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Structure Engineering of Polymers Used in Lithium-ion Battery Electrodes for Improved Performance

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Chapter 1

An Introduction:

Polymers in Lithium-ion Battery

1.1 Development of Lithium-Ion Battery

Lithium-ion batteries have become an extremely popular topic of research, ever since its commercialization in 1991. The widespread use, such as in mobile devices, laptops and electrical vehicles (EV), have raised a rapidly growing demand to further improve the battery performance. There is a critical need with batteries with greater energy and power densities, longer cycle life, faster charge/discharge, lower cost, better resistance to extreme temperatures, and also safer operation. A typical schematic of a commercial Lithium-ion battery is shown below in Figure 1, which consists of two electrodes (cathode and anode), a separator and electrolyte. When a battery is being charged or discharged, lithium ions move freely from one electrode to the other, creating an electronic current for the output devices. The most common batteries nowadays use liquid electrolyte which facilitates ion transport between cathode and anode, and also would require the presence of a separator, in order to avoid direct physical
contact between the two electrodes. This work here would be mostly focusing on battery electrodes. Additional information regarding electrolyte, porous separators and battery fabrication can be found in recent review articles\textsuperscript{3,4}.

**Figure 1.** A schematic for a commercial Lithium-ion battery.\textsuperscript{2}

Electrodes are generally comprised of active materials, polymeric binders and conductive additives. The most commonly used cathode materials are LiCoO\textsubscript{2}, LiFePO\textsubscript{4} and other Li\textsubscript{x}MO\textsubscript{y} metal oxides. These metal oxide cathode materials have a practical reversible capacity that is lower than the most commonly used anode material, graphite (372 mAh g\textsuperscript{-1})\textsuperscript{5–8}. This mismatch of electrode material capacity is a major limiting factor in achieving higher energy density in various cells. A more direct comparison of their practical capacities is given in Figure 2 below: graphite shows a capacity that more than doubles the capacities of LiCoO\textsubscript{2}, LiFePO\textsubscript{4} and LiMn\textsubscript{2}O\textsubscript{4}. Further, at ambient condition, LiCoO\textsubscript{2} and LiFePO\textsubscript{4} have very low intrinsic conductivity of 10\textsuperscript{-3} S/cm and 10\textsuperscript{-9} S/cm respectively\textsuperscript{9}. These challenges have motivated
researchers to develop new cathode materials with a higher capacity, allowing for the construction of batteries with higher capacities and power densities.

![Graph](image)

**Figure 2.** Practical reversible capacities of typical commercial cathodes and graphite anode. Adapted from Lee et al\(^3\).

### 1.2 Challenges and Limitations

Polymeric binders are widely used in almost all electrodes in order to maintain contact with current collector and provide mechanical enhancement\(^{17,18}\). However, most commonly used binders, such as poly(vinylidene fluoride) (PVDF), poly(tetrafluoroethylene) (PTFE), and carboxy methyl cellulose (CMC), are inactive in terms of ionic or electronic conductivity and electrochemical activity. As such, binders are added in the lowest possible quantities in order to maintain mechanical integrity without sacrificing much battery performance. This tradeoff between mechanical properties and mechanical properties can potentially be overcome by designing a multi-functional polymer binder that simultaneously improves mechanical property and battery performance.
Electronic conductivity is essential for all electrodes, since electrons produced during cycling need to be transported to the current collector. While conventional active materials (such as LiCoO₂, Si and V₂O₅) have high Li-ion capacity, their electronic conductivity is poor. In order to boost performance, conductive additives like carbon black can be added. Conjugated polymers can enhance both mechanical integrity and conductivity, and thus are attractive as alternatives. However, most conjugated polymers have to be doped to conduct. The doping and de-doping conditions also need to be studied carefully for different active materials and fabrication methods. One example is the use of PEDOT:PSS as a conductive binder for LiCoO₂ cathode. It was shown that with only a very small amount of PEDOT:PSS added (0.4%), the mass loading density of LiCoO₂ is enhanced substantially without any other additives or binders.

Ionic conductivity is another desirable property for binders. A high ionic conductivity can help lower the polarization at electrode and electrolyte interface, thereby enhancing cyclability and stability. A good example is a recent study by Wei et al., in which an ionically conductive binder, SPEEK-FSA-Li (sulfonated polyether ether ketone with pendant lithiated fluorinated sulfonic groups) gives five times greater adhesion strength and increasing cycle rate than common PVDF binders. Unfortunately, very few polymeric binders that can enhance both electronic and ionic conductivity have been reported.

Another potential way to improve battery capacity is to introduce redox activity within polymeric binders. In this way, not only will the binders improve mechanical and conductive properties, but they can also react with lithium and store more ions. Unfortunately, many conjugated polymers have a low doping levels, below one dopant per polymer unit; for example, PEDOT has a doping level of 0.33. However, a recent study by Yao et al. reported a conjugated naphthalene-diimide polymer PNDI which can incorporate up to 2 lithium ions per polymer unit.
Thus, with proper molecular engineering, achieving polymeric binders that enhance electrode capacity is possible.

In short, technical challenges in the development of polymeric binders include: (1) low electronic conductivity; (2) poor or no ionic conductivity; (3) mixing and processing with active material using conventional solvents can be a challenge; (4) mechanical properties of these polymeric binders are poorly understood; (5) most binders have little or no reactivity with lithium compared with active materials.

1.3 Structure Engineering

In order to provide a potential solution for many of the above mentioned challenges, we propose to use structure engineering while searching for polymers used in battery electrodes. A general design schematic for polymers that can be used in electrodes is shown below in Figure 3. If we break a polymer down into different functional groups or small units, we can systematically study the influence of different components and determine how each would affect the electrode properties and thereby the final battery performance.
Figure 3. A design Schematic of Ideal Polymer Binders. (Top) Hybrid electrode with active material, conductive additives and polymer binders (Bottom) Building blocks and design strategy for polymer binders.

As shown in Figure 3, some promising units for polymer design include (1) conjugated backbone, which promotes electron conductivity; (2) NDI unit which participates in redox
activity and would therefore help improve the total energy storage; (3) ethylene glycol unit, which has been reported many times before to show high ionic conductivity\textsuperscript{16}.

For the side-chains, we are interested in incorporating ethylene glycol (EG) as a way to further facilitate ion diffusion within the electrodes. An ionically conductive electrode will have lower interfacial polarization at the electrolyte interface, allowing the system to be more stable\textsuperscript{20}. The oxygen on the chains also makes it more hydrophilic, and will make our mixing process easier. In order to incorporate EG group, we can use two different methods. First, we can attach PEG side-chains onto the monomer, then use the monomer to undergo Suzuki coupling and create a polymer with PEG side-chains. The challenge in this approach will be to synthesize the desired monomer with high yield and purity. During our past synthesis of 2,7-Dibromo-9,9(di(oxy-2,5,8-trioxadecane))-fluorene, the most difficult step is to purify the acquired products. Right now, silicon column purification seems to be able to produce high-purity product; however, there is still difficulties in completely separating the final product from other substances, resulting in a low yield of ~60%. The second method will be to make a regular polymer and then end-cap the polymer with PEG chains. The advantage of this method is that we can easily control the overall molecular weight of PEG by modifying the size of end-cappers. However, a longer PEG end-capper will also make it more difficult to react with the polymer end.

Another side-chain candidate is the ionic group that would help dope the conjugated backbone. This type of polymers is also known as the “self-doped” polymer. It is very hydrophilic and also electronically conductive. Mai et al has shown that doping these side-groups with different salt through dialysis can influence its conductivity\textsuperscript{26}. We have been working on side-chains doped by H+ so far, but it will be useful to investigate other doping groups.
For the backbone design, we have been focusing on polyfluorene backbones so far. Some promising groups include CPD\textsuperscript{26} (Figure 11 Bottom), which is intrinsically conductive, and PNDI, \textsuperscript{36} which has been reported for fast charging/discharging. Electronic conductivity is essential for electrodes because it facilitates electron transport from the electrochemical reaction site to the current collector. Common conductive additives are carbon black, carbon nanotubes and graphene. With the use of a conjugated polymer backbone, which can provide both mechanical integrity and conductivity, we want to reduce the amount of conductive additive required in the hybrid electrode.

1.4 Previous Work with Polymeric Binders

In our previous work with V\textsubscript{2}O\textsubscript{5} electrode\textsuperscript{16}, we synthesized conjugated block copolymer poly(3-hexylthiophene)-block-poly(ethyleneoxide) (P3HT-b-PEO) to form a highly flexible self-assembled cathode. Upon addition of only 5wt\% of P3HT-b-PEO, the hybrid electrode has a substantial increase in flexibility, and also shows improved lithium-ion diffusion and boosted cyclability.
Figure 4. (a) Images of hybrid electrodes; (b) SEM images of hybrid electrodes after CV test; (c) Cycling behavior of V2O5, P5, and P10 electrodes at a discharge rate of 1C. Adapted from ref. 16.

From Figure 4 (a) and (b), we can see that the hybrid electrodes containing P3HT-b-PEO display no sign of formation of cracks and flakes after a few cycles of CV tests, compared with pure V2O5 electrode. Additionally, although hybrid electrodes P5 and P10 (i.e. with 5 wt% and 10wt% polymer) have a lower initial capacity than pure V2O5, after 200 cycles of charging and discharging, they actually show a higher final capacity due to conditioning of V2O5/polymer hybrid and gradual failing of pure V2O5 electrode. This is an evidence for P3HT-b-PEO to slow down the progression of mechanical failure in V2O5 electrodes due to severe volume expansion.

This proposed work is going to build upon our previous study with P3HT-b-PEO and V2O5 electrode. Conjugated P3HT polymer only has high electronic conductivity when doped, and it is in fact quite hydrophobic, which increases the difficulty in electrode processing with water. We would like to investigate some new conjugated polymers by tailoring the structure of side-chains and back-bone groups, in order to design a multi-functional binder with both mechanical and electrochemical enhancement.

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Chapter 2

Polymer as Binders:

Self-Doped Conjugated Polymeric Binders for V2O5 Cathodes

2.1 Abstract

Polymeric binders serve to stabilize the morphology of electrodes by providing adhesion and binding between the various components, and successful binders must serve multiple functions simultaneously, including providing strong adhesion, improving conductivity, and providing electrochemical stability. A tradeoff between mechanical integrity and electrochemical performance in binders for lithium-ion batteries is one of the many challenges in improving capacity and performance. In this paper, we demonstrate a self-doped conjugated polymer, poly(9,9-bis(4′-sulfonatobutyl)fluorene-alt-co-1,4-phenylene) (PFP), which not only provides mechanical robustness but also improves electrode stability at temperatures as high as 450°C. The self-doped PFP polymer is comprised of a conjugated polyfluorene backbone with sulfonate terminated side-chains that serve to dope the conjugated polymer backbone, resulting in stable
conductivity. Composite electrodes are prepared by blending PFP with V$_2$O$_5$ in water, followed by casting and drying. Structural characterization with X-ray diffraction and wide-angle X-ray scattering shows that PFP suppresses crystallization of V$_2$O$_5$ at high temperatures (up to 450°C), resulting in improved electrode stability during cycling and improved rate performance. This study demonstrates the potential of self-doped conjugated polymers for use as polymeric binders to enhance mechanical, structural, and electrochemical properties.

2.2 Introduction

The widespread use and rapidly-growing demand of lithium-ion batteries has raised many researchers’ interest in further improving the lithium storage capacity, long-term stability and safety[1–7]. A necessity in stable lithium-ion batteries is a binder to hold together the various components of the electrode and provide structural stability[8–10]. Most commonly-used binders, such as poly(vinylidene fluoride) (PVDF), poly(tetrafluoroethylene) (PTFE), and carboxy methyl cellulose (CMC), are inactive in terms of ionic or electronic conductivity or electrochemical activity. As such, these binders are added in the lowest possible quantities (typically less than 5 wt % in cathodes) in order to maintain essential mechanical integrity without significantly sacrificing battery capacity. The tradeoff between electrochemical performance and mechanical properties can be potentially overcome by using a multifunctional binder, which provides not only mechanical robustness, but electronic conductivity as well.

Conjugated polymers that are doped can provide good intrinsic electronic conductivity while also enhancing mechanical properties. For example, the commercially available conductive polymer poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS) has been
widely studied in device applications including as a functional binder in carbon black free LiFeO$_4$ cathodes for Li-ion battery, resulting in improved stability and comparable capacity with conventional electrodes\cite{11}. PEDOT:PSS has also been used as a conductive additive and binder in silicon anodes\cite{12,13}. PEDOT:PSS was shown to help form homogeneous and continuous conducting bridges within the composite Si anode, which results in improved cycling and rate performance\cite{12}.

However, the performance of PEDOT:PSS can change dramatically with processing conditions, including the choice of solvent, concentration, and the presence of other additives, and achieving significant conductivity often requires post-processing treatment\cite{14,15}. Self-doped conjugated polymers contain pendant, covalently bound ionic groups that serve to dope the conjugated polymer backbone. The resulting materials are more stable with respect to electronic properties and do not require the addition of external dopants\cite{16–18}. These conducting polymers are commonly used in biosensors, transistors and rechargeable batteries\cite{19–21}. As the active material in lithium-ion batteries, the sulfonic groups from self-doped polymers help limit the participation of anions during charge compensation process, leading to higher specific capacity and stability\cite{22–24}. They have also been implemented as polymer electrolytes for solid-state batteries, showing improved lithium transference number and ionic conductivity\cite{25}. They are also typically soluble in water.

In this work, we investigate a self-doped conjugated polymer as a binder in vanadium pentoxide (V$_2$O$_5$) cathodes. V$_2$O$_5$ is a promising cathode material with high theoretical capacity of 443 mAh$^{-1}$ (assuming intercalation of three lithium ions) and specific energy of 1,218 mWhg$^{-1}$ (assuming nominal 2.75V discharge voltage)\cite{26}. However, V$_2$O$_5$ lacks intrinsic conductivity, requiring the use of conductive additives along with polymeric binder\cite{27–29}. We
focus on the self-doped polymer PFP [poly(9,9-bis(4'-sulfonatobutyl)fluorene-alt-co-1,4-phenylene)], which has been used previously as a work-function modifier for organic solar cells[30] and in thermoelectric devices[31]. Critically, the polymer is water soluble and can be incorporated in V₂O₅ layers during aqueous processing. We incorporate PFP into V₂O₅ cathodes and characterize the binder’s impact on the structure, crystallinity, and electrochemical performance. Grazing-incidence X-ray scattering measurements and X-ray diffraction measurements show that PFP suppresses the transition of layered V₂O₅ to the a-crystal phase, resulting in improved stability and performance. This study demonstrates the potential of self-doped conjugated polymers for use as polymeric binders to enhance mechanical, structural, and electrochemical properties.

2.3 Materials and Methods

2.3.1. Materials

All the reagents and solvents used were purchased commercially from Sigma-Aldrich and VWR, and they were used as received unless noted otherwise. Lithium ribbon was purchased from Alfa Aesar. All coin cell-related products including CR2032 coin cell cases, springs, and stainless steel coins (15.8 mm diameter × 0.5 mm thickness) were purchased from MTI Corporation.

2.3.2. Synthesis of V₂O₅ xerogel

V₂O₅ xerogel was synthesized using a slightly modified procedure reported by Liu et al[26]. A solution of sodium metavanadate (0.1 M) in DI water was passed through an ion-exchange column filled with (Dowex-50-WX2, 50–100 mesh). The column was washed with Millipore
water until the eluent appeared colorless and had a neutral pH value. The eluent (HVO$_3$ in water) was collected and aged for 3 weeks at room temperature to produce a dark red V$_2$O$_5$ dispersion. The final homogeneous V$_2$O$_5$ xerogel solid was obtained through freeze-drying the aged solution at low temperature and under vacuum.

2.3.3. Synthesis of poly(9,9-bis(4'-sulfonatobutyl)fluorene-alt-co-1,4-phenylene), (PFP)

In a 10-mL microwave reaction tube, benzene-1,4-diboronic acid (100 mg), 2,7-dibromo-9,9-bis(40-sulfonatobutyl)fluorene (157 mg) were added, followed by 3 mL of DMF solvent and 1.2 mL of 2 M aqueous sodium carbonate. Upon addition of 1 – 2 drops of Aliquat 366, the mixture was stirred while purging through N$_2$ for 15 minutes. The catalyst (PPh$_3$)$_4$Pd(0) (34 mg) was then added quickly to the mixture, and the reaction vial was sealed. The mixture was allowed to react via microwave at 160°C for 1 hour. The raw product was obtained through precipitation in acetone. Precipitate was collected by filtration, and washed with large amount of acetone and methanol, until no obvious color can be seen in the filtrate. The precipitate was then completely dissolved in 25 mL of Millipore water and transferred to a dialysis bag (MWCO: ~5000). The dialysis bag was placed in a 1-L beaker filled with water and stirred for 3 days; the water inside the beaker was changed every 12 hours. After dialysis, the final purified product was recovered from water through freeze-drying.

2.3.4. Preparation of Electrodes

Before use, the stainless steel spacers were washed thoroughly by sonication in soap water, followed by DI water, IPA and acetone, each for 15 min. All electrode solutions were prepared in Millipore water. V$_2$O$_5$ and PFP polymer were first dissolved in water separately and sonicated
to provide a uniform solution. Then the two solutions were mixed in different ratios to obtain a series of 0 – 20 wt% PFP with V$_2$O$_5$ solution. The hybrid electrode solution was drop-casted on stainless steel coins, targeting a dried solid mass of ~ 1 mg. After preliminary drying under a fume hood, the resulting electrodes were transferred into a nitrogen-filled glove box to be heated at 90°C overnight, in order to further remove residual water.

Thermally annealed samples were prepared in a similar fashion. After drying at 90°C overnight, the sample was annealed at a certain temperature (ranging from 150°C to 450°C) under N$_2$ for 30 minutes. The sample was always placed under N$_2$ atmosphere after annealing in order to prevent re-absorption of water in air, until it was removed for testing purposes.

2.3.5. Coin Cell Assembly and Testing

Coin cells were assembled inside a water-free, oxygen-free Ar glove box, and pure lithium metal was used as the anode. The electrolyte used was 1M LiTFSI in propylene carbonate, and the separator was Celgard 3501. All coin cells were tested for cyclic voltammetry and galvanostatic charge-discharge measurements, with Arbin Battery Testing Instrument.

2.3.6. Structural Characterization

X-ray spectroscopy characterization was carried out by a Rigaku Ultima II vertical powder diffractometer using Cu K-alpha radiation ($\lambda = 1.5418$ Å) with Bragg-Brentano para-focusing optics at 40 kV. All XRD samples were prepared on cover glass to eliminate any background noise from substrate. Sample solutions were drop-cast onto the cover glass and dried in vacuum chamber. Thermal annealing was conducted under a N$_2$ atmosphere.
Grazing incidence x-ray-scattering in wide-angle regime (GIWAXS) was performed on the beam line 8-ID-E at Advanced Photon Source, Argonne National Laboratory[32]. A monochromator with a Si (111) single crystal was used to provide x-ray beam of 7.35 keV. All samples were prepared on a 1”x1” silicon wafer via drop-casting, then annealed under nitrogen for 30 minutes. The test was carried out at room temperature under vacuum.

2.3.7. Mechanical Measurements

Samples for peel test were prepared in the exact same way as cell electrodes. 3M Scotch tape was applied to the whole surface of each sample, flattened, and then gradually peeled off. The amount of electrode remaining adhered to the substrate was determined visually.

Dynamic mechanical analysis (DMA) failure test was conducted using ARES G2 rheometer. Free-standing films of various PFP/V$_2$O$_5$ blends were prepared by drop-casting on a small plastic weigh boat and peeling off the film after drying in the fume hood. The film was then cut into approximately 10 mm height X 3 mm width segments and both ends were fixed by Kapton tape. A constant strain rate (0.001 mm/s) was applied, and the sample was stretched until failure.

2.4 Results

2.4.1 Structural Analysis with Thermal Annealing

The structure of the self-doped polymer PFP is shown in Figure 1A along with an SEM micrograph of the V$_2$O$_5$ xerogel layered structure. The layered structure with water molecules as “pillars” between V$_2$O$_5$ sheets provides a high storage capacity for lithium, and our first goal was
to determine the impact that the self-doped polymer PFP had on the layered structure. X-ray measurements were used to quantify the structure and periodicity of the V$_2$O$_5$ xerogel.

We conducted X-ray diffraction measurements to characterize the structure of V$_2$O$_5$ with thermal annealing and with and without the PFP polymeric binder. Thermal annealing is critical to improving the storage capacity of V$_2$O$_5$ since water molecules within V$_2$O$_5$ layered structure can react with lithium to form Li$_2$O, resulting in a poor cycle life without annealing.[33][34] However, excessive annealing can lead to collapse of the layered structure[26] and crystallization of V$_2$O$_5$ to form the orthorhombic phase, which can only intercalate one Li ion while the xerogel phase can intercalate three equivalents[35]. The increased distance between adjacent layers in the xerogel phase also improves the diffusion of Li ions through the electrode, hence improving the overall Li ion capacity[36].
Figure 1. (a) Chemical structure of PFP; (b) SEM image of V$_2$O$_5$ layered structure; (c)(d) XRD patterns with thermal annealing from room temperature 90°C to 450°C for (c) pure V$_2$O$_5$, (d) V$_2$O$_5$ blends with 5 wt % PFP respectively.

Figure 1C shows that prior to thermal annealing the V$_2$O$_5$ has the expected layered structure characteristic of the xerogel phase, with a layer spacing of 1.47 nm, shown by the typical (001), (003), (004) and (005) diffraction peaks. With heating, the layered structure is maintained up to 300°C with a noticeable decrease in the layered spacing, reflected in a shift of the primary diffraction peak to higher angles. At annealing temperatures at and above 350°C, crystallization occurs, evidenced by a crystallization peak at 20°. Crystallization and complete transition to the orthorhombic phase is achieved at 400°C and above, also corresponding to the indexed orthorhombic V$_2$O$_5$ structure (JCPDS card No 41-1426) [26,36,37].

The phase behavior of V$_2$O$_5$ with added PFP polymer exhibits a very different trend with thermal annealing. Initially, prior to thermal annealing, a layered xerogel structure with (00l) peaks is observed similar to that for pure V$_2$O$_5$ with a slightly larger interlayer spacing of 1.60 nm. With heating, a larger shift in the primary peak position is observed, but the layered structure is maintained up to an annealing temperature of 450°C. The relative intensities of the diffraction peaks change significantly with annealing, which may be related to the loss of water during annealing, affecting the scattering length density of the region between the layers, and/or a change in the contrast due to the decrease in the layer size. Thermogravimetric analysis (TGA) measurements were conducted to verify that the materials and polymer are stable to annealing temperatures up to 450°C (see Supporting Information).
As a control study, we examined the spectrum of another conjugated polymeric binder, PFO-F, which has a similar chemical structure with PFP except with uncharged, oligo-ethylene glycol side-chains. The molecular structure of PFO-F and XRD analysis of cathodes of PFO-F in V2O5 are provided in Figure 2(a). This analysis shows that crystallization of V2O5 occurs with PFO-F additive just like that of pure V2O5. One hypothesis is that PFO-F has poor intercalation with V2O5 layers without the charged sulfonate group, which gives PFP higher water solubility and thereby better mixing with V2O5 xerogel. Furthermore, we also investigated the possible effect of adding carbon nanotubes (CNTs), which is a common non-polymeric additive to enhance electronic conductivity. As shown in Figure 2(b), once again the crystallization of V2O5 is not suppressed. These experiments indicate that PFP stabilizes the xerogel structure of V2O5 to high annealing temperatures, up to 450 °C.
Figure 3. GIWAXS 2D images with ex-situ thermal annealing from 25°C to 450°C for (a) pure V₂O₅, and (b) V₂O₅ blended with 5% PFP.

To further investigate crystallization of V₂O₅ xerogel under thermal annealing, we conducted 2-D grazing-incidence X-ray (GIWAXS) measurements for all the above annealed samples. In Figure 3(a), we can clearly see that at 350°C, multiple sharp diffraction peaks reflecting crystallization of V₂O₅ appear, consistent with the powder XRD studies. When the temperature is increased to 400°C and 450°C, complete crystallization of V₂O₅ occurs. All the residual water molecules are removed from the V₂O₅ sheets and the layered structure collapses. In Figure 3(b), GIWAXS again confirms that PFP stabilizes the layered structure to high temperatures. As discussed previously with the XRD patterns, initially the blend has a similar structure with pure V₂O₅ at room temperature. When the sample is heated, no multiple ring structure can be observed, up to 450°C. We repeated the same procedure with the other two samples, which can be referred to in the Supporting Information. Neither of the V₂O₅/PFO-F or
the V₂O₅/CNT blends showed any signs of suppressing crystallization. The GIWAXS images once again confirmed our finding with XRD results in Figure 1.

2.4.2. Electrochemical Performance with Thermal Annealing

We have demonstrated that self-doped polymer PFP as a binder helps to suppress the crystallization of V₂O₅ at high temperature. Past research has shown that V₂O₅ crystallization is unfavorable towards battery behavior[34,36]; even though crystallized V₂O₅ electrodes had initial high capacity, its cycle life is severely damaged and capacity degrades rapidly. We carried out electrochemical measurements for our own pure V₂O₅ and V₂O₅ + 5%PFP electrodes, and the results are shown below in Figure 4.
Figure 4. (a) Respective cycling performance of pure V$_2$O$_5$ and V$_2$O$_5$ + 5%PFP at 250°C and 400°C; (b) respective rate performance of pure V$_2$O$_5$ and V$_2$O$_5$ + 5%PFP at 250°C and 400°C.

We evaluated energy storage performance through galvanostatic charge-discharge tests. All cells were analyzed for 5 cycles at 0.5C rate, followed by 5 cycles at 1C, 2C, 5C, 10C and 20C rates respectively. After rate performance tests, we cycled these cells at 1C rate for 200 cycles. As a result, the pure V$_2$O$_5$ electrode annealed at 400°C showed a slightly higher initial discharge capacity of ~210 mAh/g, when compared with V$_2$O$_5$ electrode before crystallization temperature (at 250°C). However, its capacity starts to drop rapidly after about 30 cycles, and soon goes below the capacity of the V$_2$O$_5$ electrode annealed at 250°C after 80 cycles. This rapid degradation is attributed to the crystallization of V$_2$O$_5$, which not only reduced the layer spacing for Li$^+$ ion storage, but also compromised the mechanical robustness of the electrode, making it more vulnerable towards irreversible structural change.

On the other hand, with the addition of 5% PFP, this hybrid electrode shows a marginally higher capacity at 250°C than pure V$_2$O$_5$ electrode. We do want to point out the consistent capacity drop for 5% PFP sample between about 130 to 160 cycles is due to an unfortunate
instrument interruption. This, however, does not change the overall performance of this electrode. When the annealing temperature is raised past the usual crystallization temperature to 400°C, although the PFP hybrid cell does not have a high initial capacity like the pure cell does, it is much more stable during cycling. Since the crystallization of V₂O₅ is suppressed in this case, we believe that less irreversible structural damage occurs during cycling of this hybrid electrode annealed at 400°C, thus contributing to an improved cycle life. Based on CV plots for both 5% PFP and pure V₂O₅ (see Supporting Information), at the annealing temperature of 400°C, 5% PFP shows a single redox peak. We therefore believe that the drop of capacity for 5% PFP at 400°C is due to reduced number of Li-ion intercalation with each V₂O₅ unit. It has been reported that the second Li ion intercalation with V₂O₅ would result in a less reversible phase transition than that for the first Li ion[38,39].

Similarly for the rate performance tests, crystallized V₂O₅ electrodes displayed slightly higher capacity at slow charge/discharge rate; but its performance worsens quickly at higher C-rates. Meanwhile, the 5%PFP hybrid electrode with crystallization suppression at 400°C has a more stable pattern, and shows less capacity loss from 0.5C to 20C.

2.4.3. Mechanical Analysis of PFP hybrid electrodes

DMA failure tests were conducted to examine the effect of PFP binder in the overall mechanical property of V₂O₅ hybrid electrodes. Samples of pure V₂O₅ and V₂O₅ + 5%PFP were stretched at a constant strain rate until failure. The resulting diagram is shown in Figure 5. As we can clearly see, pure V₂O₅ electrodes have a very small %strain at failure of ~2%; while upon implementing even a small amount of PFP (5%), the blend is almost 8 times more extensible.
than before. Therefore, PFP as a binder greatly enhances the general stretchability and durability of the hybrid electrode.

![DMA failure tests for pure V$_2$O$_5$, and V$_2$O$_5$ with 5% PFP added.](image)

**Figure 5. DMA failure tests for pure V$_2$O$_5$, and V$_2$O$_5$ with 5% PFP added.**

Finally, we evaluated the adhesion ability of these electrodes during thermal annealing with a series of peel tests. Images of samples annealed at various temperatures before and after peeling are listed in Figure S2. Generally speaking, as annealing temperature increases, the adhesion of V$_2$O$_5$ worsens. Unfortunately, adding only 5 wt% of PFP as a binder, in this case, does not seem to improve this situation during thermal annealing. From Figure 9(b), we can see that at least 20 wt% of PFP needs to be added for a clean peel result, which is 4 times more than what we used in this study. However, the reason we did not focus on PFP polymer content higher than 5 wt% is because of the poor battery performance at higher binder content. Figure S3 displays the galvanostatic charge-discharge cycling and various rate performances 20 wt% PFP with V$_2$O$_5$. The energy storage capacity dropped to an extremely low level at higher binder content. Therefore, although increasing the PFP binder content helps to enhance the adhesion of
material to substrate, it also harms the electrochemical behavior of the hybrid electrode. This tradeoff between capacity and mechanical property should be taken into careful consideration.

2.5 Discussion

In this work, we conducted a systematic study of a fully water-processable, thermally-annealed V$_2$O$_5$ cathode with self-doped PFP polymer as the binder. Thermal annealing of V$_2$O$_5$ is favorable towards battery behavior up to the point when V$_2$O$_5$ starts to crystallize around 300°C. Crystallization of V$_2$O$_5$ at high temperature disrupts the layered structure in the V$_2$O$_5$ xerogel, making it more vulnerable towards permanent structural damage and thereby greatly reduces the cycle life of the battery. By adding only 5 wt% of PFP as a binder, we found that V$_2$O$_5$ crystallization is suppressed up to 450°C. As a result, PFP improves the stability of V$_2$O$_5$ annealed at higher temperatures and helps to maintain desirable layer spacing within the V$_2$O$_5$ system for Li ion storage and diffusion. Cycling data has indicated that 5%PFP/ V$_2$O$_5$ hybrid electrode is stable for at least 200 cycles even if it’s annealed at 400°C.

In addition, PFP as a binder can also improve mechanical stretchability and reduce stiffness of V$_2$O$_5$. Both properties contribute to a more stable electrode and longer cycle life during repeated charging and discharging. 5 wt% of PFP has been used to increase the hybrid electrode’s %strain at failure by ~8 times. However, there are still some remaining problems with incorporating higher binder content in this system. Although a higher PFP content provides much better adhesion in peel test, the electrochemical performance is largely diminished. We would need to carefully consider this tradeoff between battery performance and adhesion to current collector.
Even though PEDOT:PSS has been a very popular research subject for its electrochemical behaviors, very few researches have been carried out for other self-doped polymers as binders. PFP is just one example of a synthesized self-doped polymer used as a binder in Li-ion batteries, and there is still a broad library of self-doped polymers beyond PEDOT:PSS of interest. These polymers have a good combination of electronic properties, hydrophilicity, solubility etc. and therefore are good candidates for battery binders. Further research can be done in order to improve their conductivity, mechanical properties, electrolyte uptake and more.

2.6 References


2.7 Supporting Information

Figure S1. Thermogravimetric analysis for pure PFP, and pure V$_2$O$_5$
Figure S2. GIWAXS 2D images with ex-situ thermal annealing from 25°C to 450°C for $V_2O_5$ blended with (A) 5% PFO-F, and (B) 2.5% CNT.

Figure S3. Images of peel tests, showing before and after peeling at different temperature ranging for 90°C to 450°C for (A) pure $V_2O_5$, (B) $V_2O_5 + 5\%$ PFP; (C) images of peel tests,
showing before and after peeling at 250°C for different PFP polymer content from 0% to 80%.

Figure S4. Galvanostatic charge-discharge tests for \( \text{V}_2\text{O}_5 + 20\% \text{PFP} \).

Figure S5. Galvanostatic charge-discharge tests for \( \text{V}_2\text{O}_5 + 10\% \text{PVDF} + 10\% \text{Super-P} \) Carbon.
Figure S6. Cyclic Voltammetry for (a) Pure V$_2$O$_5$ and (b) 5% PFP + V$_2$O$_5$ annealed from 150°C to 450°C.
Chapter 3

Polymer as Active Material:

Side-chain Engineering of NDI-based Organic Electrode with Ultra-fast Energy Storage

3.1 Abstract

Polymer-based electrode materials are attractive for the development of lightweight, low-cost, and flexible electrodes. Specifically, electrodes based on conjugated polymers have shown impressive stability and rate capabilities, but further work is needed to improve capacity and reduce the amount of conductive additives needed to produce working electrodes. While a variety of conjugated polymers have been studied, the impact of the side-chain on electrochemical performance has been overlooked relative to the conjugated polymer backbone. Here, we demonstrate that side-chain engineering is a promising approach to boost electrochemical performance of conjugated polymer-based electrodes. We synthesized naphthalene dicarboximide (NDI) polymers with alkyl (PNDI-T2) or oligo-ethylene glycol side-
chains (PNDI-T2EG) and analyzed their performance in half-cell electrodes as a function of electrode thickness, charge-discharge rate, conductive additive content, and number of charge discharge cycles. While PNDI-T2EG exhibited lower specific capacities (42.9 mAh/g compared with 54.2 mAh/g for PNDI-T2), PNDI-T2EG electrodes were able to maintain their capacities for much thicker electrodes, faster charge-discharge rates, and lower contents of conductive additives. With a 1.2 mg/cm² active material loading in composite electrodes comprised of 60 wt % polymer and 40 wt % conductive additives, the electrode was able to retain 81% of its original capacity at an ultrafast charge/discharge rate of 100 C and 60 % of its capacity at 200 C. Electrodes with a reduced conductive carbon content of 20% wt % still retained 75% capacity at 100 C. Through a comparison of these results to previously reported electrode materials, we show that PNDI-T2EG nanocomposite electrodes outperform most previously reported materials both in terms of performance at high cycling rates, high mass loadings, and high active material content. This work demonstrates a route for increasing the rate of ion transport in conjugated polymers and improving the performance and capacity of conjugated-polymer based electrodes.

3.2 Introduction

Organic electrode materials offer a number of advantages over inorganic materials. They are rich in carbon and hydrogen and do not contain heavy metals, resulting in materials that are relatively inexpensive to manufacture and that can be potentially recycled. They are soft and lightweight, enabling the incorporation into portable and flexible batteries. In addition, they do not require the high processing temperatures commonly required for processing inorganic electrode materials. Therefore, they are more favorable from an economical and environmental-impact perspective. A broad range of organic electrode materials have been
developed for energy storage\textsuperscript{4-7}, including hydrocarbons\textsuperscript{8-10}, amines\textsuperscript{11-13}, thioethers, disulfides\textsuperscript{14-16}, nitroxy radicals\textsuperscript{17-19} and carbonyls\textsuperscript{20}.

Conjugated polymers are attractive organic materials for energy storage. When doped, these materials exhibit intrinsic conductivity which can help transport charges. This can result in little or no capacity loss even to very high charge/charge rates\textsuperscript{21}. Furthermore, conjugated polymer-based electrodes are more stable than small molecular based electrodes due to limited or no solubility in the liquid electrolyte\textsuperscript{22}.

However, conjugated polymer electrodes require significant amounts of conductive additives, typically 30-50 wt % of the electrode mass\textsuperscript{5-7}. This is due to the lack of conductivity in the materials prior to electrochemical doping. Furthermore, they generally exhibit low Li-ion conductivities, and as a result storage capacities drop significantly with electrode thickness.

Here, we propose that these issues can be addressed through side-chain modification of the conjugated polymers. While a variety of different conjugated polymer chemistries have been studied, these primarily focus on the composition of the backbone repeat unit rather than the side-chain\textsuperscript{6,7}. We hypothesized that the composition of the conjugated polymer side-chain could impact a number of properties directly relevant to energy storage. This includes the solubility and processability of the material, the Li-ion mobility in the conjugated polymer electrode, and the nature of electrochemical interactions between the lithium ions and the conjugated backbone.

In this work, we investigated the impact of the side-chains on the electrochemical performance of NDI-based polymers. We synthesized an NDI-based polymer with short oligo(ethylene glycol) (OEG) side-chains, as shown in Figure 1. Oligo- and poly-ethylene glycol-based materials have excellent lithium conductivity and are commonly used as solid electrolytes to transport lithium\textsuperscript{23-25}, and we hypothesized that by covalently attaching EG side-chains to the NDI backbone, we
could improve the diffusivity of lithium in the polymer electrodes enabling faster charge/discharge kinetics and better performance for both thicker and higher polymer-content electrodes. Below, we describe the synthesis of NDI-based polymers with OEG side-chains **PNDI-T2EG** and its electrochemical performance in composite batteries. We compared these materials to NDI-based polymers with octyldodecyl sidechains **PNDI-T2**, and our results demonstrated that the rate performance was improved through incorporation of OEG side-chains. This work demonstrates side-chain engineering as an effective approach to improve the electrochemical performance of polymer-based batteries.

**Figure 1.** Chemical structures of poly{[N,N'-bis(2-octyldodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)} (PNDI-T2), and poly{[N,N'-bis(2-ethoxyethyl 2-(2-(methoxyethoxy)ethoxy)acetate)-1,4,5,8-naphthalenedicarboximide-
2,6-diyl-alt-5,5′-(3,3′-bis(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2′-bithiophene) (PNDI-T2EG).

3.3 Experimental

3.3.1. Materials

All the reagents and solvents used were purchased commercially from Sigma-Aldrich and VWR, and they were used as received unless noted otherwise. Lithium ribbon was purchased from Alfa Aesar. All coin cell-related products including CR2032 coin cell cases, springs, and stainless steel coins (15.8 mm diameter × 0.5 mm thickness) were purchased from MTI Corporation.

3.3.2. Synthesis of PNDI-T2EG

A schematic for PNDI-T2EG synthesis is shown in Figure 2. A detailed description of the synthesis of NDI-Br2EG and T2-EG monomers can be found in the Supporting Information, along with 1H and 13C NMR spectra for each isolated intermediates. For PNDI-T2EG synthesis, a mixture of NDI-Br2EG (92 mg, 0.1 mmol), T2-EG (82 mg, 0.1 mmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 0.005 mmol) and tris(o-tolyl)phosphine (6.1 mg, 0.02 mmol) in anhydrous chlorobenzene (1 mL) was loaded in a microwave vial and degassed by nitrogen. The mixture was placed in a microwave reactor and heated at 100 °C for 5 min, 120 °C for 5 min, 140 °C for 5 min, 160 °C for 5 min, 180 °C for 5 min and 200 °C for 25 min. After cooling to room temperature, a solution (0.2 mL) of 2-(tributylstannyl)thiophene (0.1 mL) and tris(dibenzylideneacetone)dipalladium(0) (0.75 mg) in chlorobenzene (0.5 mL) was added and the mixture was heated at 180 °C for 5 min in the microwave reactor. After cooling to
room temperature, a solution (0.2 mL) of 2-bromothiophene (0.1 mL) in chlorobenzene (0.5 mL) was added and the mixture was heated to 180 °C for 5 min in the microwave reactor. After cooling to room temperature, the reaction mixture was added to hexanes, and the precipitate was filtered through a thimble. Soxhlet extraction was carried out with hexanes, acetone, methanol, tetrahydrofuran and chloroform. The chloroform fraction was concentrated and added to hexanes to precipitate the polymer PNDI-T2EG as a dark green solid (71 mg, 50%). $^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 8.84 (s, 2H), 7.19-6.91 (m, 2H), 4.41-3.31 (m, 72H). MALDI-TOF: $M_w = 7.93$ kg·mol$^{-1}$, $M_n = 7.55$ kg·mol$^{-1}$.

![Synthetic scheme for preparation of PNDI-T2EG](image)

**Figure 2.** Synthetic scheme for preparation of PNDI-T2EG. Reagents and conditions: Pd$_2$(dba)$_3$, P(o-tol)$_3$, chlorobenzene, N$_2$.

3.3.3. Electrochemical Testing
Polymer electrodes were prepared by drop casting a dispersion of polymer and conductive additives onto a clean stainless steel spacer. The electrode dispersion was prepared by mixing the polymer with Super-P carbon in chloroform using heating (~40 °C) and sonication (15 minutes). The resulting total solids concentration was approximately 10 mg/mL. 10 μL of this dispersion was drop-cast on a clean stainless steel spacer and dried under ambient conditions. To increase the electrode thickness, this drop-casting process was repeated up to four times. Afterwards, the electrodes were dried further on a hot plate at 100 °C for 1 hr to ensure complete removal of solvent. The final total mass of a “thin” electrode was about 1 mg (0.3 mg/cm² in terms of active material loading), and that of a “thick” electrode was about 4 mg (1.2 mg/cm² in terms of active material loading). Thin and thick electrodes had thicknesses of approximately 5 and 20 μm, respectively.

Coin cells were assembled inside a water-free, oxygen-free argon glove box, and pure lithium metal was used as reference/counter electrode. The electrolyte used was 1M lithium perchlorate (LiClO₄) in 1:1 v/v dioxalane-dimethoxyethane solution, and the separator used was Celgard 3501. All coin cells were tested using an Arbin Battery Testing Instrument. The voltage range used for all cells was from 1.6 V to 3.2 V. Each cell underwent a total of 25 cycles of cyclic voltammetry at varying scan rates, followed by 45 cycles of rate performance (at varying charge-discharge rates) and 5000 cycles of long-term cycling.

3.4. Results and Discussions

We synthesized two NDI-based polymers, one (PNDI-T2) containing alkyl side-chains and another (PNDI-T2EG) containing oligo(ethylene glycol) (OEG) side-chains, with the goal of
understanding how the incorporation of EG side-chains could enhance ion diffusion and doping of the conjugated backbone. PNDI-T2 was synthesized using previously reported methods\textsuperscript{26}, while a modified synthetic strategy was implemented to synthesize PNDI-T2EG. Briefly, 1,4,5,8-naphthalenetetracarboxylic dianhydride was first brominated, and then ethylene glycol side-chains were attached through a coupling reaction with 2-[2-(2-methoxyethoxy)ethoxy]acetic acid. The resulting monomer NDI-Br\textsubscript{2}EG was purified by column chromatography prior to polymerization. The bithiophene monomer T2-EG was synthesized in five steps including attaching the OEG side-chains, dimerization, and stannylation. The polymerization conditions for both PNDI-T2EG and PNDI-T2 were similar, and the final materials were purified by precipitation in methanol and extensive soxhlet washing with methanol, acetone, and chloroform. Detailed experimental procedures along with characterization of intermediates are provided in the Supporting Information (Figure S1 to S12).

While both polymers precipitated or partially precipitated out during polymerization, the final PNDI-T2 product had a much higher molecular weight and better solubility compared with PNDI-T2EG. The molecular weight of PNDI-T2 was 108 kg/mol as determined through size-exclusion chromatography with multi-angle light scattering analysis. The molecular weight of PNDI-T2EG was 7.55 kg/mol, determined through matrix-assisted laser desorption spectroscopy time-of-flight (MALDI-ToF). While it is unclear what the potential effect of molecular weight is on performance, prior studies on polythiophene-based electrodes have shown that electrode performance may be relatively insensitive to polymer molecular weight\textsuperscript{27}.

Differential scanning calorimetry (DSC) and X-ray powder diffraction (XRD) measurements were conducted to investigate the crystallinity of the two polymers, and these data are provided in Supporting Information Figure S13. PNDI-T2 is a highly crystalline material as reflected by
sharp diffraction peaks at $2\theta = 4^\circ$ and $23^\circ$ and a crystal melting transition above 300°C. PNDI-T2EG does not exhibit any detectable phase transitions below 350 °C by DSC and only one diffraction peak at $2\theta = 4^\circ$. This peak representing reflects interchain lamellar stacking with a d-spacing of approximately 22 Å$^{28,29}$.

To test the electrochemical performance, we fabricated nanocomposite electrodes by blending the polymers with conductive carbon. We first tested nanocomposite electrodes with 60 wt % polymer, and each electrode composition was tested at two different electrode thicknesses, approximately 5 μm and 20 μm, corresponding to active material loadings of 0.3 mg/cm$^2$ and 1.2 mg/cm$^2$. Assuming two-electron reaction with each NDI unit$^{30}$, the theoretical capacity was 54.2 mAh/g for PNDI-T2 and 42.9 mAh/g for PNDI-T2EG. This difference in their theoretical capacities was due to the higher mass of the OEG side-chains in PNDI-T2EG. The initial electrochemical storage capacities were above 93 % of the theoretical capacities for each electrode, and for comparison we calculated the normalized discharge capacity, defined as the measured capacity relative to the maximum measured at 1C.

We investigated the rate performance of both thin and thick nanocomposite electrodes containing 60 wt % polymer. We performed charge-discharge tests over the voltage range of 1.6 V to 3.2 V in which we systematically varied the charge-discharge rate (called the C-rate, where $xC$ represents the current rate required to discharge the battery in $1/x$ hours). We performed 5 cycles at each C-rate, and increased the C-rate from 1 C up to 500 C. The measured normalized capacities for PNDI-T2 and PNDIT2-EG are presented in Figure 3a and b.

At low mass loadings, both polymers exhibit similar trends in the normalized capacities as a function of C-rate, as shown in Figure 3a. Both electrodes exhibit excellent rate performance, with only a small drop in capacity with C-rate up to 100 C in which both polymers were able to
maintain 81% of their initial capacities. A significant difference in the normalized capacities of the two electrodes is only observed for C-rates greater than 200 C. At 500 C, PNDI-T2 was only able to retain 40% of its capacity while PNDI-T2EG exhibited a normalized capacity of 53%.

A much greater difference in rate performance was observed in thicker electrodes, which contain a fourfold increase in electrode mass and thickness. With increasing C-rate, the charge storage capacity of PNDI-T2 electrodes dropped significantly above 10 C (Figure 3(b). The PNDI-T2 electrodes were able to maintain less than 30% of their full capacity at 100 C and failed to store any charge at C-rates of 200 and greater. In contrast, PNDI-T2EG electrodes were relatively insensitive to the increase in electrode thickness, and the performance of the thick electrodes matched that for thinner electrodes up to 100 C. The capacity retention at 100 C was 81%, exactly matching the capacity retention for the thinner electrodes (Figure 3(a)). At 200 and 500 C, there was a significant drop in capacity, but the electrodes were still able to maintain 60 and 20% of their storage capacity, respectively. These results clearly demonstrate the improvement in electrode kinetics by incorporating OEG side-chains onto NDI-based polymers.

We also investigated the cycling stability of the nanocomposite electrodes at both thicknesses. Figure 3c shows long-term cycling studies (up to 5000 charge-discharge cycles) at a charge-discharge rate of 10 C. As shown in Figure 3(c), the initial specific discharge capacity for PNDI-T2 electrodes was significantly higher than that for PNDI-T2EG, as expected based on the different theoretical capacities for each electrode material. Both materials exhibited excellent stability under long-term cycling. After 5000 cycles, very little capacity loss was observed for either polymer in thin electrodes. For the thicker electrodes, PNDI-T2EG exhibited excellent stability while PNDI-T2 lost significant capacity. After 5000 cycles, the specific discharge capacity of thick PNDI-T2EG electrode was roughly equal to that of thick PNDI-T2 electrodes.
Next, we varied the content of conductive additives in the nanocomposite electrodes. Conductive additives such as Super P carbon are needed because conjugated polymers like PNDI-T2 and PNDI-T2EG are intrinsically non-conductive. In the case of conjugated polymer electrodes like PNDI-T2, conductive additive contents of 30 – 60 wt % are typically used\cite{5,7,21,31}. The conductive additives do not directly contribute to the storage capacity of the electrodes, and therefore minimizing the content of conductive additives is desirable to increase the charge storage capacity of the nanocomposite electrode.

![Graphs showing electrochemical studies](image)

**Figure 3.** Electrochemical studies investigating the rate performance (a) and (b) and cycling stability (c) of PNDI-T2 and PNDI-T2EG nanocomposite electrodes with 60 wt% polymer and
40 wt % carbon cycled over the voltage range of 1.6 V to 3.2 V. Thin and thick electrodes denote 0.3 and 1.2 mg/cm$^2$ active mass loadings, respectively. Normalized capacities reflect the specific capacity measured relative to that at 1 C. Cycling stability tests were performed at 10 C. Discharge capacity was calculated based on active polymer mass.

We fabricated PNDI-T2 and PNDI-T2EG nanocomposite electrodes with 80 wt % polymer (active mass=0.3 mg/cm$^2$) and repeated both rate performance and cycling stability studies. As above, we performed charge-discharge tests over the voltage range of 1.6 V to 3.2 V and performed 5 charge-discharge measurements at each C-rate, ranging from 1 C up to 500 C. The specific capacities for PNDI-T2 and PNDI-T2EG are presented in Figure 4. While the discharge capacity of PNDI-T2 nanocomposite electrodes decreases significantly with increasing C-rate over the entire range tested, the discharge capacity of PNDI-T2EG electrodes did not change significantly up to a C-rate of 50 C. For C-rates higher than 20 C, the discharge capacity for PNDI-T2EG was higher than that for PNDI-T2 electrodes despite the higher theoretical capacity of the latter. In terms of normalized capacity, the PNDI-T2EG nanocomposite electrodes at 100 C retained 81 % of their normalized capacity compared with just 25 % for PNDI-T2 electrodes. The results of cycling stability studies are presented in the Supporting Information. Both nanocomposite electrodes exhibited excellent stability over 5000 charge-discharge cycles, and the PNDI-T2 nanocomposite electrodes retained a high percentage of their capacity after long-term cycling.
Figure 4. Electrochemical studies investigating the rate performance of PNDI-T2 and PNDI-T2EG nanocomposite electrodes with 80 wt% polymer and 20 wt % carbon, cycled over the voltage range of 1.6 V to 3.2 V. Active mass loadings are 0.3 mg/cm$^2$ for both electrodes.

The PNDI-T2EG nanocomposite electrodes outperform most previously reported materials both in terms of performance at high cycling rates, high mass loadings, and high active material content. In Table 1, we compiled selected results from studies of state-of-art battery materials and compared them with results from PNDI-T2EG. Very few studies for organic electrodes have explored nanocomposite electrodes with active material loadings exceeding 1 mg/cm$^2$, C-rates above 100 C, and electrodes with 80 % active material, and none exhibit the excellent rate performance observed for the PNDI-T2EG electrodes. Additional examples for comparison are provided in the Supporting Information Table S3.
### Table 1. Comparison of capacity retention for different electrode materials as a function of polymer content and electrode mass loading.

The Active % is the weight fraction of active electrode material in the nanocomposite electrode. The Mass Loading is the active material mass per electrode cross-sectional area. The Capacity Retention is the percentage of storage capacity retained at the specific C-rate, relative to the storage capacity at 1C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Active %</th>
<th>Mass Loading (mg/cm²)</th>
<th>Capacity Retention</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Thin electrodes (≤ 0.3 mg/cm²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PNDI-T2EG</td>
<td>60%</td>
<td>0.3</td>
<td>81% (100C)</td>
<td>53% (600C)</td>
</tr>
<tr>
<td>PNDI-T2</td>
<td>60%</td>
<td>0.3</td>
<td>79% (100C)</td>
<td>40% (600C)</td>
</tr>
<tr>
<td>PVK</td>
<td>55%</td>
<td>0.3</td>
<td>78% (100C)</td>
<td></td>
</tr>
<tr>
<td>PTCDA-PI2</td>
<td>60%</td>
<td>n/a</td>
<td>28% (600C)</td>
<td></td>
</tr>
<tr>
<td>2. Thick electrodes (≥ 1.2 mg/cm²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PNDI-T2EG</td>
<td>60%</td>
<td>1.2</td>
<td>88% (50C)</td>
<td>81% (100C)</td>
</tr>
<tr>
<td>PNDI-T2</td>
<td>60%</td>
<td>1.2</td>
<td>58% (50C)</td>
<td>25% (100C)</td>
</tr>
<tr>
<td>P(NDI2OD-T2)</td>
<td>60%</td>
<td>1.3</td>
<td>85% (20C)</td>
<td></td>
</tr>
<tr>
<td>HATN-CMP</td>
<td>55%</td>
<td>1.4</td>
<td>33% (6.7C)</td>
<td></td>
</tr>
<tr>
<td>3. High active polymer ratio (≥ 80%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PNDI-T2EG</td>
<td>80%</td>
<td>0.3</td>
<td>94% (10C)</td>
<td>75% (100C)</td>
</tr>
<tr>
<td>PNDI-T2</td>
<td>80%</td>
<td>0.3</td>
<td>80% (10C)</td>
<td>35% (100C)</td>
</tr>
<tr>
<td>P(NDI2OD-T2)</td>
<td>80%</td>
<td>0.3</td>
<td>81% (10C)</td>
<td></td>
</tr>
<tr>
<td>Li4C6O6</td>
<td>80%</td>
<td>n/a</td>
<td>27% (6C)</td>
<td></td>
</tr>
</tbody>
</table>

In order to further quantify the rate performance of PNDI-T2EG and compare it to other materials reported in the literature, we relied on a recently reported semi-empirical equation for the rate dependence of capacity in batteries. The mode provides three parameters that describe the rate performance of batteries: the low-rate specific capacity $Q_M$, the characteristic time associated with charge and discharge $\tau$, and a power-law exponent $n$ that describes the decay of the capacity with increasing rate ($Q \sim R^{-n}$, where $R$ is the charge-discharge rate). The semi-
empirical equation is provided in the Supporting Information and described in more detail by Tian et al.\textsuperscript{32} Using this model, we determined values for $Q_M$, $\tau$, and $n$ for each polymer electrode tested at each thickness by fitting the semi-empirical equation to the discharge capacity data as a function of discharge rate. The results of this analysis are presented in the Supporting Information Table S2. This analysis shows that, for thin composite electrodes with 60 wt % carbon black, the characteristic time $\tau$ for discharge is smaller for PNDI-T2EG (1.1 s) compared with PNDI-T2 (2.6 s). For thicker electrodes, the characteristic time constants increase for both electrode materials, but much more significantly for PNDI-T2: 3.0 s for PNDI-T2EG and 15.8 s for PNDI-T2. These values of $\tau$ can be used to calculate a transport coefficient $\theta = L_E/\tau$, where $L_E$ is the thickness of the electrodes. The transport coefficient provides a method to compare the rate performance of different electrodes, and for the thick PNDI-T2EG, $\theta = 1.4 \times 10^{-10}$, which is among the highest value for organic materials and compares favorably against a broad range of Li-ion batteries reported in the literature.\textsuperscript{32}

We hypothesized that the exceptional rate performance and discharge capacity retention at high active polymer content and mass loadings was due to the improved ionic diffusivity in the PNDI-T2EG electrodes imparted by the OEG side-chains. To test this hypothesis, we conducted electrochemical impedance spectroscopy (EIS) measurements on both nanocomposite electrodes and on pristine PNDI-T2 and PNDI-T2EG. All electrodes were tested as half-cells with an active material mass-loading of 0.3 mg/cm$^2$. For both polymers, a series of EIS tests were carried out first at different potential values, and then with varying polymer content. The Nyquist plots ($Z''$ vs. $Z'$) resulting from these studies are presented in Figure 5. The Nyquist plot demonstrates a depressed semi-circle at high frequency region followed by a Warburg tail in the low frequency region. The Nyquist plots were fit using an equivalent circuit model with either one or two RC
circuits in series followed by a Warburg element ($W_0$). For a better fitting, all capacitor elements were replaced by constant phase elements.

EIS measurements indicate improved ion diffusion in PNDI-T2EG nanocomposite electrodes compared with PNDI-T2. The solid state diffusion coefficient ($D_{Li^+}$) of both PNDI-T2 and PNDI-T2EG polymers was calculated according to previous reports. At 60 wt% polymer content, the ion diffusivity is comparable between the two polymers: $2.65 \times 10^{-12}$ and $2.97 \times 10^{-12}$ cm$^2$/s for PNDI-T2EG and PNDI-T2 electrodes at 2.6 V respectively. However, as we reduce the amount of carbon additives, the difference becomes more significant. With 80 wt% polymer in the electrode, the ion diffusivity of PNDI-T2EG almost triples to $7.01 \times 10^{-12}$ cm$^2$/s, much higher than that of 80 wt% PNDI-T2 ($3.96 \times 10^{-12}$ cm$^2$/s). The results confirm our previous observations: for thin electrodes (0.3 mg/cm$^2$), both polymers at 60 wt% active polymer content show similar capacity retention, whereas PNDI-T2EG outperformed PNDI-T2 at 80 wt% due to the higher ion diffusivity as a result of OEG side-chains.

Additionally, EIS analysis showed reduced charge transfer resistance during charge transport within PNDI-T2EG electrodes at both polymer contents tested (60 wt %, 80 wt %). The charge transfer resistance ($R_{CT}$) represents the resistance for electron transfer during redox reaction and can be interpreted as a measure of reactivity at a given discharge state. At the peak redox potential (2.6 V), PNDI-T2 nanocomposite electrodes have an order-of-magnitude higher $R_{CT}$ (246 $\Omega$) than that of PNDI-T2EG (45.5 $\Omega$). We can also compare the change in $R_{CT}$ for both electrodes with varying polymer content. From 60 wt % to 80 wt % polymer content, the charge transfer resistance of PNDI-T2 electrodes increased from 114 $\Omega$ to 200 $\Omega$, which is expected for many organic electrodes. Due to the lowered amount of conductive additives, the resistance against electron flow within the electrode increases, thus increasing the charge transfer.
resistance. Nevertheless, $R_{CT}$ only increased by 25 $\Omega$ for PNDI-T2EG from 60 wt % to 80 wt %, leading to a fast redox kinetics even at reduced carbon content. This result corresponds with our findings earlier of PNDI-T2EG electrode’s high capacity retention at 80 wt % and further supports our theory that OEG side-chains assist in ion transport within the electrodes.

Figure 5. (a) Electrochemical impedance spectroscopy (EIS) tests for PNDI-T2 and PNDI-T2EG with varying polymer content at 2.6V, (b) charge transfer resistance calculated from EIS for both polymers at varying polymer content (measured at 2.6 V) and varying potentials (measured with 80 wt% polymer content).
In summary, we demonstrated that modification of conjugated polymer side-chains had a significant impact on the electrochemical performance of nanocomposite electrodes, in particular enabling excellent performance at high charge-discharge rates. For a high mass loading of 1.3 mg/cm² and ultrafast charge-discharge rate of 100 C, our PNDI-T2EG is able to retain an unprecedented 81% of its energy storage capacity. In addition, PNDI-T2EG shows excellent performance even when carbon content is reduced to 20 wt%, and has a capacity retention of 94% at 10 C and 75% at 100 C. The presence of the OEG side-chains improved both the redox reaction rate and the ion diffusivity inside the electrode. This work demonstrates a promising conjugated polymeric material for energy storage in PNDI-T2EG and also provides a general strategy for improving the performance of conjugated polymer based electrodes. Other promising polymer-based electrode materials can similarly be modified to potentially increase Li-ion diffusivity, improve rate capacity, and improve overall capacity. Current studies are focused on understanding how systematic variation of the EG content of the PNDI materials impacts electrochemical performance.

3.5. References


3.6. Supporting Information

Scheme S1. Synthetic scheme of PNDI-T2EG and PNDI-T2. Reagents and conditions: (i) 1,3-dibromo-5,5-dimethylhydantoin, conc. H$_2$SO$_4$, 50 °C, 16 h; (ii) 2-(2-aminoethoxy)ethanol, 2-[2-(2-methoxyethoxy)ethoxy]acetic acid, o-xylene, 120 °C, 16 h; (iii) triethylene glycol monomethyl ether, Cul, t-BuOK, rt, 1 h, 100 °C, 16 h; (iv) n-BuLi, THF, N$_2$, 0 °C, 2 h, Fe(acac)$_3$, THF, N$_2$, reflux, 2 h; (v) n-BuLi, THF, N$_2$, -78 °C, 2 h, 0 °C, 15 min, trimethyltin chloride, -78 °C → rt, 16 h; (vi) Pd$_2$(dba)$_3$, P(o-tol)$_3$, chlorobenzene, N$_2$, MW, 100 °C, 5 min, 120 °C, 5
min, 140 °C, 5 min, 160 °C, 5 min, 180 °C, 5 min, 200 °C, 25 min, 2-(tributylstannyl)thiophene, chlorobenzene, N₂, MW, 180 °C, 5 min, 2-bromothiophene, chlorobenzene, N₂, MW, 180 °C, 5 min; (viii) 5,5′-bis(trimethylstannyl)-2,2′-bithiophene, Pd₂(dba)₃, P(o-tol)₃, chlorobenzene, N₂, MW, 100 °C, 5 min, 120 °C, 5 min, 140 °C, 5 min, 160 °C, 5 min, 180 °C, 5 min, 200 °C, 25 min, 2-(tributylstannyl)thiophene, chlorobenzene, N₂, MW, 180 °C, 5 min, 2-bromothiophene, chlorobenzene, N₂, MW, 180 °C, 5 min.

**Synthesis of Compound 1, Reaction (i):** In a round bottom flask with stopper, 1,4,5,8-naphthalenetetracarboxylic dianhydride (8.0 g, 30 mmol) was dissolved in concentrated sulfuric acid (50 mL) at room temperature, followed by the addition of 1,3-dibromo-5,5-dimethylhydantoin (12.9 g, 45 mmol) in 4 portions over 1 h. The mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the mixture was poured into ice/water mixture (500 mL). The precipitates were collected by filtration, washed with water and methanol, and dried under vacuum to afford crude product 1 as yellow solid (12.8 g, 84%). ¹H NMR (600 MHz, DMSO-d₆, δ): 8.78 (s, 2H). ¹³C NMR (150 MHz, DMSO-d₆, δ): 157.9, 156.4, 137.5, 129.4, 127.4, 124.2, 123.4.

**Synthesis of Compound 2, Reaction (ii):** In a round bottom flask with septum, 2-(2-aminoethoxy)ethanol (3.1 mL, 31.0 mmol) and 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (38.9 mL, 253.5 mmol) were added to a suspension of 1 (6.0 g, 14.1 mmol) in o-xylene (90 mL). The reaction mixture was heated at 120 °C for 16 h. After cooling to room temperature, the reaction mixture was poured into brine and extracted with chloroform twice. The combined organic phase
was dried over anhydrous magnesium sulfate and the mixture was filtered. The solvent was removed under reduced pressure and the liquid residue was purified via column chromatography, eluting with dichloromethane and then ethyl acetate/dichloromethane (9:1, v/v) to afford crude product. The step of column chromatography was repeated. The crude product was recrystallized in ethyl acetate twice. The almost pure product was further purified via column chromatography, eluting with ethyl acetate/dichloromethane (9:1, v/v), and then recrystallized in ethyl acetate to afford the pure product 2 as a yellow solid (1.9 g, 15%). $^1$H NMR (600 MHz, CDCl$_3$, δ): 8.98 (s, 2H), 4.46 (t, 4H), 4.27 (t, 4H), 4.12 (s, 4H), 3.84 (t, 4H), 3.75 (t, 4H), 3.71-3.70 (m, 4H), 3.67-3.66 (m, 4H), 3.64-3.62 (m, 4H), 3.55-3.53 (s, 4H), 3.37 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$, δ): 170.4, 160.9, 160.8, 139.1, 128.4, 127.8, 125.3, 124.1, 71.9, 70.9, 70.6, 70.5, 68.5, 68.5, 67.5, 63.6, 59.0, 40.0.

**Synthesis of Compound 3, Reaction (iii):** A mixture of copper iodide (1.5 g, 8 mmol) and potassium tert-butoxide (6.7 g, 60 mmol) in triethylene glycol monomethyl ether (12.8 mL, 80 mmol) was stirred in a sealed vial at room temperature for 1 h. To the mixture, 3-bromothiophene (3.8 mL, 40 mmol) was added and the reaction was heated at 100 °C for 16 h. After cooling to room temperature, the mixture was put through a short silica plug eluting with dichloromethane/methanol (9:1, v/v) to remove inorganics. The solvent was removed under reduced pressure and the residue was purified via column chromatography, eluting with hexanes/ethyl acetate (2:1, v/v) to afford the product 3 as a light brown liquid (6.8 g, 69%). The freshly prepared product was used immediately for next step. $^1$H NMR (600 MHz, CDCl$_3$, δ): 7.15 (dd, J = 5.2 Hz, 1H), 6.76 (dd, J = 5.2 Hz, 1H), 6.25 (dd, J = 3.1 Hz, 1H), 4.10 (t, 2H), 3.82
Synthesis of Compound 4, Reaction (iv): In a three neck round bottom flask, a solution of 3 (1.3 g, 5.2 mmol) in anhydrous tetrahydrofuran (10 mL) was stirred under nitrogen at 0 °C for 15 min. To this solution, n-butyllithium (3.5 mL, 1.6 M in hexanes) was added dropwise over 10 min, and the reaction mixture was stirred at 0 °C for 2 h. The solution was transferred via cannula to a suspension of iron(III) acetylacetonate (2.0 g, 5.7 mmol) in anhydrous tetrahydrofuran (20 mL) in a three neck round bottom flask equipped with condenser under nitrogen at 0 °C. The mixture was heated to reflux for 2 h. After cooling to room temperature, anhydrous magnesium sulfate was added to the mixture and the inorganics were filtered. The solution was washed by saturated ammonium chloride solution and extracted by chloroform. The organic phase was dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure and the residue was purified via column chromatography, eluting with dichloromethane/ethyl acetate (6:1, v/v) twice to afford nearly pure product, which was recrystallized in diethyl ether in a freezer to afford pure product 4 as a yellow solid (316 mg, 11%). The freshly prepared product was used immediately for next step. $^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 7.07 (d, J = 5.6 Hz, 2H), 6.85 (d, J = 5.6 Hz, 2H), 4.24 (t, 4H), 3.90 (t, 4H), 3.76-3.75 (m, 4H), 3.68-3.67 (m, 4H), 3.65-3.64 (m, 4H), 3.54-3.53 (m, 4H), 3.37 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 151.8, 121.9, 116.6, 114.8, 72.0, 71.4, 70.9, 70.7, 70.6, 70.0, 59.0.
**Synthesis of Compound 5, Reaction (v):** In a three neck round bottom flask, a solution of 4 (245 mg, 0.5 mmol) in anhydrous tetrahydrofuran (10 mL) was stirred under nitrogen at -78 °C for 15 min. To this solution, n-butyllithium (0.69 mL, 1.6 M in hexanes) was added dropwise over 10 min, and the reaction mixture was stirred at -78 °C for 2 h, warmed to room temperature for 15 min, and then cool down to -78 °C. To this mixture, trimethyltin chloride (1.5 mL, 1.0 M in THF) was added in dropwise for 5 min. The cooling bath was removed, and the reaction was allowed to warm to room temperature overnight. The reaction was quenched by water, and the mixture was washed by brine and extracted by chloroform. The organic phase was dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to afford a yellow oil, which was dissolved in diethyl ether. The solution was stirred and cooled down to -78 °C for recrystallization. The precipitates were collected, washed by diethyl ether, and dried under vacuum at room temperature to afford pure product 5 as a pale-yellow solid (132 mg, 32%). The freshly prepared product was used immediately for next step. $^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 6.89 (d, J = 5.6 Hz, 2H), 4.27 (t, 4H), 3.91 (t, 4H), 3.79-3.77 (m, 4H), 3.68-3.67 (m, 4H), 3.65-3.64 (m, 4H), 3.54-3.53 (m, 4H), 3.37 (s, 6H), 0.36 (s, 18H). $^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 153.6, 133.9, 124.2, 120.7, 72.0, 71.5, 71.0, 70.8, 70.6, 70.1, 59.0, -8.3.

**Synthesis of PNDI-T2EG, Reaction (vi):** In a microwave vial with a sealing cap, a mixture of 2 (92 mg, 0.1 mmol), 5 (82 mg, 0.1 mmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 0.005 mmol) and tris(o-tolyl)phosphine (6.1 mg, 0.02 mmol) in anhydrous chlorobenzene (1 mL) was degassed by nitrogen. The mixture was placed in a microwave reactor and heated at 100 °C for 5 min, 120 °C for 5 min, 140 °C for 5 min, 160 °C for 5 min, 180 °C for 5 min and 200 °C for 25 min. After cooling to room temperature, a solution (0.2 mL) made of 2-
(tributylstannyl)thiophene (0.1 mL) and tris(dibenzylideneacetone)dipalladium(0) (0.75 mg) in chlorobenzene (0.5 mL) was added and the mixture was heated at 180 °C for 5 min in the microwave reactor. After cooling to room temperature, a solution (0.2 mL) made of 2-bromothiophene (0.1 mL) in chlorobenzene (0.5 mL) was added and the mixture was heated at 180 °C for 5 min in the microwave reactor. After cooling to room temperature, the reaction mixture was added to hexanes, and the precipitate was filtered through a thimble. Soxhlet extraction was carried out with hexanes, acetone, methanol, tetrahydrofuran and chloroform. The chloroform fraction was concentrated and added to hexanes to precipitate the polymer PNDI-T2EG as a dark green solid (71 mg, 50%). $^{1}$H NMR (600 MHz, CDCl$_3$, $\delta$): 8.84 (s, 2H), 7.19-6.91 (m, 2H), 4.41-3.31 (m, 72H). MALDI-TOF: $M_w$ = 7.93 kg·mol$^{-1}$, $M_n$ = 7.55 kg·mol$^{-1}$.

**Synthesis of PNDI-T2, Reaction (vii):** In a microwave vial with a sealing cap, a mixture of 4,9-dibromo-2,7-bis(2-octyldodecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetrone (92 mg, 0.1 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (82 mg, 0.1 mmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 0.005 mmol) and tris(o-tolyl)phosphine (6.1 mg, 0.02 mmol) in anhydrous chlorobenzene (1 mL) was degassed by nitrogen. The mixture was placed in a microwave reactor and heated at 100 °C for 5 min, 120 °C for 5 min, 140 °C for 5 min, 160 °C for 5 min, 180 °C for 5 min and 200 °C for 25 min. After cooling to room temperature, a solution (0.2 mL) made of 2-(tributylstannyl)thiophene (0.1 mL) and tris(dibenzylideneacetone)dipalladium(0) (0.75 mg) in chlorobenzene (0.5 mL) was added and the mixture was heated at 180 °C for 5 min in the microwave reactor. After cooling to room temperature, a solution (0.2 mL) made of 2-bromothiophene (0.1 mL) in chlorobenzene (0.5 mL) was added and the mixture was heated at 180 °C for 5 min in the microwave reactor. After
cooling to room temperature, the reaction mixture was added to methanol, and the precipitate was filtered through a thimble. Soxhlet extraction was carried out with methanol, acetone, hexanes, and chloroform. The chloroform fraction was concentrated and added to methanol to precipitate the polymer PNDI-T2 as a dark blue solid (90 mg, 91%). $^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 8.79-7.34 (s, 6H), 1.26-0.86 (m, 82H). GPC: $M_w$ = 256 kg·mol$^{-1}$, $M_n$ = 108 kg·mol$^{-1}$. 
Figure S1. $^1$H NMR of crude 1 in DMSO-d$_6$.

Figure S2. $^{13}$C NMR of crude 1 in DMSO-d$_6$.
Figure S3. $^1$H NMR of 2 in CDCl$_3$.

Figure S4. $^{13}$C NMR of 2 in CDCl$_3$.
Figure S5. $^1$H NMR of 3 in CDCl$_3$.

Figure S6. $^{13}$C NMR of 3 in CDCl$_3$. 
Figure S7. $^1$H NMR of 4 in CDCl$_3$.

Figure S8. $^{13}$C NMR of 4 in CDCl$_3$. 
Figure S9. $^1$H NMR of 5 in CDCl$_3$.

Figure S10. $^{13}$C NMR of 5 in CDCl$_3$. 
Figure S11. $^1$H NMR of PNDI-T2EG in CDCl$_3$.

Figure S12. $^1$H NMR of PNDI-T2 in CDCl$_3$. 
Figure S13. (a) DSC tests and (b) XRD spectrums for PNDI-T2 and PNDI-T2EG.

Figure S14. Cycling performance for 80 wt% PNDI-T2 and 80 wt% PNDI-T2EG at 10 C.
Figure S15. SEM surface imaging at different magnification for (a) PNDI-T2 and (b) PNDI-T2EG, with 80 wt% polymer and 20 wt% carbon.
Figure S16. Images of 60 wt% PNDI-T2 and PNDI-T2EG electrodes before and after cycling for 5000 cycles, for both thin (0.3 mg/cm$^2$) and thick (1.2 mg/cm$^2$) electrodes.

<table>
<thead>
<tr>
<th>Active Material</th>
<th>Active material : Carbon ratio</th>
<th>Total electrode mass (mg)</th>
<th>Active material loading (mg/cm$^2$)</th>
<th>Thickness (um)</th>
<th>Specific Discharge Capacity (mAh/g)</th>
<th>Areal Discharge Capacity (mAh/cm$^2$)</th>
<th>Volumetric Discharge Capacity (mAh/cm$^3$)</th>
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<td>PNDI-T2</td>
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<td>~20</td>
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Table S1. Detailed information for PNDI-T2 and PNDI-T2EG electrodes tested at 1 C.
Figure S17. Cyclic voltammetry of 60 wt% PNDI-T2 and 60 wt% PNDI-T2EG electrodes tested as (a) thin electrodes (0.3 mg/cm²), and (b) thick electrodes (1.2 mg/cm²); (c) cyclic voltammetry of 80 wt% PNDI-T2 and 80 wt% PNDI-T2EG electrodes with 0.3 mg/cm² active material loading. Reference electrode is lithium metal for all three CV plots.
Figure S18. Charge/discharge voltage profiles for PNDI-T2 and PNDI-T2EG with 60 wt% polymer content and 0.3 mg/cm² active material loading.

Figure S19. Charge/discharge voltage profiles for PNDI-T2 and PNDI-T2EG with 60 wt% polymer content and 1.2 mg/cm² active material loading.

Figure S19. Equivalent circuit models used for EIS analysis.
\[
\frac{Q}{M} = Q_M \left[ 1 - (R\tau)^n \left( 1 - e^{-(R\tau)^n} \right) \right]
\]  
Equation (1)

\[
\theta = \frac{L_E^2}{\tau}
\]  
Equation (2)

where \( \frac{Q}{M} \) is the measured specific capacity, \( Q_M \) is the low rate specific capacity, \( \tau \) is the characteristic time associated with charge/discharge, \( \theta \) is the transport coefficient, and \( L_E \) is the thickness of electrode.

<table>
<thead>
<tr>
<th></th>
<th>PNDI-T2 (Thin)</th>
<th>PNDI-T2 (Thick)</th>
<th>PNDI-T2EG (Thin)</th>
<th>PNDI-T2EG (Thick)</th>
<th>PNDI-T2 (Thin)</th>
<th>PNDI-T2EG (Thin)</th>
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<td>80%</td>
<td>80%</td>
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<tr>
<td>( Q_M ) (mAh/g)</td>
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<td>54.2</td>
<td>42.9</td>
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<tr>
<td>( n )</td>
<td>0.62</td>
<td>0.75</td>
<td>0.51</td>
<td>0.73</td>
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<tr>
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<td>1.14</td>
<td>3.00</td>
<td>10.6</td>
<td>2.15</td>
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<tr>
<td>( \Theta ) (m²/s)</td>
<td>( 9.9 \times 10^{-12} )</td>
<td>( 2.6 \times 10^{-11} )</td>
<td>( 2.3 \times 10^{-11} )</td>
<td>( 1.4 \times 10^{-10} )</td>
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<tr>
<td>( \log_{10}(\theta) ) (m²/s)</td>
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<td>-10.6</td>
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<tr>
<td>( R^2 )</td>
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<td>0.993</td>
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<td>0.999</td>
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Table S2. Fitting parameters and transport coefficients calculated from the rate performance model using Equation (1) and Equation (2).
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<th>Active Ratio</th>
<th>Areal Loading (mg/cm²)</th>
<th>Capacity Retention</th>
<th>Ref.</th>
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<td>PNDI-T2EG</td>
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<td>81% (100C)</td>
<td>this work</td>
</tr>
<tr>
<td>PNDI-T2EG</td>
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<td>1.2</td>
<td>88% (50C)</td>
<td>this work</td>
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</tr>
<tr>
<td>P(NDI2OD-T2)</td>
<td>60%</td>
<td>1.3</td>
<td>85% (20C)</td>
<td></td>
</tr>
<tr>
<td>HATN-CMP</td>
<td>55%</td>
<td>1.4</td>
<td>33% (6.7C)</td>
<td></td>
</tr>
<tr>
<td>Li4-p-DHT</td>
<td>67%</td>
<td>n/a</td>
<td>74% (5C)</td>
<td></td>
</tr>
<tr>
<td>Li4-p-DHT NS</td>
<td>59%</td>
<td>1.2</td>
<td>65% (5C)</td>
<td></td>
</tr>
</tbody>
</table>

1. Average active polymer ratio (≥ 50%)
<table>
<thead>
<tr>
<th>Material</th>
<th>Ratio</th>
<th>Charge</th>
<th>Rate 10C</th>
<th>Rate 100C</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(S-TTN)</td>
<td>70%</td>
<td>n/a</td>
<td>77%</td>
<td>n/a</td>
<td>77% (10C)</td>
</tr>
<tr>
<td>CTF BPPF</td>
<td>70%</td>
<td>n/a</td>
<td>42%</td>
<td>n/a</td>
<td>42% (15C)</td>
</tr>
<tr>
<td>Na4C8H2O6 NR</td>
<td>65%</td>
<td>1.0</td>
<td>55%</td>
<td>n/a</td>
<td>55% (5C)</td>
</tr>
</tbody>
</table>

2. High active polymer ratio (≥ 80%)

<table>
<thead>
<tr>
<th>Material</th>
<th>Ratio</th>
<th>Charge</th>
<th>Rate 10C</th>
<th>Rate 100C</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNDI-T2EG</td>
<td>80%</td>
<td>0.3</td>
<td>94%</td>
<td>75%</td>
<td>this work</td>
</tr>
<tr>
<td>PNDI-T2</td>
<td>80%</td>
<td>0.3</td>
<td>80%</td>
<td>35%</td>
<td>this work</td>
</tr>
<tr>
<td>P(NDI2OD-T2)</td>
<td>80%</td>
<td>0.3</td>
<td>81%</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>Li4C6O6</td>
<td>80%</td>
<td>n/a</td>
<td>27%</td>
<td>n/a</td>
<td></td>
</tr>
</tbody>
</table>

Table S3. Comparison table for rate retention between PNDI-T2/PNDI-T2EG and previously reported organic electrodes.
4.1 Polymeric Binders for Silicon

Silicon has a theoretical charge capacity for lithium-ion storage of 3579 mAh/g, roughly ten times higher than that of graphite (372 mAh/g). Replacing graphite with silicon could significantly reduce the size of anodes and/or increase the cell energy density. However, current formulations of composite silicon anodes are not sufficiently stable under long-term cycling for practical applications. Failure has been attributed to the large volume changes of silicon particles during charge and discharge, which result in particle disintegration and continuous reformation of the solid electrolyte interphase (SEI) layer, which further aggravates the inherently nonpassivating behavior of Si in organic carbonate electrolytes.

Polymeric binders play a critical role in the electrochemical performance and stability of composite Li-ion electrodes. Binders in silicon anodes typically comprise more than 10 wt % of the composite electrode and serve multiple functions, which include maintaining the mechanical integrity of the composite electrode, suppressing pulverization of the electrode film, and
preventing delamination from the copper current collector. Effective polymeric binders must satisfy a number of properties, including chemical and electrochemical stability within the potential window of electrode operation, strong adhesion to silicon, a high modulus and high elasticity, and, ideally, self-healing behavior, as detailed in a number of reviews on binders for silicon anodes.4–8 The interaction of the binder with the electrolyte and the amount of swelling or uptake by the binder are also important characteristics that can influence mechanical properties, electrochemical stability, and Li-ion mobility.9–12 While several promising polymeric binders have been identified, for many of these materials, there is a lack of fundamental understanding in how polymeric binder properties influence performance and how the relationship between various physicochemical properties—including adhesion, mechanical integrity, electrochemical stability, and ion diffusion—determines stability and performance of the silicon anode.

A few recent studies have shown that polyacrylamide (PAM) is a promising binder material for Si anodes. Zhu et al. synthesized a cross-linked PAM network in situ, inspired by the chemistry that produced highly stretchable hydrogel networks. Their work showed that Si anodes with cross-linked PAM as a binder resulted in impressive stability.13 Yoo et al. also studied a cross-linked PAM network as a binder in Si anodes and found that systematic variations of the cross-link density had a significant impact on performance and stability.14 While these studies indicate that PAM is a promising material for Si anodes, these studies did not conduct an analysis of various physicochemical properties relevant to battery performance, including adhesion strength, electrolyte uptake, and electrochemical stability. These studies also utilized in situ cross-linking and/or polymerization to produce the binder, which increases the complexity of the electrode fabrication process.
We study commercially available samples of partially hydrolyzed polyacrylamide (HPAM) as binders for Si anodes. HPAM is produced industrially at the large scale for enhanced oil recovery applications and is a low-cost, widely available material. Partial hydrolysis introduces acrylic acid groups along the polymer chain, which enhances stability in oilfield conditions; however, for battery applications, it can potentially improve adhesion to Si, as has been shown in a number of studies with poly(acrylic acid) (PAA) binders. One study utilized HPAM in silicon anodes and found low capacities, but here we show that HPAM is an effective binder and can be used to produce electrodes with performance comparable to other state-of-the-art binder materials.

We present a comprehensive study of a series of high Mw (ranging from 3 to 20 × 10^6 g/mol) HPAM binders to understand the relationship between the physicochemical properties of the polymeric binder and the electrode stability and performance. Our work shows that HPAM satisfies many of the properties generally believed to be favorable, including good adhesion, high strength, and electrochemical stability. The resulting electrodes exhibit an electrochemical
storage capacity greater than 3000 mAh/g initially and 1639 mAh/g after 100 cycles. We attribute capacity fade to failure of mechanical properties of the binder or an excess of the solid electrolyte interphase (SEI) layer being formed at the Si surface. The highest-molecular-weight sample exhibited the strongest adhesive forces to silicon and copper and as a result was expected to perform the best. Interfacial adhesion has been cited as a key determinant of good cell cycling in Si anodes. However, we found that HPAM of moderate molecular weight produced more stable and higher capacity electrodes. We attribute this to a trade-off in mechanical strength and uniformity of the resulting electrode. This work demonstrates promising performance of a low-cost polymer as a binder material for Si anodes and provides insight into the physical and chemical properties that influence electrochemical performance.

4.2 Continued Study of NDI-based Organic Electrode

Redox-active organic materials are promising for energy storage due to their low cost, versatility, and favorable mechanical properties. However, organic materials generally exhibit lower specific, volumetric, and areal capacities compared with intercalation layered transition metal oxides. As a follow-up study from our previous PNDI-T2EG work, we show that side-chain engineering of redox-active conjugated polymers significantly increases charge storage capacity. We studied a series of conjugated polymers with varying contents of oligo(ethylene glycol) (EG) side-chains and found that the EG side-chains increased ionic and electronic conductivities in nanocomposite and pure polymer electrodes. This led to improved rate performance, with 85 % capacity retention at 200 C, and increased capacities in thick electrodes. The EG side-chains also enabled nanocomposite electrodes with a much higher content of the redox-active polymer, including pure polymer electrodes with significant electrochemical
activity. Finally, the EG side-chains led to additional charge storage processes. Altogether, these findings demonstrate that side-chain engineering is a powerful approach to improving the specific, volumetric, and areal capacities of organic electrodes based on redox-active conjugated polymers.

Figure 2. (a) Structure of the PNDI-EGX polymers studied, where X represents the molar content of EG side-chains (R1) relative to 2-octyldodecyl side-chains (R2). (b) Reaction scheme for redox reaction in PNDI-EGX polymers showing that NDI repeat unit can store two lithium-ions.

4.3 Conclusion

In summary, this work focuses on different applications of polymer in Lithium-ion battery electrodes, with an emphasis in structure engineering of polymers in order to provide a better understanding in the fundamental relationship between polymer structure, electrode
composition, battery properties and performance. Chapter 2 studied self-doped polymeric binders in $V_2O_5$ cathodes. This fully water-processable, thermally annealed hybrid electrode shows steady cycling performance even when it is annealed at 400°C. We believe this is because the addition of 5 wt% PFP as binder helps suppress the crystallization of $V_2O_5$ xerogel and avoid the disruption of its layered structure. Chapter 3 discussed using conjugated polymer PNDI-T2EG as the active materials in electrode. We demonstrated that modification of conjugated polymer side-chains had a significant impact on the electrochemical performance of nano-composite electrodes, in particular enabling excellent performance at high charge-discharge rates. By attaching OEG side-chains, electrodes demonstrate exceptional rate performance at high charge-discharge rate, high mass loading, and high active material content. As a continued study, we look at a series of PNDI-based polymer with different ratios of OEG side-chains. All these works help to demonstrate that structure engineering of polymers is an efficient strategy when researching for the next better materials used for battery development.

4.4 References


