the reversible reductions of two carbonyl groups of the PDI units (Scheme 4.2). The capacity of the lithium-ion battery was tested with galvanostatic charge/discharge measurements (Figure 4.10b). When cycled at 0.05 C (nC is the current it would take to charge/discharge the cell fully in 1/n hours), the capacity is 75.9 mAh g⁻¹ corresponding to 78.7% of the theoretical capacity (96.4 mAh g⁻¹). When the current is increased by 2 orders of magnitude, the capacity is 22.4 mAh g⁻¹, 29.5% of that obtained at 0.05 C. Importantly, after cycling the cell 500 times at 2 C it retains 80.2% of its original capacity, showcasing the framework’s excellent cycling stability (Figure 4.10c). The coulombic efficiency over the entire cycling stability test for the PDI-Tc battery is ~100% demonstrating that no
irreversible processes take place during charging and discharging. The excellent stability of the PDI-Tc framework is the result of the highly insoluble nature of the frameworks as well as the highly reversible electrochemistry of the PDI units (Figure 4.10c, inset). The stability of the PDI-Tc framework much better than the PDI small molecule, which rapidly decays to 13.6% of the original capacity after 100 cycles, and 7.48% of the original capacity after 500 cycles (Figure 4.11). Additionally, the framework is also very stable at low charging and discharging rates, where material dissolution is more problematic, retaining 82% of its capacity after 200 cycles at 0.5 C (Figure 4.12a). The charge-transfer and equivalent series resistance, measured by EIS after 5, 100, and 200 cycles of the cycling experiment performed at 0.5 C, remain almost constant throughout the cycling experiment (Figure 4.12b, Table 4.1).

**Figure 4.10** (a) Cyclic voltammogram of the PDI-Tc battery at a scan rate of 1 mV s$^{-1}$. (b) Galvanostatic charge/discharge curves of the PDI-Tc battery at currents between 0.05 C to 5 C. (c) Capacity decay and coulombic efficiency of the PDI-Tc battery over 500 cycles at a current rate of 2 C. Inset: Photograph of PDI-Tc in a 1 M LiPF$_6$ ethylene carbonate dimethoxyethane (1:1 w/w) electrolyte.
Scheme 4.2 (a) Redox mechanism for NDI units and (b) redox mechanism for PDI units. The third and fourth carbonyl groups on the arylene diimides do not undergo reversible reductions due to the distribution in conjugation required to reduce them.

Figure 4.11 (a) Structure of the small molecule PDI and (b) capacity decay and coulombic efficiency of the small molecule PDI over 500 cycles at a current rate of 2 C.

Figure 4.12 (a) Capacity decay and coulombic efficiency of the PDI-Tc battery over 500 cycles at a current rate of 2 C. (b) Electrochemical impedance results for the cycling stability test displayed in a Nyquist plot. The dots are the data points and the solid lines represent the fits obtained using a circuit model. (c) Circuit model used for the PDI-Tc battery.
Table 4.1 EIS modelling data for the PDI-Tc battery during the cycling stability measurement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rs (Ω)</th>
<th>CPE-T (F)</th>
<th>CPE-P</th>
<th>R1 (Ω)</th>
<th>Wo-R (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 cycles</td>
<td>4.30</td>
<td>1.87x10^{-5}</td>
<td>0.73964</td>
<td>273.6</td>
<td>179.2</td>
</tr>
<tr>
<td>100 cycles</td>
<td>3.45</td>
<td>1.25x10^{-5}</td>
<td>0.81342</td>
<td>299.1</td>
<td>178.1</td>
</tr>
<tr>
<td>200 cycles</td>
<td>4.00</td>
<td>1.67x10^{-5}</td>
<td>0.79824</td>
<td>281.7</td>
<td>158.2</td>
</tr>
</tbody>
</table>

The NDI-Tc framework did not display optimal performance, likely due to the large aggregate size in the electrode and/or the poor crystallinity (Figure 4.5b, Figure 4.13). Although the PDI-Tc and NDI-Tc framework electrodes have similar redox characteristics, a different circuit model for the EIS was required for each. A modified Randles circuit was sufficient for the PDI-Tc framework while the NDI-Tc framework required an addition R/CPE element for the model to fit (Figure 4.13e). This can be explained by the large charge-transfer resistance for the NDI-Tc framework, likely due to the large non-conductive aggregates observed in the electrode (Figure 4.9c,d). In the PDI-Tc framework, only one R/CPE element is needed to model the charge-transfer resistances for both the anode and cathode. This is due to the similar resistances and capacitances for each redox reaction and they are indistinguishable. However, for the NDI-Tc framework, the charge resistance of the cathode, along with the much larger capacitance value, creates a frequency response that behaves much differently than the anode. The result is the appearance of 2 semicircles, one for the anode that appears at high frequency and one for the cathode that appears at lower frequency.

Table 4.2 EIS modelling data for the NDI-Tc battery during the cycling stability measurement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rs (Ω)</th>
<th>CPE1-T</th>
<th>CPE1-P</th>
<th>R1 (Ω)</th>
<th>CPE2-T</th>
<th>CPE2-P</th>
<th>R2 (Ω)</th>
<th>Wo1-R (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 cycles</td>
<td>4.0</td>
<td>1.12x10^{-5}</td>
<td>0.80000</td>
<td>110.8</td>
<td>0.013644</td>
<td>0.59078</td>
<td>4432</td>
<td>1.24x10^{-5}</td>
</tr>
<tr>
<td>100 cycles</td>
<td>3.7</td>
<td>1.54x10^{-5}</td>
<td>0.79314</td>
<td>105.0</td>
<td>0.015636</td>
<td>0.69207</td>
<td>5031</td>
<td>2.62x10^{-9}</td>
</tr>
<tr>
<td>200 cycles</td>
<td>3.4</td>
<td>2.14x10^{-5}</td>
<td>0.77708</td>
<td>94.00</td>
<td>0.017328</td>
<td>0.72311</td>
<td>5078</td>
<td>2.84x10^{-13}</td>
</tr>
</tbody>
</table>
Figure 4.13 (a) Cyclic voltammogram of the NDI-Tc battery at a scan rate of 1 mV s$^{-1}$. (b) Galvanostatic charge/discharge curves of the NDI-Tc battery at currents between 0.05 C and 5 C. (c) Capacity decay and coulombic efficiency of the NDI-Tc battery over 200 cycles at a current rate of 0.5 C. The jumps in capacity and coulombic efficiency are due to the potentiostatic impedance measurement run at 2.5 V that charges the battery slightly while running the measurement. (d) Electrochemical impedance results for the cycling stability test displayed in a Nyquist plot. The dots are the data points collected and the solid lines represent the fits obtained using a circuit model. (e) Circuit model used for the NDI-Tc battery.

The higher charge-transfer resistance of the NDI-Tc framework cathode is likely due to the large aggregate size of NDI-Tc in the electrode. Lithium ion conduction throughout the active material proceeds via lithium ion hopping. In PDI-Tc, the smaller size of the aggregates as well as the higher crystallinity facilitates facile lithium ion diffusion through the aggregate compared to the large, amorphous NDI-Tc aggregates. The high charge-transfer resistance of the NDI-Tc framework could also be the manifestation of a low conductivity of the NDI-Tc framework due to the lower crystallinity and lack of efficient overlap between the aromatic cores of NDI-Tc.
4 Conclusions

In summary, I have demonstrated the use of triptycene-based COFs as cathode materials for lithium-ion batteries for the first time. Using a PDI-based redox couple, a high reversibility and stability was achieved. The capacity reached 78.7% of the theoretical value with PDI-Tc at a rate of 0.05 C and retains 29.5% of this value when the current is increased by 2 orders of magnitude. The coulombic efficiency is ~100% throughout the experiment, demonstrating the almost perfect reversibility. Importantly, an excellent stability was demonstrated by cycling the battery 500 times at 2 C. The battery retained 80.2% of its capacity, which is the best reported value for PDI-based polymers or frameworks. This work demonstrates that triptycene-based COFs can form the basis of highly stable lithium-ion batteries. The NDI version of the same COF does not feature this high performance, which shows how critical molecular design is for organic battery applications. The replacement of the inorganic cathode materials with inexpensive, abundant organic materials such as the ones reported here should yield devices with a lower cost, greater sustainability, and a lower impact on the environment. I hope that this work will provide a new avenue towards the design of highly stable organic electrodes. By replacing the PDI units with ones that have a higher voltage and capacity, high-performance materials can be made without compromising stability.

5 Experimental

5.1 General Considerations

All reagents and electrolytes were purchased from Sigma-Aldrich and used as received. Organic solvents for synthetic procedures were obtained from Caledon Laboratories Ltd., dried in a solvent purification system (Innovative Technology) under argon and then further dried over 4 Å molecular sieves (Sigma-Aldrich). All electrochemical measurements and construction of lithium-ion batteries were performed at room temperature in an argon-filled glovebox (mBraun) with oxygen and moisture levels below 5 ppm. Battery capacities and C-rates are calculated based on the amount of active material in the cathode, with the theoretical capacities of PDI-Tc and NDI-Tc being 96.4 and 124.2 mAh g⁻¹ respectively.
5.2 Instrumentation and Methods

TEM was performed on a Hitachi HT-7700 C-TEM at an accelerating voltage of 80 kV. SEM was performed on a Hitachi S-5200 SEM. The FTIR spectra were recorded using a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a 10-bounce diamond/ZnSe ATR accessory. Solution NMR spectra were recorded using a Bruker Avance III 400 spectrometer operating at 400 MHz. $^{13}$C CP/MAS NMR spectra were recorded using an Agilent DD2-700 spectrometer with a recycling delay of 30 seconds and an 18 kHz spinning rate. XPS was carried out using a Thermo Scientific k-Alpha spectrometer with a monochromated Al Ka source. TGA was performed on a TA instruments Q50 TGA with a heating rate of 10°C min$^{-1}$. XRD was measured using a Rigaku MiniFlex 600 X-ray Diffractometer. All electrochemical measurements were performed on a Bio-Logic SP-200 potentiostat/galvanostat with a frequency response analyzer. Equivalent circuit modelling was performed using the Zview software. Carbon dioxide adsorption isotherms were performed by Quantachrome’s Material Characterization Laboratory with an Autosorb iQ Station 2. Prior to analysis, the frameworks were activated at 200 °C for 24 hours. Geometry optimizations were performed using the Gaussian 09 software suite at the B3LYP level of theory and the 6-31G basis set.

5.3 Synthesis and Characterization

5.3.1 Synthesis of 1

The synthesis of 1 was carried out using a previously reported procedure.$^{43}$

5.3.2 General Synthesis of Arylene Diimide-Triptycene Frameworks

1 equivalent of 1, 1.5 equivalents of the dianhydride monomer, 0.8 equivalents of zinc (II) acetate, and 260 equivalents of imidazole were mixed together to homogenize and then added to a flame-dried 3-necked flask fit with a reflux condenser. The mixture was backfilled with argon three times to remove any oxygen. The reaction mixture was stirred at 160°C for 24 hours. Upon completion, the reaction was cooled to room temperature and methanol was added to dissolve the solid imidazole. The reaction was then poured into methanol and filtered through a Soxhlet thimble. The crude material was purified by Soxhlet extraction with methanol for one day and then chloroform for 5 hours to remove imidazole, impurities, and any low molecular weight species.
5.3.3 Characterization of PDI-Tc

Performed on a 3.34 mmol scale. Quantitative yield (2.87 g). $^{13}$C CP/MAS NMR δ: 163.38, 146.55, 133.08, 124.06, 53.86 ppm. Elemental analysis calculated for C$_{56}$H$_{24}$N$_3$O$_6$: C, 80.57; H, 2.90; N, 5.03. Found: C, 70.02; H, 3.24; N, 4.36.

5.3.4 Characterization of NDI-Tc

Performed on a 0.835 mmol scale. Quantitative yield (603 mg). $^{13}$C CP/MAS NMR δ: Elemental analysis calculated for C$_{41}$H$_{17}$N$_3$O$_6$: C, 76.04; H, 2.65; N, 6.49. Found: C, 67.63; H, 2.86; N, 7.09.

5.3.5 Purification of Frameworks by Precipitation

To further purify the frameworks and decrease the particle size, 144 mg of the frameworks were dissolved in 15 mL of methanesulfonic acid overnight with stirring. The solution was then added dropwise to 2.5 L of methanol in a rapidly stirring beaker. The suspension was then concentrated on a rotary evaporator until the volume of methanol was approximately 500 mL. The suspended frameworks were collected by centrifugation, washed with methanol three times, and dried at 200°C under vacuum overnight.

5.4 Assembly of Lithium-Ion Battery Coin Cells

The cathode containing the frameworks was prepared by mixing the purified framework, carbon Super P, and PVDF in a 60:30:10 (w/w/w) ratio and suspending the mixture in NMP at a concentration of 150 mg mL$^{-1}$. The slurry was sonicated for 1 hour, stirring every 15 minutes to homogenize. The slurry was cast onto an aluminum foil current collector and dried according to a previously published procedure.$^{22}$ CR2023-type coin cells were purchased from MTI Corporation. A copper foil with a diameter of 16 mm (McMaster-Carr) was used as the anodic current collector, a lithium foil with a diameter of 16 mm was used as the anode, and a Celgard polypropylene separator with a diameter of 19 mm was used to prevent short circuiting. An electrode punch (DPM Solution Inc.) was used to cut the electrodes to a 16 mm diameter and a hydraulic press (BT Innovations) was used to hermetically seal the cells. Approximately 80 µL of electrolyte (1:1 (v/v) ethylene carbonate:dimethoxyethane, 1 M LiPF$_6$) was used to fill the cells prior to sealing.
6 References


Chapter 5
Ladder-Type Triptycene-Based Frameworks for Lithium-Ion Battery Anodes

1 Contributing Statement

Dr. Andrew Tilley performed the initial computational work, helped develop the synthetic route towards these materials, and provided the F-PDI-Tc framework. Dr. Emily Kynaston helped with electron microscopy. Dr. Sergiy Nohkrin performed the solid-state NMR and the EPR studies. I synthesized the F-NDI-Tc and F-pyro-Tc frameworks, performed the structural and electrochemical characterization, and interpreted the results.

2 Introduction

The work presented in the previous two chapters was focused on cathode materials for lithium-ion batteries. In fact, the vast majority of organic electrodes for lithium-ion batteries have been investigated as cathode materials.\(^1\) This is likely because the redox activity of most organics are well-suited for cathode materials and there is an obvious motivation for developing new cathode materials due to the environmental burden, the unfavourable mechanical properties, and the high cost of current transition metal-based cathodes. However, the development of new rechargeable anode materials is still important. The reason for this is two-fold; 1) the graphite electrodes that are used in commercial rechargeable lithium-ion batteries have a relatively low capacity of approximately 300 mAh g\(^{-1}\) compared to that of lithium metal (~3842 mAh g\(^{-1}\)); and 2) the formation of dendrites upon repeated cycling of lithium and sodium metal anodes poses serious safety concerns.\(^2\)\(^-\)\(^4\) Obviously, there is a large opportunity for development of high performance anodes.

Many strategies have been employed to replace the current low capacity anode materials. Most of these have focused on either addressing the inherent safety issues with alkali metal anodes by inhibiting dendrite formation or by replacing the anode with a new material altogether. Popular strategies to inhibit dendrite formation include using solid electrolytes with a high modulus,\(^3\)\(^,\)\(^5\) highly concentrated electrolytes,\(^4\)\(^,\)\(^6\) and plating lithium metal within a carbon material.\(^2\)\(^,\)\(^7\) Although much progress has been made in this area, these strategies are not enough to prevent lithium dendrite formation after extended cycling and safety issues are still a major concern.
On the other hand, using other low-voltage, high-capacity materials is experiencing a high degree of interest. Silicon, germanium, and phosphorus are examples of materials that have been widely investigated as new anode materials having theoretical capacities greater than 1000 mAh g\(^{-1}\) and voltages lower than 0.5 V vs Li/Li\(^+\). However, these materials have challenges associated with the large volume expansion upon lithiation, sometimes greater than 300%, leading to low cycling stability. An alternative solution is to use organic materials that typically do not experience a large volume expansion. However, the research in organic anodes materials has been relatively sparse in part because of the degradation of organic compounds at low potentials, especially ones that have saturated carbons or complex functionality. The research that has been performed on organic anodes has thus been focused on conjugated materials with a minimal amount of saturated carbons.

One of the most popular classes of organic materials for lithium-ion battery anodes are conjugated carboxylic acids. This is due to the low reduction potential of carboxyl groups (~0.5 V vs Li/Li\(^+\)) and the high abundance of carboxylic acid-containing organic compounds. However, these compounds still have a relatively low theoretical capacity of approximately 300 mAh g\(^{-1}\), which limits the energy density of the battery. Other classes of organic compounds have also been explored for lithium-ion battery anodes such as imines and carbonyls but these also suffer from low capacities of under 300 mAh g\(^{-1}\). Recently, an intriguing phenomenon has been discovered where the insertion of lithium-ions into a conjugated structure can provide a capacity of over 1500 mAh g\(^{-1}\). This phenomenon has been dubbed ‘superlithiation’ due to the large amount of lithium ions that are inserted into the conjugated organic structure. The proposed mechanism for this large capacity is a complete reduction of the sp\(^2\) framework where each carbon atom in the structure accepts an electron and a lithium ion (Scheme 5.1). This type of reduction has been observed in compounds such as aromatic and conjugated carboxylic acids and ladder-type polymers. Superlithiation compounds can greatly increase the energy density of the resulting batteries, however, one of the main limitations of these materials is their slow kinetics, leading to their low power density. A possible solution to this kinetic issue is to use frameworks with inherent porosity that can facilitate ion diffusion.
Scheme 5.1 Proposed electrochemical insertion of lithium ions into the conjugated structure of naphthalene dianhydride. Adapted from reference 28.

Here, I describe my work towards triptycene-based frameworks that incorporate benzimidazole linkers. These compounds are shown to undergo superlithiation at low potentials, providing a high capacity of 557 mAh g\(^{-1}\) for the F-PDI-Tc framework. Importantly, this capacity is obtained at room temperature and the framework is stable for over 500 cycles. By studying the effect of the linker on battery performance, I draw conclusions on the structure-property relationships for the performance of organic framework materials for lithium-ion battery anode.

3 Results & Discussion

3.1 Synthesis and Characterization

The frameworks were synthesized in acidic or basic conditions using the corresponding dianhydride and the hexamino triptycene hydrochloride salt (1) or the free-base (2) respectively (Scheme 5.2). Using the hydrochloride salt of hexamino triptycene (1) allows a gram scale preparation of 1 without the need for anhydrous or oxygen-free conditions compared to a synthesis using the highly air sensitive free-base 2.\(^{34}\) F-pyro-Tc and F-NDI-Tc were synthesized in 61.9% and quantitative yields, respectively, using the acidic conditions. However, attempts to synthesize F-PDI-Tc using the same acidic conditions only led to the recovery of starting material as indicated by the FTIR spectra (Figure 5.1a). When F-PDI-Tc was synthesized in basic conditions, a new peak at 1690 cm\(^{-1}\) was observed that corresponds to the C=O stretch and the C=N stretch in the new 5-membered ring, which is consistent with similar small molecule organic compounds (Figure 5.1b).\(^{31,35,36}\) However, the majority of the peaks are very similar to that of the perylene dianhydride starting material suggesting that the degree of functionalization is low and/or there
are many defects in the framework. This could be due to the higher number of equivalents of the anhydride used for the synthesis of the F-PDI-Tc framework in basic conditions to try and functionalize the triptycene core as much as possible with the redox active perylene groups, the strong $\pi$-$\pi$ stacking of the perylene units limiting solubility, or to degradation of the highly sensitive amine precursor that occurs prior to functionalization.\textsuperscript{34} When F-NDI-Tc and F-pyro-Tc were synthesized in acidic conditions, new peaks in the FTIR spectra emerged. Notably, the broad peaks at 1701 cm\textsuperscript{-1}, 1634 cm\textsuperscript{-1}, and 1549 cm\textsuperscript{-1} in F-NDI-Tc and 1721 cm\textsuperscript{-1}, 1625 cm\textsuperscript{-1}, and 1436 cm\textsuperscript{-1} in F-pyro-Tc are due to the C=O and C=N stretches (Figure 5.1b).\textsuperscript{31,35,36} This indicates that the F-NDI-Tc and the F-pyro-Tc frameworks are functionalized to a much larger degree than the F-PDI-Tc framework.

\textbf{Scheme 5.2} Synthesis of fused frameworks in (a) acidic and (b) basic conditions.
**Figure 5.1** (a) FTIR spectra of F-PDI-Tc synthesis in acidic conditions, F-PDI-Tc synthesized in basic conditions and the perylene dianhydride starting material. (b) FTIR spectra of all synthesized frameworks.

The XRD pattern of F-PDI-Tc shows diffraction peaks that are similar to the flexible framework reported in Chapter 4, other PDI-based polymers linked through the diimide nitrogen, and also that of the perylene dianhydride starting material (Figure 5.3a).\(^{37}\) This suggests that the diffraction peaks are coming from the stacking of the perylene units. The F-NDI-Tc and F-pyro-Tc XRD patterns show broad amorphous halos with the F-NDI-Tc framework having two peaks corresponding to a spacing of 6.14 Å and 3.79 Å while the F-pyro-Tc framework has one very broad peak corresponding to a spacing of 4.29 Å. Since the arylene dianhydride starting materials are crystalline, this shows that the frameworks are functionalized to a relatively high degree, which breaks up the crystal packing between the arylene units. The differences between the resulting crystallinity of the frameworks are likely the result of the stronger interactions of the perylene cores leading to low solubility, similar to that reported in Chapter 4. The low solubility leads to the F-PDI-Tc compound precipitating out of solution after a low degree of functionalization.

Solid-state \(^{13}\)C NMR was performed to further characterize the frameworks (Figure 5.4). The spectra of the frameworks are consistent with reports of similar compounds and the assignments correlate with those calculated by DFT (Section 5.2).\(^{35}\) The chemical shift of the carbonyl and benzimidazole ring are at 159 ppm, 158 ppm, and 166 ppm, for F-PDI-Tc, F-NDI-Tc, and F-pyro-Tc respectively. Additionally, the sp\(^3\) carbon peak in the triptycene unit is observed at 49 ppm, 52 ppm, and 53 ppm for F-PDI-Tc, F-NDI-Tc, and F-pyro-Tc respectively indicating that the
incorporation of the triptycene unit into the material is successful. Other peaks in the spectra correspond to the various aromatic carbons in the phenyl groups of the triptycene and the aromatic carbons in the arylene units. As the linker in the frameworks decreases in size from perylene to pyromellitic, the signal in the spectra decreases dramatically. Increasing the number of scans in the measurement did not provide greater resolution, which suggests that the frameworks exhibit some paramagnetic character. Indeed, electron paramagnetic resonance (EPR) measurements show that all frameworks possess radical character with a small degree of anisotropy and hyperfine coupling for the F-pyro-Tc and F-NDI-Tc frameworks and no hyperfine coupling for the F-PDI-Tc framework (Figure 5.5). The g-factor is 2.0034 for F-PDI-Tc, 2.0031 for F-NDI-Tc, and 2.0030 for F-pyro-Tc. The g-factors for the frameworks are similar to that observed for a similar ladder-type polymer, polybenzimidazobenzoisoquinoline (BBL), which has a g-factor of 2.0034.\textsuperscript{38,39} EPR studies of BBL show similar spectra to that obtained with F-pyro-Tc and F-NDI-Tc, having a small degree of anisotropy and hyperfine coupling. The origin of the unpaired electrons in BBL was attributed to the formation of bond alternation charged defects that result in polarons, which was supported by an optical absorption below 2000 nm. This suggests that polarons are present in all of the synthesized frameworks, with the concentration of the polarons increasing from F-PDI-Tc to F-pyro-Tc. Further characterization to confirm this hypothesis is underway.

![TGA of fused frameworks under a running nitrogen atmosphere.](image)

**Figure 5.2** TGA of fused frameworks under a running nitrogen atmosphere.
Figure 5.3 XRD patterns of (a) F-PDI-Tc, (b) F-NDI-Tc, and (c) F-pyro-Tc.

Figure 5.4 CP-MAS $^{13}$C NMR spectra of (a) F-PDI-Tc, (b) F-NDI-Tc, and (c) F-pyro-Tc with the corresponding assignments calculated by DFT.

Figure 5.5 EPR spectra of the frameworks.
The C1s XPS spectra shows that all frameworks possess the correct carbon environments expected for the frameworks (Figure 5.6). Each framework possesses an sp\(^3\) carbon signal corresponding to the aliphatic carbon in the triptycene unit, an sp\(^2\) carbon signal attributed to the carbon atoms in the aromatic rings, a signal corresponding to the carbons in the triptycene rings bonded to nitrogen atoms, a signal corresponding to the benzimidazole carbons double bonded to oxygen and nitrogen, and a broad shake-up feature corresponding to the π-π* transition. Additionally, the N1s XPS spectra shows two nitrogen bonding environments. The peak at 399.18 eV, 398.98 eV, and 399.08 eV in the F-PDI-Tc, F-NDI-Tc and F-pyro-Tc framework corresponds to the sp\(^2\) nitrogen while the peak at 400.88 eV for F-PDI-Tc and F-NDI-Tc and the peak at 400.58 eV for F-pyro-Tc corresponds to the sp\(^3\) nitrogen (Figure 5.7). The results of the N1s spectra show that the benzimidazole ring is formed between the dianhydride and the triptycene unit.

**Figure 5.6** C1s XPS spectra of (a) F-PDI-Tc, (b) F-NDI-Tc, and (c) F-pyro-Tc.

**Figure 5.7** N1s XPS spectra of (a) F-PDI-Tc, (b) F-NDI-Tc, and (c) F-pyro-Tc.

The porosity and surface of the materials were examined by CO\(_2\) gas adsorption at room temperature. All frameworks show a typical type I isotherm that is consistent with microporous materials. The surface area of the materials increases with decreasing aromatic linker size with F-PDI-Tc, F-NDI-Tc, and F-pyro-Tc frameworks having surfaces areas of 124.0 m\(^2\) g\(^{-1}\), 276.5 m\(^2\) g\(^{-1}\).
and 328.2 m² g⁻¹ respectively. The pore size distribution calculated by DFT shows that all frameworks have similar pore sizes of 3.5 Å, 4.8 Å, and 8.2 Å for F-PDI-Tc, and 3.5 Å, 5.0 Å, and 8.2 Å for F-NDI-Tc and F-pyro-Tc.

Figure 5.8 CO₂ gas adsorption and pore size distribution of (a,d) F-PDI-Tc, (b,e) F-NDI-Tc, and (c,f) F-pyro-Tc.

3.2 Electrode Characterization

To test the applicability of the frameworks for lithium-ion battery anodes, electrode films were cast as a composite of the active framework materials, carbon Super P, and a PVDF binder in a weight ratio of 60:30:10 (Experimental Section). The electrodes were first examined by SEM to characterize the morphology, which is important for the performance of the resultant lithium-ion batteries (Figure 5.9). The SEM images of the F-PDI-Tc electrode show a homogenous distribution of the materials. The F-PDI-Tc material appears as small aggregates with an average length of less than 2 μm and a diameter of ~300 nm, which are distributed within the carbon Super P matrix. The F-NDI-Tc electrode has large aggregates distributed throughout the electrode of varying sizes with some less than a 3 μm in diameter and some up to 80 μm in length. However, there are some areas of the electrode that have a homogenous distribution of the F-NDI-Tc material. The F-pyro-Tc electrode also has large aggregates in the electrode, although they are
smaller in size than the F-NDI-Tc aggregates with lengths around 20 µm. The F-pyro-Tc electrode also has some regions where there is a homogenous distribution of material.

Figure 5.9 SEM images of (a,b) F-PDI-Tc electrodes, (c,d) F-NDI-Tc electrodes, and (e,f) F-pyro-Tc electrodes.

The large aggregate size in the F-NDI-Tc and F-pyro-Tc electrodes could have an effect on the electrochemical performance of the resultant lithium-ion battery due to the large lithium-ion diffusion length to penetrate the aggregate as well as the non-conductive nature of the frameworks. In order to decrease the aggregate size in the F-NDI-Tc and F-pyro-Tc electrodes, and to examine its effect on lithium-ion battery performance, the materials and resultant slurry were subjected to ball milling. Examining the morphology of the resultant electrodes by SEM clearly shows a drastic reduction in the average aggregate size, and an obvious increase in electrode homogeneity (Figure 5.10). For the F-NDI-Tc electrode, ball-milling decreases the aggregate size to below 10 µm and an increase in homogeneity compared to the sample that was not ball-milled. The F-pyro-Tc electrode that was ball-milled also has a decreased aggregate size to diameters below 10 µm, there is a qualitative increase in the homogeneity of the film, and there is an apparent increase in number macropores in the film compared to the electrode cast without ball-milling. This large difference in film morphology for the F-pyro-Tc may suggest that there is chemical degradation occurring in the framework upon ball-milling. Indeed, the FTIR spectra of the ball-milled F-NDI-Tc framework shows little change in the spectra while that of the F-pyro-
Tc framework changes significantly (Figure 5.11). This shows that the F-NDI-Tc sample is stable to the ball-milling conditions while that of the F-pyro-Tc framework is not stable. Therefore, only the effect of ball-milling on the F-NDI-Tc sample is examined below.

**Figure 5.10** SEM of (a,b) F-NDI-Tc and (c,d) F-pyro-Tc electrodes that were subjected to ball-milling prior to casting.

**Figure 5.11** FTIR of ball-milled (a) F-NDI-Tc and (b) F-pyro-Tc compared to samples that were not ball-milled.
3.3 Lithium-Ion Battery Testing and Characterization

To test the electrodes, lithium-ion battery coin cells were assembled using lithium as the reference and auxiliary electrode. From the cyclic voltammogram, the frameworks exhibit an electrochemical profile that is consistent with that observed for other superlithiation compounds (Figure 5.12). For the F-PDI-Tc electrode, the first scan reveals a sharp cathodic peak at 1.90 V, which almost disappears in the consecutive scans. This peak is ascribed to the reduction of the carbonyl oxygen and the reduction of the sp$^2$ imine nitrogen. From 1 V to 0 V vs Li/Li$^+$, a reduction occurs that is attributed to the formation of the solid electrolyte interface and the insertion of lithium-ions into the aromatic carbons around the framework. When reversing the scan, there is a small, broad oxidation peak centred at 1.23 V that is ascribed to the de-insertion of lithium-ions in the framework. Beyond the first scan, the CV curves nearly overlap and there is a new anodic peak that emerges at 1.60 V. For the F-NDI-Tc framework, the evolution of the profiles and the peaks are similar to the F-PDI-Tc framework although there is much less current being drawn from the system. This may indicate that the F-NDI-Tc framework is not as electrochemically active as the F-PDI-Tc framework. The CV of the F-pyro-Tc framework, however, is much different from the other two materials. The first scan contains cathodic peaks at 1.46 V, 0.92 V, and 0.42 V that correspond to the reduction of the carbonyl groups, the reduction of the imine groups, and the formation of the solid electrolyte interface respectively. Additionally, from 1.0 V to 0.0 V, there is a broad reduction peak overlapping with the peaks at 0.92 V and 0.42 V that correspond to the insertion of lithium ions into the aromatic carbons, much like that of F-PDI-Tc and F-NDI-Tc. However, unlike the F-PDI-Tc and F-NDI-Tc frameworks, there is a much more pronounced oxidation. Two distinct peaks at 0.53 V and 1.01 V relate to the de-insertion of lithium ions. After the first scan, the peaks at 1.46 V and 0.92 V are greatly diminished and the peak at 0.42 V completely disappears. The broad reduction and oxidation peaks from 0.0 V to 1.0 V corresponding to the insertion and de-insertion of lithium ions into and out of the framework become consistent after the first scan. These results show that redox activity is occurring at low potential and is consistent with what is observed for other superlithiation compounds.

To determine the capacity of the frameworks, galvanostatic charge-discharge experiments were performed. It is important to note that since the fused framework materials are being tested as anode materials, the capacities are calculated from the galvanostatic profile going from low to
high potential with positive current, designated as the discharge profile. This is because when assembled into a lithium-ion battery, the profile going from low to high potential will determine the discharge capacity of the anode, while the profile from high potential to low potential will determine the charging capacity.

**Figure 5.12** CV (a) F-PDI-Tc, (b) F-NDI-Tc, and (c) F-pyro-Tc batteries performed at 1 mV s\(^{-1}\).

Testing F-PDI-Tc first, the battery has an initial capacity of 188 mAh g\(^{-1}\) at a current density of 50 mA g\(^{-1}\) (Figure 5.13a). Increasing the current leads to a dramatic decrease in performance, with a capacity of only 32 mAh g\(^{-1}\) at a current density of 500 mA g\(^{-1}\). The charge profile of the F-PDI-Tc material has a plateau between 0.5 V and 0.0 V and a long sloping discharge from 0 V to 3 V, consistent with other reports of superlithiation (Figure 5.13b). When the cycling stability of the F-PDI-Tc electrode is tested at 200 mA g\(^{-1}\), an almost linear increase in capacity starting from 100 mAh g\(^{-1}\) at the 3\(^{rd}\) cycle and increasing to 419 mAh g\(^{-1}\) on the 500\(^{th}\) cycle with an almost perfect coulombic efficiency is observed (Figure 5.13c). This shows that there is a long activation period required for this material and prior to this activation the material suffers from poor kinetics. After testing the cycling stability, the rate capabilities were re-examined and they show a marked improvement in performance (Figure 5.13d). At a current density of 50 mA g\(^{-1}\), the capacity of the cycled F-PDI-Tc electrodes reaches a maximum of 557 mAh g\(^{-1}\) and even at an extremely high current density of 5000 mA g\(^{-1}\), the electrode still maintains a capacity of 96 mAh g\(^{-1}\). The reason for this drastic rise in performance is likely due to an activation of the electrode by an increased penetration of the electrolyte within the crystal structure of the F-PDI-Tc framework, leading to a decreased resistance. This resistance can be quantified by the impedance data, where the charge-transfer resistance decreases from 214.7 \(\Omega\) to 57.97 \(\Omega\) from the pristine electrode to the cycled electrode (Figure 5.13f, Table 5.1).
Figure 5.13 Performance of F-PDI-Tc in a lithium-ion battery. (a) Capacity at different currents and (b) charge discharge behaviour before cycling. (c) Cycling stability at 200 mA g\(^{-1}\). (d) Capacity at different currents and (e) charge discharge behaviour after cycling. (f) Impedance of F-PDI-Tc lithium-ion battery performed at 0.1 V before and after cycling. The solid lines represent the fits.

Figure 5.14 Equivalent circuit used to model the impedance behaviour of all frameworks.

The F-NDI-Tc framework has a poor performance compared to F-PDI-Tc framework. Even at the lowest current density of 50 mA g\(^{-1}\), the framework only has a capacity of 39.6 mAh g\(^{-1}\). This is likely due to the large aggregates in the electrode. Cycling the electrode at 200 mA g\(^{-1}\) results in an initial decrease in capacity from 17.2 mAh g\(^{-1}\) to 8.2 mAh g\(^{-1}\) but the capacity slowly increases to 10.8 mAh g\(^{-1}\) after 500 cycles. Testing the rate capability afterwards shows a decrease in performance compared to the sample before cycling, with a maximum capacity of 28.0 mAh g\(^{-1}\) at 50 mA g\(^{-1}\). The impedance spectra of the F-NDI-Tc electrode before and after cycling shows a small increase in the charge-transfer resistance from 380 \(\Omega\) to 415.4 \(\Omega\).
Table 5.1 Impedance fit data of F-PDI-Tc, F-NDI-Tc, and F-pyro-Tc batteries before and after cycling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rs (Ω)</th>
<th>CPE1-T (F)</th>
<th>CPE1-P</th>
<th>R1 (Ω)</th>
<th>CPE2-T (F)</th>
<th>CPE2-P</th>
<th>R2 (Ω)</th>
<th>Wo1-R (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-PDI-Tc</td>
<td>12.44</td>
<td>1.75x10^{-5}</td>
<td>0.76738</td>
<td>214.7</td>
<td>8.63x10^{-3}</td>
<td>0.90</td>
<td>15.81</td>
<td>0.58875</td>
</tr>
<tr>
<td>before cycling</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-PDI-Tc</td>
<td>3.685</td>
<td>1.91x10^{-4}</td>
<td>0.5678</td>
<td>57.97</td>
<td>7.09x10^{-3}</td>
<td>0.81636</td>
<td>62.68</td>
<td>10.89</td>
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<tr>
<td>after cycling</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>F-NDI-Tc</td>
<td>5.359</td>
<td>1.48x10^{-5}</td>
<td>0.76379</td>
<td>380</td>
<td>9.18x10^{-4}</td>
<td>0.90</td>
<td>41.79</td>
<td>337.7</td>
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<tr>
<td>before cycling</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-NDI-Tc</td>
<td>4.067</td>
<td>1.95x10^{-5}</td>
<td>0.73431</td>
<td>415.4</td>
<td>2.38x10^{-3}</td>
<td>0.55134</td>
<td>8.12x10^{19}</td>
<td>1174</td>
</tr>
<tr>
<td>after cycling</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-pyro-Tc</td>
<td>5.252</td>
<td>2.14x10^{-5}</td>
<td>0.75916</td>
<td>339.6</td>
<td>4.20x10^{-3}</td>
<td>0.91121</td>
<td>47.57</td>
<td>14.83</td>
</tr>
<tr>
<td>before cycling</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>F-pyro-Tc</td>
<td>11.56</td>
<td>1.37x10^{-4}</td>
<td>0.7823</td>
<td>30.05</td>
<td>1.45x10^{-2}</td>
<td>0.87056</td>
<td>1.117</td>
<td>2.96x10^{-4}</td>
</tr>
</tbody>
</table>
Figure 5.15 Performance of F-NDI-Tc in a lithium-ion battery. (a) Capacity at different currents and (b) charge discharge behaviour before cycling. (c) Cycling stability at 200 mA g\(^{-1}\). (d) Capacity at different currents and (e) charge discharge behaviour after cycling. (f) Impedance of F-NDI-Tc lithium-ion battery at 0.1 V before and after cycling. The solid lines represent the fits.

The F-pyro-Tc framework has an initial performance similar to that of the F-PDI-Tc framework. At a current density of 50 mA g\(^{-1}\), F-pyro-Tc has a capacity of 137 mAh g\(^{-1}\) and at a current density of 500 mA g\(^{-1}\) it has a capacity of 79.3 mAh g\(^{-1}\) indicating that it initially has a rate capability greater than that of the F-PDI-Tc framework before cycling (Figure 5.16). Cycling the battery leads to an increase in capacity from 98.7 mAh g\(^{-1}\) in the second cycle to 278 mAh g\(^{-1}\) in the 500\(^{th}\) cycle (Figure 5.16c). Testing the rate capabilities after cycling results in a dramatic improvement in performance. The capacity at 50 mA g\(^{-1}\) is 328 mAh g\(^{-1}\) and at 5000 mA g\(^{-1}\) the capacity is 83.8 mAh g\(^{-1}\) (Figure 5.16d,e). The increase in capacity is also attributed to an activation of the electrode, similar to the F-PDI-Tc battery. The decrease in charge-transfer resistance from 339.6 Ω before cycling to 30.05 Ω after cycling shows that the activation results in an increase in the charge-transfer kinetics (Figure 5.16f).
Figure 5.16 Performance of F-pyro-Tc in a lithium-ion battery. (a) Capacity at different currents and (b) charge discharge behaviour before cycling. (c) Cycling stability at 200 mA g$^{-1}$. (d) Capacity at different currents and (e) charge discharge behaviour after cycling. (f) Impedance of F-pyro-Tc lithium-ion battery at 0.1 V before and after cycling. The solid lines represent the fits.

To determine the effect of the framework aggregate size on the performance of F-NDI-Tc, the electrode prepared by ball-milling was tested in a lithium-ion battery (Figure 5.17). Interestingly, the electrochemical profile in both CV and charge discharge experiments changes drastically compared to the sample not ball-milled. From the first CV scan of the ball-milled F-NDI-Tc framework, there are two large reduction peaks centered at 1.30 V and 1.10 V that are attributed to the reduction of the imine and carbonyl groups of the framework, a reduction peak at 0.61 V attributed to the solid electrolyte interface formation, and a long sloping reduction starting at 0.41 V that corresponds to the insertion of lithium ions into the aromatic carbons of the framework (Figure 5.17a). These peaks disappear in the subsequent scans. Scanning anodically, there is a distinct oxidation peak related to the de-insertion of lithium-ions in the aromatic carbons of the framework centered at 0.55 V that is retained in the subsequent scans. The charge-discharge profile of the ball-milled F-NDI-Tc compound at 50 mA g$^{-1}$ shows a nucleation/phase transformation event happening upon the first reduction at $\sim$0.03 V followed by a plateau at 0.12 V. The discharge shows a flat plateau at $\sim$0.555 V that has a capacity of 43.5 mAh g$^{-1}$ (Figure 5.17b). This plateau disappears in the subsequent scans, likely due to a delamination event of the
electrode that shows that the ball-milled films are not adhered well to the electrode. The impedance spectra of the ball-milled F-NDI-Tc framework show a charge-transfer event occurring at high frequency with a resistance of 340.1 Ω (Figure 5.17c, Table 5.2). This value is similar to the charge-transfer resistance in the F-NDI-Tc sample that was not ball-milled suggesting that ball-milling was unsuccessful in decreasing the kinetic barrier towards reduction.

**Figure 5.17** Performance of ball-milled F-NDI-Tc and F-pyro-Tc electrodes. (a) CV, (b) charge discharge behaviour, and (c) impedance of a lithium-ion battery made from ball-milled F-NDI-Tc.

**Table 5.2** Impedance fit data of F-NDI-Tc battery made with ball-milled electrodes before and after cycling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rs (Ω)</th>
<th>CPE1-T (F)</th>
<th>CPE1-P</th>
<th>R1 (Ω)</th>
<th>CPE2-T (F)</th>
<th>CPE2-P</th>
<th>R2 (Ω)</th>
<th>Wo1-R (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-NDI-Tc</td>
<td>5.2</td>
<td>1.10x10⁻⁵</td>
<td>0.780</td>
<td>340.1</td>
<td>1.10x10⁻³</td>
<td>0.5</td>
<td>1360</td>
<td>8.08x10⁵</td>
</tr>
</tbody>
</table>

The trend in performance of the frameworks can be explained by the crystallinity, the morphology of the electrode, and the amount of charge carriers in the frameworks. With the F-PDI-Tc framework, the favourable morphology and the high crystallinity provide short ionic and electronic conduction paths, as well as a short electron hopping distance between the perylene units due to their close π-π stacking distances. This allows F-PDI-Tc to have a high capacity, due to the usage of a relatively high amount of active material compared to that of F-NDI-Tc. The F-pyro-Tc has a relatively unfavourable morphology and a low crystallinity compared to that of the
F-PDI-Tc framework. However, its high performance can be attributed to the high number of charge carriers within the framework, indicated by the large EPR signal, providing a higher conductivity compared to the F-PDI-Tc and F-NDI-Tc frameworks. Additionally, the larger surface area could allow for a better electrolyte penetration within the active material and a higher ionic conductivity within the framework. The poor performance of the F-NDI-Tc is attributed to the low crystallinity, poor morphology, and low number of polarons.

4 Conclusions

In conclusion, novel ladder-type triptycene-based frameworks with benzimidazole linkers have been synthesized for applications as lithium-ion battery anodes. These frameworks undergo superlithiation when reduced at low potentials below 1 V vs Li/Li⁺. With the F-PDI-Tc framework, the initial capacity was 188 mAh g⁻¹ but increased to 557 mAh g⁻¹ after charging and discharging 500 times. This increase is attributed to an activation of the electrode that reduces the charge-transfer resistance, enhancing the kinetics of the redox reactions. The high performance of the F-PDI-Tc framework is attributed to the high crystallinity and small aggregate size in the electrode that allows for short lithium ion diffusion pathways and a short electron hopping distance between perylene units. The F-pyro-Tc framework showed similar performance, with an initial capacity of 98.7 mAh g⁻¹ that increases to 278 mAh g⁻¹ after 500 cycles. The high performance of the F-pyro-Tc is attributed to a high concentration of polarons in the framework, which provides a relatively high conductivity and a large pore volume that facilitates electrolyte penetration in the active material. The F-NDI-Tc electrode however showed poor performance due to the low crystallinity, the large aggregate size, and relatively low concentration of polarons. Reducing the aggregate size of the F-NDI-Tc framework seemed to have a large effect on the electrochemical profile of the framework, with more ideal battery behaviour and well-defined voltage plateaus, but the film integrity was greatly diminished resulting in delamination from the current collector. Overall, it seems that ball-milling fails to improve the electron transfer kinetics of F-NDI-Tc, evidenced by the impedance spectroscopy results showing similar charge-transfer resistances of the ball-milled sample and the sample that was not ball-milled. Improving the film integrity of the ball-milled electrode could result in a better performing electrode and further investigation is warranted. Taking these results into account, the use of ladder-type triptycene-
based frameworks for lithium-ion battery anodes results in highly stable, high capacity materials that could be used to replace the graphite-based anodes used in commercial devices. Future work should focus on producing a material with a high crystallinity, large pore volume, and a high concentration of polarons in the material that can be cast as an electrode with a small aggregate size. Further investigation into the effect of ball-milling and how to eliminate the activation period of the frameworks is planned.

5 Experimental

5.1 General Considerations

All reagents and electrolytes were purchased from Sigma-Aldrich and used as received. Organic solvents for synthetic procedures were obtained from Caledon Laboratories Ltd., dried in a solvent purification system (Innovative Technology) under argon and then further dried over 4 Å molecular sieves (Sigma-Aldrich). All electrochemical measurements and construction of lithium-ion batteries were performed at room temperature in an argon-filled glovebox (mBraun) with oxygen and moisture levels below 5 ppm. All battery capacities and current densities were calculated based on the amount of the framework material in the electrode.

5.2 Instrumentation and Methods

SEM was performed on a Hitachi S-5200 SEM. The FTIR spectra were recorded using a PerkinElmer Spectrum 100 FT-IR spectrometer equipped with a 10-bounce diamond/ZnSe ATR accessory. $^{13}$C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were recorded using an Agilent DD2-700 spectrometer with a recycling delay of 30 seconds and an 18 kHz spinning rate. EPR measurements were obtained on a refurbished Bruker EMX X-Band spectrometer equipped with a high sensitivity cylindrical cavity (0101) at a microwave frequency of 9357.967 MHz, a modulation frequency of 100 kHz, and a modulation amplitude of 1 Gauss. XPS was carried out using a Thermo Scientific k-Alpha spectrometer with a monochromated Al K$_{\alpha}$ source. TGA was performed on a TA instruments Q50 TGA with a heating rate of 10°C min$^{-1}$. XRD was measured using a Rigaku MiniFlex 600 X-ray Diffractometer. All electrochemical measurements were performed at room temperature on a Bio-Logic SP-200 potentiostat/galvanostat with a frequency response analyzer or a Bio-Logic BCS-805 battery tester with a frequency response analyzer. Equivalent circuit modelling was performed using the
Zview software. Carbon dioxide adsorption isotherms were performed by Quantachrome’s Material Characterization Laboratory with an Autosorb iQ Station 2. Prior to analysis, the frameworks were activated at 180°C for 24 hours. Geometry optimizations and NMR calculations were performed using the Gaussian 09 software suite at the B3LYP level of theory and the 6-31G basis set. The NMR output from Gaussian 09 was converted into chemical shifts in ppm by a previously reported method.

5.3 Synthesis and Characterization

5.3.1 Synthesis of 1

The synthesis of 1 was carried out using a previously reported procedure. The NMR spectra was consistent with what was reported.

5.3.2 Synthesis of 2

The synthesis of 2 was carried out using a previously reported procedure. The NMR spectra was consistent with what was reported.

5.3.3 General synthesis of frameworks in acidic conditions

The synthesis of the fused arylene diimide frameworks was based on a procedure previously reported. Briefly, polyphosphoric acid (25 g) was added to an oven-dried 3-necked flask fitted with an argon inlet. The viscous liquid was degassed by bubbling argon through it while heating at 110°C for 24 hours with stirring. The liquid was cooled to 50°C and 1 (1 equivalent) was added and the solution was then stirred at 120°C overnight. The solution was then cooled to 70°C, and the corresponding dianhydride (1.5 equivalents) was added. The reaction was slowly heated to 180°C at a heating rate of 4°C min⁻¹. Upon completion, the reaction was cooled and poured into 500 mL of rapidly stirring methanol. The residual solid in the reaction flask was dissolved in water and poured into the stirring methanol. After stirring for 20 minutes, the solid was filtered, dried, and ground with a mortar and pestle. The solid was then placed in a soxhlet thimble and extracted with methanol for 24 hours, followed by chloroform for 3 hours.
5.3.4 Characterization of F-NDI-Tc

Performed on a 0.569 mmol scale (quantitative yield). $^{13}$C CP/MAS NMR $\delta$: 157.86, 145.24, 137.03, 123.71, 51.73 ppm. Elemental analysis calculated for $C_{41}H_{14}N_6O_3$: C, 77.11; H, 2.21; N, 13.16. Found: C, 62.35; H, 3.01; N, 8.68.

5.3.5 Characterization of F-pyro-Tc

Performed on a 0.569 mmol scale (61.9% yield). $^{13}$C CP/MAS NMR $\delta$: 165.95, 142.33, 132.48, 111.06, 53.30 ppm. Elemental analysis calculated for $C_{35}H_{11}N_6O_3$: C, 74.60; H, 1.97; N, 14.91. Found: C, 55.39; H, 3.83; N, 10.38.

5.3.6 Synthesis of F-PDI-Tc in basic conditions

To a flame-dried 3-necked flask fitted with a reflux condenser, a mixture of 2 (163 mg, 0.473 mmol), zinc acetate (210 mg, 1.144 mmol), perylene-3,4,9,10-tetracarboxylic acid dianhydride (556 mg, 1.417 mmol), and 25 g of imidazole was added. The mixture was backfilled with argon three times to remove any oxygen. The reaction mixture was heated to 160$^\circ$C for 22 hours. Upon completion, the reaction mixture was cooled slightly and then poured into a stirring solution of methanol. The solid was filtered through a soxhlet thimble and was extracted with methanol for 1 day, acetone for 3 hours, hexanes for 2.5 hours, and chloroform for 18 hours to yield a dark purple solid (78.5% yield).

5.3.7 Characterization of F-PDI-Tc

$^{13}$C CP/MAS NMR $\delta$: 160.13, 142.12, 135.00, 126.46, 117.62, 48.66 ppm. Elemental analysis calculated for $C_{92}H_{32}N_6O_{12}$: C, 78.19; H, 2.28; N, 5.95. Found: C, 68.10; H, 2.58; N, 6.81.

5.4 Preparation of Lithium-Ion Batteries

5.4.1 Casting of electrodes from as-synthesized frameworks

The frameworks were initially ground up into a fine powder with a mortar and pestle. The ground frameworks were then mixed with carbon Super P and PVDF in a 60:30:10 (w/w/w) ratio and suspended in NMP at a concentration of 150 mg mL$^{-1}$ for F-PDI-Tc and F-NDI-Tc and at a concentration of 75 mg$^{-1}$ for F-pyro-Tc. The mixtures were then sonicated for 1 hour, stirring every 15 minutes to homogenize. The slurries were then cast onto copper foils (McMaster-Carr)
using a notch-bar with a height of 200 µm, according a previously published procedure. The electrodes were then dried in air on a hotplate at a temperature of 80°C and then in a vacuum antechamber at a temperature of 65°C before bringing into the glovebox.

5.4.2 Casting of electrodes from ball-milled frameworks

The frameworks were ball-milled for 30 minutes at a speed of 4000 rpm with a micro-vibration mill (MTI) with 1.5 mm zirconia beads. Super P was added and ball-milled for an additional 12 minutes, followed by the addition of pre-dissolved PVDF and NMP and ball-milled for an additional 12 minutes. The ratio of frameworks: Super P: PVDF was 60:30:10 and the concentration of the slurry was 80 mg mL\(^{-1}\). The slurries were then cast onto copper foils and dried in the same way as described above.

5.4.3 Assembly of the lithium-ion battery coin cell

CR2023-type coin cells were purchased from MTI Corporation. A copper foil with a diameter of 16 mm (McMaster-Carr) was used as the anodic current collector, a lithium foil with a diameter of 16 mm was used as the reference/auxiliary electrode, and a Celgard polypropylene separator with a diameter of 19 mm was used to prevent short circuiting. An electrode punch (DPM Solution Inc.) was used to cut the electrodes to a 16 mm diameter and a hydraulic press (BT Innovations) was used to hermetically seal the cells. Approximately 80 µL of electrolyte (1:1 (v/v) ethylene carbonate:diethyl carbonate, 1 M LiPF\(_6\)) was used to fill the cells prior to sealing.

6 References


Chapter 6
Conclusions and Future Outlook

1 Summary

In this thesis, I describe the investigation of novel organic materials for energy storage devices. It encompasses the design, characterization, and electrochemical properties of the investigated materials. Additionally, the underlying reason behind the materials performance is also investigated. From Chapter 2, a polyfullerene material was found to possess broad redox peaks that give rise to an ideal pseudocapacitive behaviour. Upon reduction, the monomeric units accept multiple electrons providing the material with a high capacitance. Additionally, since the polyfullerene is redox-active at low potentials, a high power asymmetric SC can be constructed using PEDOT as the positive electrode and the polyfullerene as the negative electrode. The superior performance is a result of the extended voltage window compared to a device with PEDOT acting as both the positive and negative electrode. Additionally, it was found that degradation occurs due to mechanical stress that the polymer experiences upon charging. Decreasing the size of the cation used to balance charge in the material increases the stability.

In Chapter 3, a polymer with pendant flavin units was investigated as a cathode material in a lithium-ion battery. The polymer was designed to mitigate the cycling stability issues discovered in the previous chapter while still avoiding dissolution of the active material in the electrolyte. Here, I found that coating the conductive additive in the electrode with the redox-active polymer affords a high capacity. Additionally, a novel degradation mechanism was elucidated that involves a large geometry change associated with the reduction of the polymer pendant groups and this is expected to be applicable to organic electronic materials in general. I also described the use of computational chemistry as a guide to predict the differences in geometry between the different redox states of organic compounds and from this, stable materials can be designed.

In Chapter 4, triptycene-based frameworks with arylene diimide linkers were studied as cathode materials for lithium-ion batteries. Here, I determined the applicability of triptycene-based frameworks as electrode materials. It was found that the performance of the electrode is highly dependent on the crystallinity and/or the size of the framework aggregates in the electrode. Having a high crystallinity and small aggregate size in the electrode leads to a relatively high conductivity of the framework and results in high usage of active material and excellent cycling stability. These
excellent results are due to the insolubility of the framework and the increased kinetics of reduction compared to amorphous frameworks with large particle size. This work shows that by appropriate choice of redox active linkers, high performance triptycene-based frameworks can be constructed.

In Chapter 5, ladder-type triptycene-based frameworks that contain benzimidazole linkers were investigated for lithium-ion battery anodes. This is the first investigation of superlithiation frameworks for anode materials. It was found that the performance of these anode materials depends on the crystallinity of the material, the morphology of the electrode, and the concentration of the radicals within the frameworks. The F-PDI-Tc framework has good performance due to its high crystallinity and the superior morphology despite its low concentration of radicals and the F-pyro-Tc has good performance due to the high concentration of radicals despite its poor crystallinity and morphology. Additionally, ball-milling the F-NDI-Tc framework to decrease the particle size leads to a different electrochemical profile and a decreased performance. Further elucidation of the nature of the radicals in the frameworks and whether they correspond to polarons needs to be performed and the effect of ball milling the samples needs to be elucidated.

2 Future Outlook

2.1 Future Outlook for Negative Charge Accepting SC Materials

To develop high stability negative electrodes for SC applications, insoluble materials that can accommodate the influx of ions are required. Our group and others have shown that COFs can address this issue due to their permanent porosity and insolubility. Attempts to increase the spacing between the monomer units of the polyfullerene material by introducing other aromatic groups into the polymerization solvent have been unsuccessful. However, by creating frameworks with other redox active compounds that exhibit pseudocapacitance at low potentials, a positive effect on stability is expected.

Conjugated polymers with redox active backbones could also fulfill these requirements. Conjugated polymers become conductive in their doped states, giving rise to pseudocapacitive properties. They also lack crosslinking that is present in the polyfullerene material, allowing easy accommodation of ions and solvent without high mechanical stress. However, negative charge accepting conjugated polymers suffer from a few drawbacks. First, the polymerization of negative
charge accepting polymers for SCs is typically challenging. The monomers are typically sparingly soluble and chemical polymerizations yield materials with inherently low molecular weight that could become soluble upon reduction in the SC electrolyte. Also, electrochemical polymerization could lead to over oxidation of the polymer and rapid degradation. This is a significant issue due to the relatively high oxidation potential required for electropolymerization of n-type polymers. Additionally, low lying LUMOs are required to avoid degradation upon reduction of the material and decomposition of the electrolyte. It is well known that in the case of polythiophenes, whose reduction potentials are typically around -2.0 V vs Ag⁺/AgCl, reduction leads to rapid degradation.⁴⁻⁷

One method that has been used to lower the LUMO level while maintaining a low oxidation potential for electropolymerization is to use donor-acceptor compounds. However, issues related to the degree of electronic delocalization of these compounds is problematic and leads to rapid self-discharge.⁸⁻⁹ Also, the capacity is inherently lower for these compounds due to the use of donor units that are required for polymerization but do not contribute to the acceptance of negative charge. Recently, our group has investigated a class of compounds called thienopyrazines that possess both n-type and p-type redox activity within a single monomer unit (Figure 6.1).¹⁰,¹¹ These compounds exhibit much higher stability than other n-type conjugated polymers, presumably due to the higher amount of delocalization, absence of cross-linking, and a narrow bandgap allowing for electropolymerization and reduction to occur at potentials where the polymer and electrolyte are stable. However, these materials do not yet have the stability required for commercial SCs. It is expected that by further tuning the electronic structure by lowering the LUMO level and raising the HOMO level, this can be resolved. I expect that materials such as these will play a large role in the development of negative charge accepting polymers for SC applications.

![Thienopyrazine Structure and Redox Mechanism](image)

**Figure 6.1** General structure and redox mechanism of thienopyrazines.
Additionally, to achieve high capacitance, the repeating units of the polymers should accept multiple charges. One of the issues with conjugated polymers is that delocalization of the charges along the backbone is accompanied by a Coulombic repulsion. Although this is likely the reason for the pseudocapacitive properties, a consequence is that conjugated polymers can only accept less than one charge per repeating unit. Strategies to overcome this limitation have been demonstrated with positive charge accepting polymers by using pendant redox groups off the conductive polymer backbone, copolymerizing the materials with redox-active substances that offer additional redox activity, or by blending the conductive polymer with redox active materials. Introduction of redox active motifs onto negative charge-accepting polymer electrodes is expected to have similar improvement in performance.

2.2 Future Outlook for Biologically-Derived Polymer Cathodes

The use of biologically-derived materials is expected to play a large role in the deployment of organic cathode materials. This is because of the increased need for sustainable lithium-ion batteries due to their widespread use and predicted growth in new applications. Using the methodology outlined in Chapter 3, biological redox molecules can be incorporated into polymers and mitigate the issues of dissolution that plague small molecule organics in general.

Additionally, the development of stable materials for organic cathodes should be guided using computational chemistry. Careful choice of the pendant redox group can also yield high capacity and high voltage materials. Recently, there has been interesting work on the use of ortho-substituted quinones for cathode materials in lithium-ion batteries. This is because of their overall increase in voltage relative to para-substituted quinones due to the favourable coulombic interaction from lithium ions coordinating with two oxygen atoms (Figure 6.2). Since quinones have an inherently high capacity and certain classes can be derived from nature, they are prime candidates for the development of new pendant polymer cathode materials.

Moreover, future work in the area of polymeric electrode materials is expected to lead to the development of flexible batteries based on these materials. The development of flexible batteries is being investigated in a number of researchers. However, the technologies that these groups use are typically based on nanostructured metal-based electrode materials and/or aqueous systems. By using polymeric electrode materials, there is an opportunity to increase the safety, electrochemical performance, and mechanical properties of the device and decrease the overall
cost. Additionally, polymeric electrode materials should have an increased compatibility with solid-polymer electrolytes that are being developed for flexible and solid-state devices. This is because there is inherent favourable interaction between organic materials, compared to inorganic-organic interfaces. Also, by casting the electrode film as a blend between the active electrode material and the polymer electrolyte, there is an opportunity for evoking a spontaneous phase separation between the two materials. This could result in micrometer or nanometer-sized structures, which should be beneficial for electrolyte diffusion and charge transport.

Figure 6.2 Redox mechanism and voltage of (a) para-substituted quinones and (b) ortho-substituted quinones. Adapted from reference 22.

Moreover, the development of carbon additive-free electrodes could be achieved using organic materials. The investigation of organic materials as pure thin-film electrodes without carbon additives has been investigated previously. However, these previously investigated systems were based on radical polymers that are able to conduct charge through the film through an electron self-exchange mechanism of radicals. By copolymerizing the active material monomer with an ionically conductive block, films up to 5 µm in thickness can be cast with a linear increase in areal capacity (Figure 6.3). If this type of behaviour could be applied to high capacity materials such as quinones, it would easily lead to the implementation of polymer electrodes for thin-film batteries.
2.3 Future Outlook for COF Cathodes

Organic frameworks are highly attractive electrode materials for energy storage due to their insolubility and permanently porous structure, leading to high cycle life as shown by the work of us and others.\(^1\)\(^{−}\)\(^3\) In order to increase the performance of batteries using these materials, improvements in capacity, rate capabilities and voltage need to be addressed. One way this can be achieved is by using high capacity/voltage redox-active linkers and/or functionalizing the vertex unit with redox active functionalities. Another strategy that can improve both rate capabilities and capacity is to infiltrate the porous framework with a conducting polymer.\(^2\) The polymer provides a conductive pathway throughout the COF, allowing thick films to be made that can charge and discharge extremely rapidly without loss in capacity.

Additionally, in the case of triptycene-based frameworks, the triptycene group offers an opportunity to functionalize the sp\(^3\) carbon linking the phenyl groups. This can be used to install additional redox functionality and/or by controlling solubility and crystal structure. Overall, designing organic cathode frameworks with a small aggregate size and high crystallinity can increase performance. Thus, special attention needs to be paid attention to how these materials organize into a crystal structure and how to prepare electrodes with a small active material particle size.
2.4 Future Outlook for Superlithiation Materials

The use of frameworks that undergo superlithiation for anode materials is a new concept and these materials require further investigation in order for them to be considered commercially viable. Specifically, decreasing the activation period required for these frameworks is important. Additionally, increasing the coulombic efficiency of the first charge to avoid a large consumption of lithium-ions and electrolyte in the formation of the solid electrolyte interface is a challenge that needs to be resolved. This last point is general to all superlithiation materials reported in the literature, where the first charge results in a coulombic efficiency of ~50%. Furthermore, the effect of ball-milling still needs to be investigated. Ball-milling seems to result in a more ideal electrochemical profile, having a defined voltage plateau compared to the long sloping plateau that is prevalent among most superlithiation materials. However, an increase in performance has not yet been observed. Improvements in film quality to avoid delamination is expected to elucidate the overall effect of this method for electrode preparation.

Overall, the investigation of superlithiation compounds is still in its infancy and there is much work to be done on the investigation into their fundamental electrochemical properties, structure-property relationships, and overall performance in a commercial device. These aspects are important to the development of these materials and eventual realization into a fully functional lithium-ion battery that uses a high voltage (~3.5 V vs Li/Li+) cathode material, such as that in a real device.

3 Future Issues to Address for Organic Electrodes

In summary, organic electrode materials are rapidly developing but there are issues that still need to be addressed prior to commercialization. First of all, the potential difference between negative and positive electrode materials needs to be increased for all energy storage devices. This needs to be accompanied by the development of electrolytes that are stable to the increase in voltage. The high voltage electrolytes that are being developed are mostly based on solid electrolytes and the applicability of these solid electrolytes with organic materials has been seldom investigated. Therefore, further investigation into the compatibility of both materials needs to be performed.

Additionally, the relatively low amount of charge stored in organic materials need to be addressed. For lithium-ion batteries specifically, the volumetric capacity of organic materials needs to be
increased to be competitive with inorganic electrode materials. The density of inorganics is approximately four times higher than that of organic materials, meaning that even if organic electrodes are competitive in terms of gravimetric capacity, the volumetric capacity will be ~25% of inorganic materials. Obviously, this is a major concern for devices that require compact energy storage, such as portable electronics. Similarly, increasing the active material content to over 90% in the electrode needs to be attained. This will require the use of inherently conductive materials able to transport charge without requiring large amounts of conductive additives.

Specifically for SC materials, the stability of the electrodes needs to reach thousands of cycles in order to replace the widely used conductive carbon materials, which are extremely stable. Obviously, there is much room for improvement, especially for negative charge accepting pseudocapacitive materials. For lithium-ion battery materials, much progress has been made in terms of cycling stability but there is still a push to have stabilities greater than 80% over 1000 cycles. This could at least be partially overcome by using a solid-state electrolyte since dissolution of the active materials would be limited.\textsuperscript{32}

Finally, the logistics of integrating organic cathodes into industrial lithium-ion battery manufacturing needs to be addressed. For commercial rechargeable lithium-ion batteries, the lithium ions originate from the cathode crystal structure and intercalate into the graphite anode upon the first charge (Figure 6.4). This contrasts with organic materials, which require a lithium source from the anode. The consequence of this is either the cathode or anode needs to be pre-lithiated prior to device construction or, typically, a metal anode is used. Since pre-lithiation is typically expensive for the redox materials currently used and alkali metal anodes are unsafe due to dendrite formation, organic cathode materials cannot easily replace the metal-based cathodes currently used in commercial devices. However, with the development of high voltage organic materials, pre-lithiation can be achieved relatively easy by synthesis in alkali conditions or by reduction with inexpensive reducing reagents.
Overall, organic materials show great promise for electrode materials in energy storage devices. However, they still require development to become commercially viable. The challenges outlined above are not insurmountable and with the correct design, the implementation of organic materials for commercial devices is foreseeable in the near future.

4 References

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