TCAQ-based polymer for electrochemically mediated separations

by

Emily Thai

Submitted to the Department of Materials Science and Engineering in partial fulfillment of the requirements for the degree of Bachelor of Science in Materials Science and Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2017

© Emily Thai, MMXVII. All rights reserved.

The author hereby grants to MIT permission to reproduce and to distribute publicly paper and electronic copies of this thesis document in whole or in part in any medium now known or hereafter created.

Signature redacted

Author ..........................................................
Department of Materials Science and Engineering

Signature redacted

May 9, 2017

Certified by.

Signature redacted

T. Alan Hatton
Ralph Landau Professor, Director, David H. Koch School of Chemical Engineering Practice
Thesis Supervisor

Signature redacted

Elsa Olivetti
Assistant Professor of Materials Science and Engineering
Thesis Supervisor

Accepted by ..... 

Signature redacted

Geoffrey Beach
Undergraduate Committee Chairman
DISCLAIMER NOTICE

Due to the condition of the original material, there are unavoidable flaws in this reproduction. We have made every effort possible to provide you with the best copy available.

Thank you.

The images contained in this document are of the best quality available.
TCAQ-based polymer for electrochemically mediated separations

by

Emily Thai

Submitted to the Department of Materials Science and Engineering
on May 8, 2017, in partial fulfillment of the requirements for the degree of Bachelor of Science in Materials Science and Engineering

Abstract

Redox-mediated separation systems offer the potential to efficiently desalinate water and to purify contaminated waste streams, among other health and environmental applications. A TCAQ-based polymer, unique for its two-electron redox reaction, was synthesized for use in redox-mediated separation systems, and its performance was quantified in low-concentration aqueous salt solutions. The polyvinyl ferrocene (PVF)//PTCAQ system displayed an ion adsorption capacity much higher than previously reported literature values for capacitive or redox deionization systems.

Thesis Supervisor: T. Alan Hatton
Title: Ralph Landau Professor, Director, David H. Koch School of Chemical Engineering Practice

Thesis Supervisor: Elsa Olivetti
Title: Assistant Professor of Materials Science and Engineering
Acknowledgments

The author would like to acknowledge Dr. Xiao Su and Dr. Johannes Elbert for their mentorship over the course of this project, as well as Prof. T. Alan Hatton and Prof. Elsa Olivetti for supervision.
# Contents

1 Introduction .................................................. 9
  1.1 Motivations ................................................. 9
  1.2 Current state of electrochemical separation technologies .... 10
  1.3 Exploring asymmetric pairs of redox polymers ................. 11

2 Materials and Methods ........................................ 15
  2.1 Synthesis of PTCAQ ......................................... 15
    2.1.1 Initial trials ......................................... 16
    2.1.2 Refined synthesis procedure ........................... 18
  2.2 Electrode fabrication ...................................... 20
  2.3 Deionization ............................................... 21

3 Results & Discussion ........................................... 23
  3.1 Characterization ............................................. 23
  3.2 Quantifying deionization performance ........................ 24
  3.3 Optimizing charge parameters ............................... 25

4 Conclusions and Future Work ................................ 31

5 References .................................................... 35
Chapter 1

Introduction

1.1 Motivations

Energy-efficient ion separation systems are of great interest for environmental purposes. As water becomes more scarce, use of desalination technologies to derive fresh, potable water from seawater is increasing. Unfortunately, current commercial desalination based on reverse osmosis technology, which uses high pressure to force water through a selective membrane, requires large amounts of energy and is extremely inefficient at low concentrations of salt. More generally, selective separation systems are also of interest for environmental protection purposes, e.g. for the selective removal of organic ion contaminants from industrial waste streams or contaminated waterways, and for pharmaceutical purposes, e.g. for the extraction of charged organic products during chemical synthesis. For these applications, the system must be able to pull certain ions out of solution, sometimes in the presence of a high concentration of background electrolytes.

One potential solution to these problems is to use electrochemical separation technologies, in which feed water flows between two electrodes, a voltage is applied across the two electrodes, and ions in the feed water are drawn to the electrodes. The adsorbed ions are later released into concentrated wastewater by discharging the electrodes with zero or negative potential. Electrochemical separation systems offer several advantages over traditional pressure-based ones, including fast kinetics, con-
trol by electrical potential, modularity, and reuse[3]. The Hatton Group has been exploring various Faradaic electrodes for this purpose. This thesis focuses on the synthesis and characterization of redox-active polymer-coated carbon electrodes for selective deionization at low salt concentrations.

1.2 Current state of electrochemical separation technologies

Current electrochemical separation technologies can be broadly divided into capacitive and redox-active systems. A capacitive deionization (CDI) cell generally consists of two electrodes, usually porous carbon, between or through which the feed to be deionized flows[2]; when a voltage is applied across the electrodes, ions in the feed form an electrical double layer at the surface of each electrode, and during discharge, ions are released into wastewater and some energy is recovered. However, because they rely solely on double-layer capacitance, CDI cells will bind all ions and are inefficient at low ionic concentrations. Redox-active electrodes, on the other hand, can selectively bind various charged and uncharged particles from solution, as shown in Figure 1-1.

In a redox-mediated separation cell, as in batteries, particular ionic species preferentially undergo intercalation into a matrix via the redox reaction. The electrode surfaces can be tuned to selectively adsorb ions of interest. Even for applications where selectivity is not important, redox-active cells can be more energy- and cost-efficient than CDI, as charge is stored in and can be released from both the electrical double layer capacitance and the pseudocapacitance of the redox reaction. Redox-based electrodes can also be more efficient at low concentrations, on the order of micromolars of the desired solute.

For these reasons, the Hatton Group is exploring redox-mediated electrochemical separation cells for both desalination, for which energy and cost are particularly important, and environmental separations, for which selectivity and efficiency at low
concentrations are particularly important. Ferrocene-based materials are one such redox material, having been studied in several energy storage applications. Ferrocene-metallopolymers contain a ferrocenium cation center that, when oxidized, can reversibly adsorb organic anions. Electrodes functionalized with polyvinyl(ferrocene) (PVF) have previously been reported by the Hatton Group to selectively and controllably bond organic anions[3].

1.3 Exploring asymmetric pairs of redox polymers

While a symmetric ferrocene-based system demonstrates high selectivity, asymmetric systems offer further improvements in efficiency. Asymmetric redox couples, in which the active centers of the two electrodes have different charges and chemical identities, can operate at high charge storage capacity while minimizing side reactions such as hydrolysis. These side reactions decrease the efficiency of the system, as well as fouling the redox electrodes, which reduces ion selectivity[4].

So far, the group has done preliminary experiments on asymmetric systems such as polypyrrole vs. ferrocene, PVF vs poly(2-(methacryloyloxy)ethyl cobaltocenium, and
PVF vs. poly[(1-carboxy-propylmethacrylate)-cyclopentadienyl]cobalt- (tetrphenyl-cyclobutadiene) (PCpCoCbMA). Asymmetric systems combine the selectivity of PVF at the anode with some desired quality of the cathode material—suppression of water splitting in the case of the cobaltocenium polymer, or cation selectivity in the case of PCpCoCbMA. Figure 1-2 shows the structures of selected redox-active polymers.

![Figure 1-2: Structures of redox-active polymers used for fabricating electrodes.](image)

Drawing inspiration from materials used in organic batteries, this thesis examines the behavior of poly(2-methacrylamid-TCAQ) (PTCAQ) in such asymmetric redox-mediated deionization systems.

Poly(2-methacrylamid-TCAQ) (PTCAQ) is a particularly attractive candidate for redox-mediated separations due to its unique structure. PTCAQ contains a 11,11,12,12-tetracyano-9,10-anthraquinodimethane moiety, or TCAQ. TCAQ normally adopts a “butterfly” shape, in which the central benzene ring is bent and the two side rings remain planar. During reduction, if TCAQ gains a single electron, its structure becomes twisted and unstable, causing it to gain another electron to become symmetric and stable again, at which point it adopts a fully planar shape. The respective structures of neutral and reduced TCAQ moieties are shown in Figure 1-3. TCAQ thus gains or yields two electrons in a single reaction. Once the first reduction has taken place, the energy for the second reduction is actually lower than that of the first[8]. Due to this unique property, TCAQ-based materials have found a wide variety of electrochemical applications.

To explore PTCAQ’s applications in redox-mediated separations, the polymer was synthesized and dropcast onto porous carbon paper electrodes. The electrochem-
Figure 1-3: Structure of TCAQ ("butterfly" shape, left) and TCAQ$^{-2}$ (planar, right).[8]

Chemical performance of symmetric and asymmetric cells composed of electrodes made from different redox-active polymers, including PVF, PCpCoCbMA, and poly(2-methacrylamid-TCAQ) were characterized and compared via cyclic voltammetry and chronopotentiometry. PTCAQ demonstrates a remarkably high ion adsorption compared to other polymers tested, as well as compared to previously reported electrochemical deionization systems in literature.
Chapter 2

Materials and Methods

2.1 Synthesis of PTCAQ

PTCAQ was synthesized based on procedures in Wild et al.[5] and Wannalerse et al.[6]. The three-step synthesis is shown in Figure 2-1. The amino group in the commercially available 2-aminoanthraquinone is substituted with a methacrylamino group, which will become the backbone of the polymer chain. The oxygens on the anthraquinone are then substituted by two dicyanomethyl groups to form the TCAQ-methacrylamide. Finally, the monomer TCAQMA is polymerized via free radical polymerization to form PTCAQ.

Figure 2-1: Synthesis of PTCAQ (7) from 2-aminoanthraquinone (4).[5]
2.1.1 Initial trials

Synthesis of 2-AAQMA

In the first step, the amino group in 2-aminoanthraquinone is substituted for methacrylamide to form N-(anthraquinone-2-yl)methacrylamide. 2-aminoanthraquinone (6g = 21.5 mmol) and pyridine (8.7 mL = 108 mmol) were added to a flask under nitrogen atmosphere and dissolved in anhydrous dichloromethane (about 100 mL). The flask was placed into an ice bath and methacryloyl chloride (11 mL = 108 mmol) was added. The mixture was stirred at 0°C for 1 hour and room temperature for 3 hours. Previously, a 1.2:1 ratio of pyridine to quinone was used. The product was characterized by nuclear magnetic resonance spectroscopy, which indicated that about half the quinone remained unreacted. Therefore, the high excess (5:1) of pyridine and methacryloyl chloride was found to be necessary in order to react all of the anthraquinone. Figure 2-2 compares the NMR spectra of each trial.

The mixture from the successful synthesis was then precipitated in water. Dichloromethane and chloroform were added. Water was added again, and the organic phase was extracted; this step was repeated with water once more and then with saturated sodium chloride solution (brine). The remaining mixture was dried over magnesium sulfate and the solvents were evaporated under reduced pressure, yielding a brown paste. This product was dissolved in 1:2 v/v chloroform/ethyl ether and left at 0°C overnight, forming a precipitate. The solids were extracted using vacuum filtration and left in
a vacuum oven for 1 hour to remove any remaining solvent, yielding 1.9204 g of a brown powder.

**Synthesis of TCAQMA**

In the second step, N-(9,10-bis(dicyanomethylene)-9,10-dihydroanthracen-2-yl)methacrylamide (TCAQMA) was synthesized from 2-AAQMA. 2-AAQMA (1.9 g = 6.59 mmol) was dissolved, along with malonitrile (4.35 g = 65.9 mmol), in chloroform (about 80 mL) under a nitrogen atmosphere. The flask was placed into a water bath and pyridine (10.63 mL = 131.7 mmol) and aluminum chloride (5.27 g = 39.5 mmol) were added. The mixture was stirred at room temperature for 40 minutes, then at 40°C for 19 hours. Thin-layer chromatography (TLC) in 1:1 v/v ether/hexane of the mixture was compared to TLC of the step 1 product to confirm that none of the step 1 product remained. The organic phase was extracted using water (500 mL) and chloroform (150 mL). The product was washed twice with water (100 mL each) and once with brine (50 mL), then dried over magnesium sulfate, filtered through filter paper, and evaporated under reduced pressure. Ethyl ether was added and the mixture was kept at 0°C for 1 hour to precipitate the product. Vacuum filtration was used to extract a brown solid. The mixture was left in a vacuum oven overnight, yielding 1.99 g of solid. NMR spectra indicated that the precipitate was mostly pure.

**Synthesis of (poly(2-methacrylamide-TCAQ)**

In the third step, poly(N-(9,10-bis(dicyanomethylene)-9,10-dihydroanthracen-2-yl)-methacrylamide) was synthesized from the monomer via free radical polymerization. 0.5 g of TCAQMA and 6.36 mg of AIBN, an initiator, were dissolved in 0.86 mL of NMP. The mixture was evacuated and filled with nitrogen three times, then evacuated again in order to remove any dissolved air. (No crosslinker was used because high molecular weight was not needed for this application. Nitrogen flushes instead of freeze-pump-thaw cycles were used because without the crosslinker, the mixture contained no volatile components.) The mixture was then placed into an oil bath and stirred at 75°C for 22 hours, precipitated dropwise into diethyl ether/DCM (1/1 v/v)
(40 mL), and centrifuged for 3 min. Excess liquid was decanted and the solid was left in a vacuum oven for 2 days, yielding 0.4744 g of a brown solid.

**Electrochemical characterization of monomer (2-AAQMA)**

The synthesized monomer was characterized via cyclic voltammetry in two forms: in solution and as a paste electrode. For the solution test, 100 mM tetrabutyl ammonium hexafluorophosphate (387 mg) in acetonitrile (10 mL) was used as electrolyte in a 3 electrode cell with a glassy carbon working electrode, platinum counter, and Ag/AgCl reference. 20 mV/s scans from -1.5 to 0.5 V were run. Peaks were observed at -0.4 and -0.8 V, with the latter being twice the magnitude and irreversible. Scans from -0.6 to 0.3 V kept the reversible reaction peak at -0.4 V.

For the paste electrode, the monomer was ground with carbon paste with about a 1:4 ratio of monomer to carbon. The paste was pressed into the working electrode; the same platinum counter and Ag/AgCl reference were used. Similarly, a large cyclic voltammetry scan, from -1.5 to 0.3 V, showed a large peak for an irreversible reaction, whereas a smaller scan from -0.4 V to 0 V was reversible.

Finally, thin layer chromatography of the sample yielded three distinct regions, likely the intended product with two substitutions, half-reacted product with only one substitution, and unreacted AAQMA. As such, it was determined that additional purification steps would be necessary.

### 2.1.2 Refined synthesis procedure

The synthesis was repeated for better purity and higher yield, as well as with a higher amount of starting material to yield more overall product.

**Synthesis of 2-AAQMA**

2-aminoanthraquinone (80%, 7g = 31.3 mmol) and pyridine (19 mL = 235.2 mmol) were added to a flask under nitrogen atmosphere and dissolved in chloroform (200 mL). The flask was cooled to 0°C. Methacryloyl chloride (24.5 g = 235.2 mmol) was
added dropwise. The mixture was stirred at 0°C for 16 h. The mixture was diluted with 200 mL dichloromethane, washed with water (3 × 200 mL) and brine (200 mL), dried over MgSO₄, filtered and concentrated to 30 mL under reduced pressure. The product was precipitated by adding 400 mL hexane. The orange-brown product was collected by filtration, washed with hexane and dried under reduced pressure. The 5.5 g (75%) product were used without further purification in the synthesis of Nη(9,10ηbis(dicyanomethylene)η9,10ηdihydroanthracenη2ηyl)methacrylamide.

**Synthesis of TCAQMA**

N-({Anthraquinone-2-y1}-methacrylamide (4.5 g, 15.5 mmol) and malononitrile (10.3 g, 155.5 mmol) were dissolved in CHCl₃ (200 mL) under nitrogen atmosphere. Pyridine (25.1 mL, 311 mmol) and aluminum chloride (15.5 g, 116.6 mmol) were added and the reaction mixture was stirred at room temperature for 10 min, followed by stirring at 40°C for 24 h. The mixture was poured into water (500 mL). Chloroform (200 mL) was added, the phases were separated, the organic phase was washed with water and brine dried over MgSO₄, filtered and evaporated under reduced pressure. The obtained crude product was purified by column chromatography yielding 3.2 g (53%) of TCAQMA-m as a yellow powder.

¹H-NMR (300 MHz, CDCl₃, δ): 8.84 (1H, Ar), 8.37–8.25 (3H, Ar), 8.15 – 8.10 (1H, Ar), 7.91 – 7.82 (2H, Ar), 5.92 (s, 1H, C=C-H), 5.60 (s, 1H, C=C-H), 2.04 (s, 3H, CH₃)

**Free radical polymerization of (poly(2-methacrylamide-TCAQ)**

TCAQMA (500 mg, 1.3 mmol) and AIBN (10 mg, 0.06 mmol) were dissolved in 0.6 mL NMP in a Schlenktube. The vessel was flushed with nitrogen, and the mixture was heated to 70°C for 24 h. The product was precipitated in 40 mL diethyl ether, the polymer was collected by filtration and dried under reduced pressure, yielding 330 mg (66%) PTCAQ.
2.2 Electrode fabrication

CNT, PVF, and PCoCpCb electrodes were prepared via dropcasting or dipcoating a polymer-CNT solution onto carbon paper. To prepare the solution for polymeric electrodes, two stock solutions were used: one of 80 mg polymer (PVF: Polysciences, Inc; PCoCpCb: synthesized as in Su et al 2016[3]) and 40 mg multi-walled carbon nanotubes (MWCNT, Sigma) in 10 mL chloroform, and one of 40 mg CNT in 10 mL chloroform. Each solution was sonicated in ice water for 45 minutes. The solutions were mixed in a 1:1 ratio and sonicated for another 45 minutes in an ice bath. To prepare CNT-only electrodes, 80 mg multi-walled CNT was dissolved in 20 mL chloroform and sonicated in an ice bath for 40 min.

To prepare a dropcast electrode, the appropriate solution was drop-cast in 50 µL increments onto pieces of Teflon-coated carbon fiber (Toray carbon paper, Electrochem Inc). The chloroform was evaporated at ambient temperature. Copper tape was used to attach copper wire to each electrode. To prepare dipcoated electrodes, the two stock solutions were prepared with the same procedure and mixed in a 1:1 ratio. The carbon paper was immersed into solution for 3 s, below the line of the copper tape, then left to dry in ambient temperature for 15 s. The drop or dipcoat was repeated several times to achieve the desired amount of active material for a given test. All electrodes used in this paper were 2-drop, resulting in 2 µmoles of active units.

PTCAQ-CNT electrodes were prepared via dropcasting, using different solvents due to PTCAQ's low solubility in chloroform. 8 mg MWCNT were dispersed in 1.5 mL chloroform by sonication for 45 min. 8 mg PTCAQ were dissolved in 0.5 mL dimethylformamide, added to the MWCNT dispersion, and sonicated for an additional 45 min. 100 µL was dropcast on Teflon-coated carbon fiber. The chloroform was evaporated under ambient conditions and the DMF was evaporated by drying the electrodes for 16 h in a vacuum oven at 60°C.
2.3 Deionization

Deionization performance was assessed by measuring changes in conductivity of an aqueous salt solution as voltage is applied in a two-electrode cell. Solutions were prepared from stock made with Millipore deionized water and solid salts. The two electrodes were submerged in 2 mL of salt solution, which was continuously stirred. Conductivity was measured using a VWR sympHony Benchtop Meter.

Chronopotentiometry scans used are described in Figure 2-3. In most tests, the cell was charged at 1.2 or 1.5 V and discharged at -1 V. For comparison, some tests were done at 1 V charge or -0.1 V discharge, both of which were found to be too low to adsorb or desorb, respectively, the system's maximum ion capacity. A PVF-CNT composite, except in baseline tests of CNT//CNT, was used as the working electrode, and a polymer-CNT composite of interest (PCoCpCb or PTCAQ) was used as the counter electrode.
Chapter 3

Results & Discussion

3.1 Characterization

Electrochemical performance of the synthesized PTCAQ electrode was first assessed via cyclic voltammetry. The results are shown in Figure 3-1. The scan showed a strong oxidation peak at -0.4 V, a smaller peak at -0.3 V, and a strong reduction peak at 0.25 V. The reaction was also fully reversible over multiple scans. These results match with results from literature[8].

![Cyclic voltammetry scan of PTCAQ](image)

Figure 3-1: Cyclic voltammetry scan of PTCAQ.
3.2 Quantifying deionization performance

A carbon fiber//carbon fiber deionization cell was prepared as a control, to assess the effects of solely double layer capacitance-based deionization in this system. As shown in Figure 3-2, the concentration of sodium chloride did not change under positive or negative voltage. Double layer capacitance alone is not enough to adsorb a significant amount of ions to the electrode surface; the additional adsorption in CNT and polymer-CNT systems can therefore be attributed to adsorption to the CNT or polymer-CNT composite itself.

![Figure 3-2: Conductivity of carbon fiber//carbon fiber cell during chronopotentiometry.](image)

Figure 3-3 compares the ion adsorption performance of PVF//PCoCpCb and PVF//PTCAQ cells against baselines CNT//CNT and PVF//CNT cells. Each cell contained 1 mM sodium chloride as electrolyte and was charged at 1.5 V for 20 min. CNT//CNT alone shows no decrease in concentration. PVF//CNT shows a slight decrease, but the concentration goes up after an initial dip, implying that the adsorption may not be stable over time despite continued applied potential. With the addition of a polymeric anode, a clear drop in ion concentration is observed. PTCAQ adsorbs more than twice the amount of ions as PCoCpCb. For both polymers, the concentration had not yet reached equilibrium after 20 minutes, so further tests were
Figure 3-3: Comparison of deionization performance of CNT//CNT, PVF//CNT, PVF//PCoCpCb, and PVF//PTCAQ.

conducted using a 40 minute charge.

3.3 Optimizing charge parameters

The behavior of the PVF//PTCAQ system was further explored under varying conditions to optimize the deionization; the results of these tests are shown in Figure 3-4. Concentration of the salt solution and applied voltage on charge were varied. Discharge voltage was -1 V for all except the 1.5 V, 1 mM test, which was discharged at -0.1 V and did not completely discharge. Except for 1.5 V, 0.5 mM, which was run for a 25 minute charge and 25 minute discharge, each test was run for 40 minute charge and 40 minute discharge.

The PVF//PTCAQ system is shown to adsorb ions over a range of charging voltages and initial ion concentrations. However, there are some inconsistencies in behavior. For 1.5 V charge and 1 mM NaCl, conductivity rapidly falls, but then slowly rises before discharge potential is applied. This trend is not seen in any other charge/concentration combination. It may be due to a side reaction that happens at higher voltages and concentrations, desorption of ions over time, or some other unknown factor. The large increase in conductivity during discharge for the two 0.5
mM NaCl trials, possibly for the same reasons. Further work is needed to determine whether either or both of these behaviors is consistent and if so their causes.

Figure 3-5(a) displays the charging portions of the same trials as Figure 3-4, normalized to the initial conductivity of each. Figure 3-5(b) emphasizes varying potential. Applying a higher potential, unsurprisingly, increases both the amount and rate of ion adsorption. The trials at lower voltages may not have reached equilibrium concentration, so there is potential for more ion adsorption over longer times. On the other hand, applying too high voltage, while saving time, may result in the increase in conductivity shown by the 1.5 V trial. Figures 3-5(c) and 3-5(d) compare across constant voltage—1.2 V and 1.5 V, respectively. For a constant voltage, the deionization performance is roughly equal at different ion concentrations up to 1 mM. The lower ion concentrations reach equilibrium conductivity more quickly, despite a lower total ion adsorption.
(a) Percent change in conductivity for selected deionization runs of PVF vs PTCAQ.

(b) Varying voltage, constant concentration (1mM NaCl)

(c) Varying concentrations, constant voltage (1.2 V)

(d) Varying concentrations, constant voltage (1.5 V charge)

Figure 3-5: Percent change in conductivity for selected deionization runs of PVF vs PTCAQ.
Ion adsorption at varying low concentrations (<1 mM) is explicitly shown in Figure 3-6. However, the polymer electrodes were found to be unstable at 5 mM, despite a variety of conditions attempted: using NaCl, NaClO₄, and NaNO₃ solutions, using both drop-cast and dip-coated PVF working electrodes, and using both 1.2 and 1.5 V charge. The PVF was found to leech from the electrode into the solution. The data (not shown) show that conductivity, and by extension ion concentration, first fall slightly, then begin to rise after 5 to 10 minutes despite a charging potential being applied. Further work is needed to determine the cause of the instability.

Regardless, the PVF//PTCAQ system performs extremely well for low concentrations. Figure 3-7 compares adsorption capacity per gram of material of PVF//PTCAQ, PVF//PCoCpCb, baseline materials, and values for systems previously reported in the literature. The PTCAQ system is over five times as effective as the highest previous literature value. PTCAQ, and redox polymers more generally, have significant potential to form the basis of new, highly efficient, and highly effective deionization and separation systems.

![Figure 3-6](image-url)

Figure 3-6: Ion uptake in mmol NaCl with varying experimental parameters—concentration of NaCl and applied potential during charge. (0.25 mM, 1.5 V was not run.)
Figure 3-7: Comparison of ion uptake by PVF/PTCAQ and other comparable sys-

Adsorption capacity (mg/g)

<table>
<thead>
<tr>
<th>Material</th>
<th>Adsorption Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li (Graphene)</td>
<td></td>
</tr>
<tr>
<td>Li (Graphene Oxide)</td>
<td></td>
</tr>
<tr>
<td>Farmer (Carbon Aerogel)</td>
<td></td>
</tr>
<tr>
<td>PVF/PTCAQ</td>
<td></td>
</tr>
<tr>
<td>CNT/CNT</td>
<td></td>
</tr>
<tr>
<td>PVF/PCoCpCb</td>
<td></td>
</tr>
<tr>
<td>Cn//Cn</td>
<td></td>
</tr>
<tr>
<td>Peng (CNT-mesoporous)</td>
<td></td>
</tr>
</tbody>
</table>

[2]
Chapter 4

Conclusions and Future Work

The redox polymer PTCAQ was synthesized and incorporated into polymeric electrodes for electrochemically mediated separations. The synthesis and purification process of PTCAQ was adjusted slightly from literature for maximum yield and lower molecular weight. PTCAQ-CNT composite electrodes were prepared and combined with PVF-CNT working electrodes to form an asymmetric redox deionization system. PVF//PTCAQ deionization cells were compared to solely double layer capacitance-based deionization (carbon fiber//carbon fiber cell), CNT//CNT and PVF//CNT alone, and a different redox polymer-based system (PVF//PCoCpCbMA).

PVF//PCoCpCbMA and PVF//PTCAQ were also compared to results in the literature for capacitive deionization. Systems containing PTCAQ were shown to have much higher ion uptake than previously reported capacitive and redox deionization systems—about 27mg/g adsorbed ions per g of active material—with reliable performance at concentrations up to 1 mM.

Future work must be done to assess PTCAQ’s viability for real-world desalination systems. Thus far, the PVF//PTCAQ system has not been shown to effectively adsorb ions at concentrations of 5 mM or above—when tested, the polymer-CNT composite becomes unstable and dissolves in the salt solution, the conductivity does not observably decrease, or both. Relatively low-salinity real-world systems, such as brackish water, are in the 1 to 10 mM range, so further research should examine how to stabilize the electrodes at higher concentrations. One potential path is to increase
the molecular weight of both the PVF and PTCAQ chains; short polymer chains can dissolve in solution in either their charged or uncharged state, reducing the capacity of the electrode and eventually destroying it[10].

The PVF//PTCAQ system has also not yet been tested for cycleability. While cyclic voltammetry indicated that the redox reaction of PTCAQ was reversible, there may be additional complications involving the physical ion adsorption, which is partially dependent on interactions between chemical structures as well as the applied potential. Ideally, applying a negative potential would fully discharge any adsorbed ions and regenerate the electrodes to their original state, such that a deionization cell could be discharged and recharged repeatedly to deionize multiple batches of water. Current results show significant variation in the regeneration process (as referenced in Chapter 3 and Figure 3-4): while in some cases nearly all of the ions are recovered into solution, i.e. the conductivity returns to its original value, in other cases the ending conductivity is significantly lower or even higher. Further work should be done to examine the causes of this variation—whether they are side reactions in solution, electrode capacity loss or degeneration, both, neither—and to choose a charge and discharge potential and time that balances efficient and complete desorption with minimal side reactions.

Figure 4-1: Example of deionization performance over multiple cycles in a CDI system.[9]
An immediate next step will be to examine the regeneration performance of the PVF//PTCAQ desalination cell. An example graph of performance over multiple cycles for a CDI system is shown in Figure 4-1. Over multiple cycles, the shape of the conductivity curve remains roughly the same, and the overall conductivity should ideally not change over time. While this figure references a deionization cell in which feed water flows through and conductivity of the discharge is measured, the same consistency of behavior is expected in a batch mode deionization.

Further, the PVF//PTCAQ system can be explored for electrochemical separations outside of deionization. The PVF//PCoCpCbMA system has been previously shown to preserve PVF’s anion selectivity[3]. The PVF//PTCAQ system can be tested in the same way for ion selectivity, suppression of side reactions, and extending its own high ion adsorption beyond simple salts.

Applying these principles of CDI and the growing redox desalination field to the PVF//PTCAQ system, we have found that PTCAQ is highly effective at desalination over low concentrations. Future work will focus on stabilizing the PTCAQ-CNT composite at higher ion concentrations and over multiple adsorption/desorption cycles to expand its desalination applications.
Chapter 5

References


