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Scale-up of Polyaniline Cellulose Membranes

A thesis submitted in partial
fulfillment of the requirements for
the degree of Bachelor of Sciences
in Chemical Engineering

By Isaac Bodemann

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Scale-up of Polyaniline Cellulose Membranes

Abstract

Polyaniline coated cellulose membranes show impressive conductive properties that may be used to innovate traditional charged separation techniques, such as electrodeionization. However, these membranes are not sold to consumers, so they cannot be easily integrated into such systems. This research focuses on the scale-up and development of positively charged anion exchange membranes to be used in EDI cells. Novel cellulose membranes were made using lab-specific cellulose. These membranes were then coated using a polyaniline technique adopted from a paper titled, "Flexible Electrically Conductive Nanocomposite Membrane Based on Bacterial Cellulose and Polyaniline" [1]. This paper details the methods used to add the polyaniline coating to lab-scale cellulose membranes. Fourier transfer infrared spectrometry (FTIR) was used to determine that the chemical composition of the material was altered. The carboxyl functional groups were most likely altered to imine groups judging by the shifted FTIR peaks. The theoretical chemical analysis performed before the experiment supports this conclusion. More work needs to be done to compile important data on the novel material, but the proof of concept has been shown within this research.

Introduction

Separation technologies have become heavily researched over the last few decades. Methods such as reverse osmosis, electrodeionization, and electrodialysis are still finding new applications throughout a variety of fields. Electrodeionization (EDI) has proven to be particularly interesting. It is a recyclable, continuous separation technique that utilizes ion-exchange resin (often made into wafers) and charged membranes [2]. Electrodeionization is a process primarily used for the ultra-purification of distilled water, mostly used in the fields of microelectronics, pharmaceuticals, and biology [3]. Figure 1 provides a basic illustration of ion separation occurring within an electrodeionization cell.

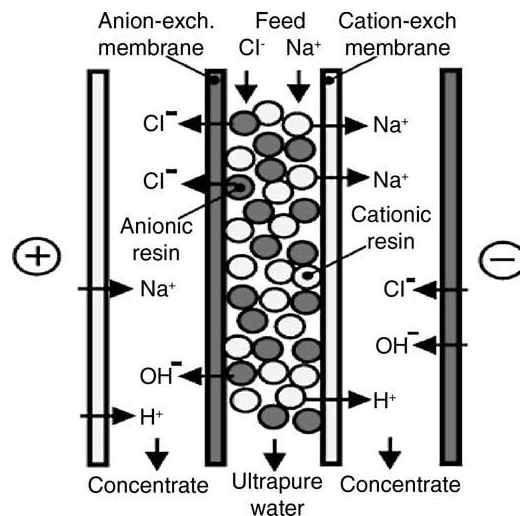


Figure 1 - Visual diagram of electrodeionization process separating sodium and chloride from water. Adopted from Tongwen Xu [6].

This project's origin stems from the idea that organic acids may be effectively separated from batch solutions using EDI [4]. Traditionally, organic acids are acquired through sensitive fermentation processes that can be difficult to uphold. The bacteria used to produce organic acids often die from the acidity of such a process, and purifying the organic acids is not energy efficient [5]. However, if the sugar molecules were broken down into organic acids without having to use bacterial enzymes, the process would become much more reliable and expedited. It

has been hypothesized that by using bi-metallic nanocatalysts as enzymes, these sugar molecules may be negated to more valuable organic acids. If this process were undergone with an EDI cell, the organic acids would be continually formed and separated from the bulk solution. The potential profitability of such an innovative leap is massive.

A few significant roadblocks had to be addressed. First, the bi-metallic nanocatalysts must operate like enzymes within a certain energy threshold. A graduate student is currently investigating this. Second, an EDI cell must be able to supply the necessary energy for these catalysts to operate. This energy can be transmitted using an electrical current; However, EDI is notorious for its reduced utilization of electrical current [6]. Therefore, the motivating factor of this research is to develop an EDI cell that proficiently conducts electricity. The three major components that inhibit this conductivity are the ion-exchange resin, charged membranes, and solution within the cell. The resin should be as conductive as the solution it resides, as it is very porous. If a high salinity solution is used, then moderate levels of electrical conductivity can be achieved. Therefore, the charged membranes are of the most significant concern. Electrically conductive membranes have been developed but are only retailed commercially or for specific applications at a high cost. This research focuses on synthesizing electrically conductive, positively charged membranes to address this discrepancy.

Theory

Polyaniline is an electrically conductive polymer with interesting mechanical properties. By crosslinking the polymer on cellulose membranes to form a nanocomposite, the electrical conductivity of these membranes can be increased by multiple orders of magnitude [3]. However, these membranes have only been synthesized and examined on small, pilot scales. The goal of this research is to create large scale membranes that may be further investigated. One

ideal use of these membranes, as mentioned earlier, is the simultaneous catalysis and selective separation using electrodeionization.

Ammonium persulfate is used as an oxidant in the oxidative polymerization of aniline, while a cellulose membrane is used as the template [1]. The extent of reaction limits the density of the polymeric layer. This affects the electrical conductivity. According to Weili Hu, optimal conductivity is achieved with a reaction time between 60 and 90 minutes [1].

Aniline infiltrates the carboxyl functional groups of the cellulose to form nitrogen-based groups, such as imine or nitro groups [7]. The extent of reaction likely determines the quantity of such nitrogen-based functional groups. Due to the unusual nature of the novel cellulose membranes, the formation of certain groups might be inconsistent. It is possible that aniline does not remove the carboxyl group but instead forms a link between the oxygen atoms. The repercussions of such chemistry on the conductivity have yet to be determined. Also, a thorough analysis of the mechanical properties and surface charge of the membrane would likely form a valuable understanding of the material's surface composition.

It must be noted that most of the data pertaining to this research was cut short due to the coronavirus pandemic, resultingly shutting down the research lab. Most of the project was spent developing in-situ cellulose membranes and a safe procedure to perform polyanilization. FTIR data was compiled for the polyaniline membranes to determine that the chemistry had been altered. Further characteristics that were meant to be investigated are electrical conductivity, weight percent polyaniline, tensile strength, and ion conductivity.

Synthesis of Novel Cellulose Membranes

Some details about the membrane synthesis process will be withheld due to a potential patent¹. The membranes were formed using lab-specific tempo oxidized cellulose. A cellulose solution was developed that can synthesize membranes using phase inversion. Phase inversion utilizes a cold water bath to separate the membrane's carbon-based backbone (cellulose) from the solvent [8]. Performing this synthesis requires the solution to be drawn across a glass plate, then flattened to a predetermined, measured thickness. The glass plate is dipped in a water bath, and phase inversion occurs. After the glass plate is removed from the bath, most of the solvent is pulled from the membrane. The membrane is left to dry, then washed again to ensure any remaining solvent has been removed. **Figure 2** provides an image of the novel cellulose membranes directly after phase inversion.

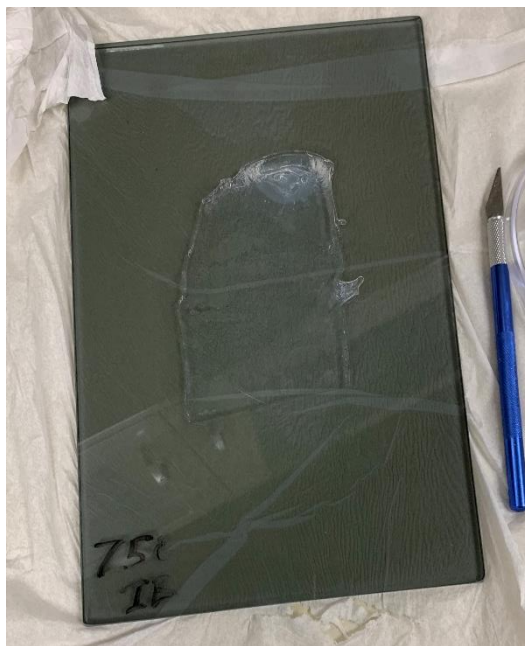


Figure 2 - Photo of a novel cellulose membrane with a thickness of 750 microns.

¹ A U.S. patent has been submitted on the OTO-CNM Form I and Form II with a potential royalty stream to the inventors. International Publication Number WO 2019/023702 A1. International Publication Date: 31 January 2019
An Invention disclosure was submitted in regard to the technology presented in this report under Invention ID: C2020-40

Standard cellulose membranes are usually not clear, so the novelization of this particular membrane synthesis procedure should be noted. **Figure 3** below shows the similarity between these novel cellulose membranes compared to traditional cellulose. Hypothetically, both membranes should share similar power densities since their compositions are analogous. Unfortunately, there was not enough time available to examine the power density of the polyaniline coated cellulose membranes. The power density would likely increase due to better electrical conductivity but must be further investigated.

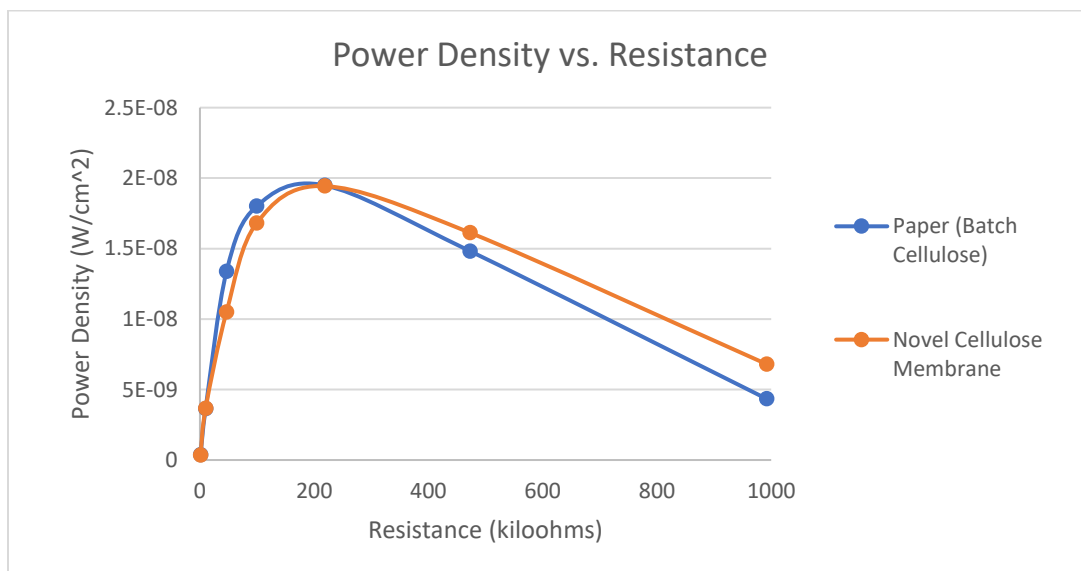


Figure 3 - Illustrates the power density of the novel cellulose membranes versus batch cellulose membranes (in this case paper).

Safety Considerations

Aniline, ammonium persulfate, and hydrochloric acid are all hazardous compounds. Aniline and ammonium persulfate result in a highly exothermic reaction. Also, aniline is notable for its acute toxicity. The environmental health and safety committee had to approve the use of these hazardous substances before proceeding towards experimentation. Dr. Tammy Lutz-

Rechtin, the Chemical Engineering Safety Coordinator, significantly helped prepare an appropriate standard of procedures.

The oxidative polymerization of aniline was performed under a fume hood, with three layers of containment. No metal was used within the setup to avoid a spontaneous reaction with aniline. All the handling tools used were composed of glass and plastic. Waste from the process was stored within the fume hood in an appropriately labeled container. Three layers of containment were utilized for the storage of aniline to alleviate its strong odor and avoid potential spills. An ice bath was used to cool the previously mentioned exothermic reaction during experimentation. The temperature of the solution had to be consistently monitored throughout the experiment.

Select personal protective equipment (PPE) was used for the polyaniline addition step. As always, the primary research lab PPE standards were met (pants, close-toed shoes, safety goggles). Also, a splash shield was worn to protect the eyes and face. Silver-shield gloves and a lab coat were also used to protect against the risks of aniline. Plans to address spills in and outside of the fume hood were developed in the case of an emergency. The Environmental Health and Safety committee commended the thorough risk and safety analysis. No incidents occurred throughout the length of the project, due to the necessary precautions being taken.

Polyanilization Procedure

As mentioned earlier, this experimental procedure was adapted from Weili Hu [1]. First, the experimental setup consisted of a two-neck flask with a stir bar, a rocker with three layers of containment, and a variable speed motor to control the rocker. Beakers, a waste container, plastic tweezers, and glass/plastic syringes were also vital components used. A picture of the experimental setup is provided below in **figure 4**.



Figure 4 - Picture of experimental setup. Variable motor is glossy teal object on left, waste container in back left, two-neck flask with stirrer towards center left above hot plate, and mechanical rocker with three layers of containment on right.

First, the cellulose membranes were washed to avoid possible contamination. Initially, the membranes were dried to constant weight under vacuum, but it was later determined that this step was unnecessary since the weight was not of significant concern. 6.66 mL of water was added to the two-neck flask, followed by 3.33 mL of 6M hydrochloric acid. This first step dilutes the hydrochloric acid to 2M. The temperature was allowed to plateau before moving forward. Next, 0.76 mL of pure aniline monomers was added dropwise using a plastic syringe. The solution was then transferred to the glass plate attached to the mechanical rocker. The membrane

was added to the solution and stirred for one hour while monitoring the temperature. Next, ice was added to the container surrounding the glass plate to cool the forthcoming exothermic reaction. Lastly, two mL of 2M ammonium persulfate was added dropwise. At this step, the temperature must be closely monitored. The membrane may be allowed to stir for 30-180 minutes. In most cases, the solution was stirred for thirty minutes. After the reaction has occurred, the liquid waste is drained into the waste container. The membrane is preserved and washed thoroughly three times using distilled water and 75% ethanol. The membrane is left to air dry for at least 24 hours.

Some aspects of the process must be noted. First, unique pipettes and syringes were used for each compound added to avoid cross-contamination. Also, the variable motor is used to switch on/off the mechanical rocker since the switch on the rocker is somewhat tricky to access. Membranes with a thickness of 750 microns were used for every coating. This thickness was chosen because of its interesting ion selectivity and promising mechanical properties.

Results

Three batches of polyaniline cellulose membranes were synthesized throughout this project. A membrane from each batch is pictured in **figure 5**. They exemplify the necessary scale-up of membrane size needed to experiment in a lab-scale separation cell. The final and largest membrane could handily fit within an EDI cell.



Figure 5 - Photos of a membrane from each batch of polyanilization. Smallest to largest membrane from left to right.

Fourier-transform infrared spectroscopy (FTIR) was used to determine if the membrane was coated in polyaniline. FTIR provides valuable information about the molecular composition of materials. Infrared radiation is shot at the material. Some of the radiation passes through the material, while the rest is absorbed [9]. This creates a signal that is translated into absorbance peaks. Peaks within specific absorbance ranges are indicative of certain atomic bonds. Using FTIR, it was determined that the experimental setup successfully altered the chemistry of the membrane. **Figure 6** below shows a new peak around 1650-1700 for the polyaniline membrane.

This means that an imine group likely replaced the double-bonded oxygen of the carboxyl groups [10]. This is a promising sign that the aniline properly bonded to the functionalized cellulose. It also depicts the removal of a peak around 1600 that is present in the raw cellulose and cellulose membrane data. This peak is likely the result of a carboxylic oxygen-carbon double bond [11]. These carboxyl functional groups are either removed or altered by the polyaniline coating.

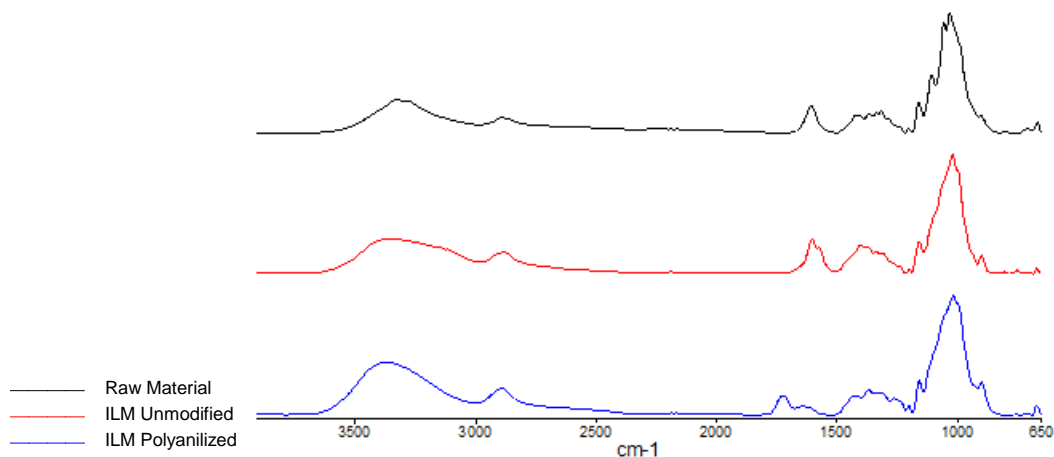


Figure 6 – FTIR data of the cellulose powder (black), unmodified cellulose membrane (red), and polyaniline cellulose membrane (blue).

The membranes proved to be rather stable under ambient conditions and presented relatively promising strength. Minor flexibility was examined but seemed to be mostly dependent on the level of moisture. The polyaniline coating should supplement a positive surface charge on the membrane due to polarization. This property is responsible for the improved electrical conductivity of the membranes [1].

Conclusion

Overall, this project accomplished its primary objective, to synthesize a polyaniline cellulose membrane large enough to be integrated into lab-scale separation systems. First, a process to create novel cellulose membranes was used to provide a template for the polyaniline coating. Next, these membranes were coated with polyaniline utilizing the procedures detailed above. Lastly, a change in chemical composition was detected using FTIR. The shift in peaks is believed to be the result of imine groups forming on the carboxyl functional groups of the cellulose. The surface chemistry is thought to be dependent on the length of exposure to ammonium persulfate after polyaniline has coated the membrane. These scaled-up polyaniline cellulose membranes show great promise; However, due to unfortunate circumstances, a large amount of valuable data has yet to be obtained. These membranes should be further studied to determine their applicability towards an electrically conductive EDI cell.

Recommendations for Future Work

It is suggested that more data be acquired on the polyaniline coated membranes. First, the electrical conductivity should be examined to determine if the coating works effectively on larger membranes. The four-probe method may be used to test the electrical conductivity. Also, the ion conductivity and morphology of the membranes should be investigated. Lastly, experiments should be performed to determine the surface charge of the membrane [12].

In terms of improvements to the experimental process, there are a few. First, some techniques should be used to ensure the membranes remain flat. From **figure 5**, it is evident that the membranes tend to roll up around the edges as they dry. This may hinder the membrane's potential applications by degrading the consistency of its physical properties. Second, the

membrane should be stirred for ninety minutes once the ammonium persulfate is added. This seems to be the duration that the optimal conductivity is achieved [1]. Lastly, a larger mixing apparatus would allow more membranes to be synthesized. If scaling up is essential for increased experimentation, then the mixing equipment will be the limiting factor.

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