A Novel Approach to Renewable Energy: Light Stimulated Active Cation Transport Membrane Via Covalent Modification with a Photoacid

Matthew Fosdick

Empire High School

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Abstract

Today, there exists the growing challenge of climate change. Solar is a popular renewable energy source to combat climate change. Today solar panels are approximately 15% efficient and due to the limitations of the materials used to manufacture them, the maximum efficiency is 34%. This research utilizes a completely different renewable solar system than current technology and stands to be more cost efficient and more energy efficient than current solar energy. Photoacids have recently been recognized as potential solar generators. They have benefits over current solar cells with a longer life and potentially more cost-efficient design. Furthermore, they produce few harmful emissions during production unlike current photovoltaic technology. As demonstrated for the first time in late 2017, a photoacid, HPTS has the ability to covalently bond to a cation exchange membrane, nafion, making it an active membrane. When a light excites this modified membrane in an electrochemical cell, it demonstrates power generation. The problem is that the efficiency is very low. This research project successfully synthesized the first active membrane to be made with a photoacid other than HPTS and demonstrated a nearly 5000% increase in efficiency. This synthesis was accomplished through modification of HPTS through several reactions and a long reflux of the membrane in the solution of the HPTS derivative The successful use of this photoacid is very promising for future research because it indicates that at least 4 more photoacids of similar structure could be used. Furthermore, it is very possible that the single novel membrane created is far from optimized and could further increase in eficiency. Ultimately this experiment demonstrates rapid growth in the active membrane field and could produce the next viable renewable energy source.

1 Introduction

1.1 Impact

Today, there exists the growing challenge of climate change. Current solar technology is only 15-20% efficient and leaves much room for improvement. However, progress has stalled with this type of solar technology due to the lack of pathways for improvement. Even if the technology was perfected, the efficiency is capped at 34% due to the chemical properties of silicon used in current solar panels. This research utilizes a completely different renewable solar system than current technology and stands to be more cost efficient and more energy efficient than current solar energy. Photoacids have recently been recognized as potential solar generators. They have benefits over current solar cells with a longer life and potentially more cost-efficient design. Furthermore, they produce few harmful emissions during production unlike current photovoltaic technology. Photoacids have such a short history in power generation that some predict that the efficiency could increase tenfold (White et al.). This makes it a worthy candidate for the next type of green energy production.

1.2 Objectives

Main objectives to this research:

- Create a regenerative active membrane through modification with 8-Hydroxypyrene-1,3,6-Trisulfonic Acid (HPTS)
- Demonstrate the modified membrane's ability to transfer hydrogen ions across the membrane when excited by light mimicking sunlight
- Demonstrate reverse transfer during immediate periods of darkness
- Compare the relative ability of membranes modified by HPTS derivatives to transfer hydrogen ions across the membrane when excited by light and reverse transfer during immediate periods of darkness to the HPTS modified membrane
- Optimize procedures for cost

2 Background

The solar cell that is utilized in this experiment creates electricity with the same method as a typical electrochemical cell, with the traditional membrane replaced by a regenerative active membrane. In a typical electrochemical cell, there are two chambers, with each chamber containing an acidic solution or a basic solution. An electrode is inserted in each solution with the electrodes connected by a wire to allow for the transfer of electrons. Each solution contains metal ions of the electrode that is in that solution. The acidic side of the cell, the anode undergoes a chemical reaction which oxidizes the anode.

Electrons travel from the anode and into the wire, creating cations, or positively charged molecules, on the surface of the anode which dissolve into solution. The electrons travel from the anode to the other electrode, the cathode. At the cathode, a reduction reaction occurs and metal ions travel out of solution and bond to the cathode while absorbing electrons. The flow of electrons in the wire sets up the surrent of electricity. However, this process of adding cations to the acidic solution and removing the cations from the basic solution changes the pH of each solution. When this pH change becomes too extreme, the cell cannot work. To fix this, the solutions are connected through a salt bridge or in the case of the electrochemical cell in this experiment, a membrane. The salt bridge or membrane transfers cations from the acidic solution to the basic solution to control the pH and keep the cell running.

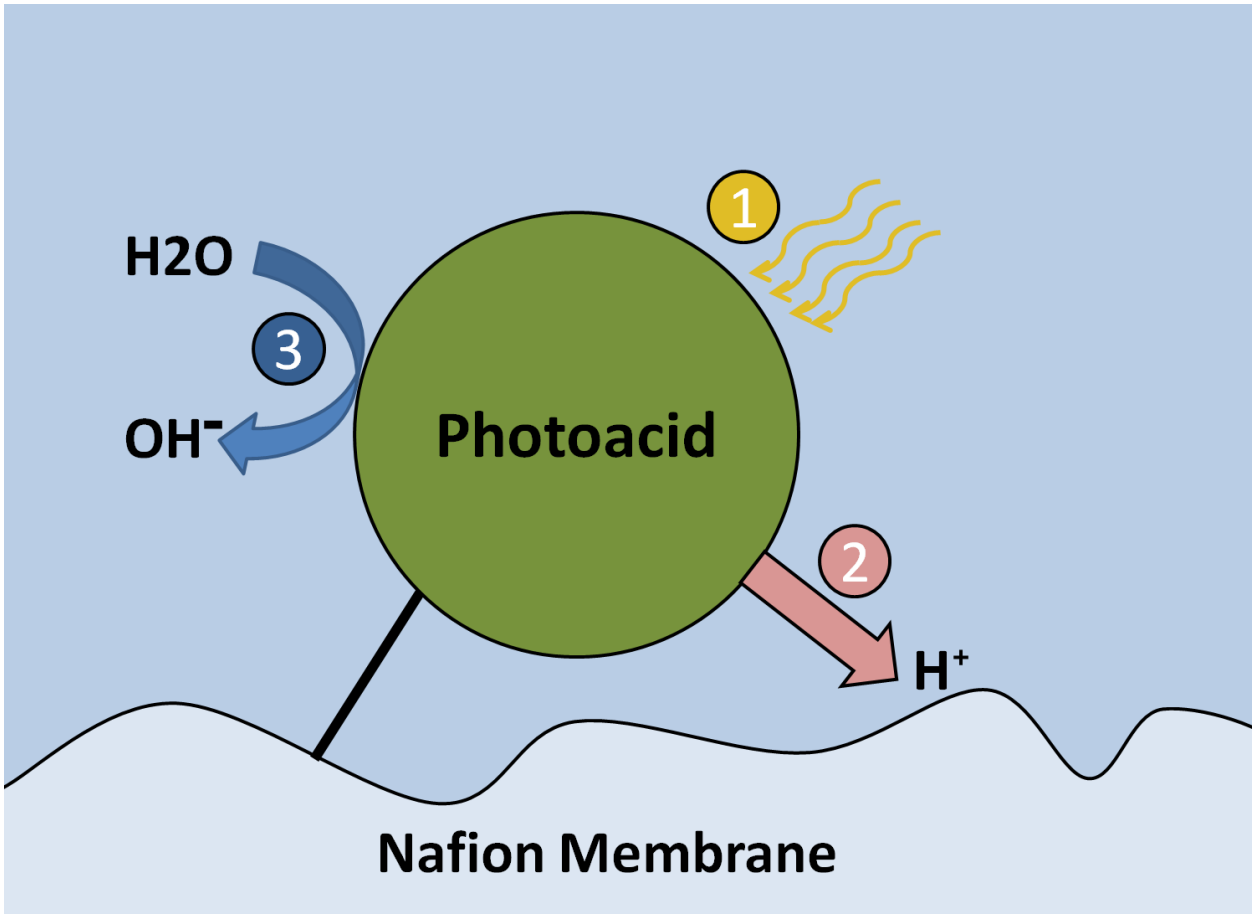
An electrochemical cell can only work for a limited amount of time and stops working when it runs out of metal ions to bond to the anode. In a cell that uses an active membrane like the ones in this experiment, this problem is not an issue. When the membrane is no longer stimulated by light, the reaction is reversed so that the metal on the cathode oxidizes again and dissolves back into solution. Not only is the cell reset but as electrons move again, albeit in the opposite direction, electricity is generated. This is what makes regenerative active membrane technology so useful, electricity is generated in sunlight and darkness driven solely by solar energy, creating a potentially superior solar panel. This technology is a very recent discovery and has only been tested in the last two years. The first and only use of this technology estimated that only a tenth of the reasonable potential of the technology had been unlocked with the first cells, the research also only examined one photoacid which limited the scope of the experiment while this experiment will analyze HPTS derivatives.

The regenerative active membrane works by converting light energy into the transfer of cations. A photoacid is a molecule that dissociates when it is stimulated by a photon and then re-protonates after stimulation. This cycle not only allows the reverse reaction to occur in darkness, generating electricity, it also is an integral part of the forward reaction. Nafion is a membrane that is commonly used in normal electrochemical cells and allows the passage of cations but no other molecules through it. When a photoacid is covalently bonded to the nafion membrane, light can cause a hydrogen ion to dissociate from the photoacid which is transferred through the membrane. Even though some cations can return to the side with the photoacid, there is a positive bias and most cation transport is in the direction that the photoacids are pushing the hydrogen ions The pH of the solution changes when the hydrogen ion dissociates from the photoacid and transfers through the membrane, this can be harnessed to generate electricity.

The ultimate goal is to create an electrochemical cell that can operate as a typical cell in the dark and then in the presence of sunlight push cations in the reverse direction of normal operation so the cell charges and metal ions bond back to the anode, dissolving from the cathode. During this charging cycle,

the cell continues to generate electricity. This research will determine methods of bonding different photoacids to nafion and testing them in cells to find the efficiency of the active membranes. As this technology advance, it can rival other existing solar technologies.

2.2 Membrane Mechanism Diagram



This is a diagram illustrating the course that the photoacid follows when it is bonded to the membrane. First the photoacid is struck by light which causes dissociation and this hydrogen molecule goes through the membrane finally, the photoacid reprotonates with water from the side it is on.

3 Literature Review

3.1 Active Membrane Literature

A research paper from UC Irvine titled "Observation of Photovoltaic Action from Photoacid-Modified Nafion Due to Light-Driven Ion Transport" (White et al.) details covalent modification of nafion, a cation exchange membrane with a photoacid HPTS. This was achieve by refluxing a small piece of the membrane in isopropyl alcohol with HPTS and small amounts of triethylamine and NaOH for 7

days. they then tested the membrane by putting it into a cell and shining a laser on it and measuring the current and potential output, however this procedure was not very well documented and it was hard to recreate. They found that the membrane did create a potential difference between the two sides of the cells and induce a current when the laser was activated. They used three lasers and found that only one worked very much at all. They could have improved the explanation of their procedures and tried multiple photoacids to expand on the research.

3.2 Photoacid Literature

A second paper, "Highly photostable 'super'-photoacids for ultrasensitive fluorescence spectroscopy" (Finkler et al.) detailed the modification of HPTS into multiple other photoacids. They accomplished this by first reacting it with acetic anhydride to change the structure of HPTS and then they reacted it with thionyl chloride to chlorinate it. At this point the procedures differed for each photoacid they created but generally, they combined the modified HPTS with a salt that would have a part of it ultimately bonded to the modified HPTS, this was reacted in dimethylamine at 0 degrees C. This would produce a molecule with similar structure to HPTS but with an extra group attached to the ends. The research didn't have many applications for these new photoacids but and this decreased the value of the paper.

3.3 Novel Directions

The research in this project attempts to achieve a completely new membrane by utilizing modified HPTS bonded to nafion to respond to light. The photoacid used is stronger than HPTS and has an increased affinity to dissociate when struck by light, making it more acidic and able to produce more power. This modified HPTS has never been applied to active membrane research and is also very young so there is great potential with applying it. Additionally, Using a modified HPTS can be more cost effective because the required purity is reached through the modification procedures with no need for an extra purifying step which can be costly. Finally, this research in both active membranes and modified photoacids is extremely new and has great ability to expand to new horizons especially in renewable energy.

4 Experimental Section

4.1 Modification of HPTS

(*1*) Reflux 4.56 g of HPTS with 71.4 mg of sodium acetate in 50 ml of acetic anhydride for 35 hrs. Dilute this with THF and vacuum filter. Dry this precipitate to yield pure HPTS.

(*2*) Suspend 4.36g of *1* in 20 ml thionyl chloride. Add 120 µL of DMF and heat to reflux for 5 hours. Pour on ice to form precipitate and vacuum filter this to yield a chlorine salt of pyranine.
(*3a*) Add 508µL of the borate salt to 4.72mL of methylene chloride, cool to 0oC, add 364µL of triethylamine. Add 262.4 mg of *2* dissolved in 24 mL of methylene chloride dropwise, warm to room temp and stir for 48 hrs. Dilute with 40 mL of 1M HCl and extract organic phase with separatory funnel. Dry over sodium sulfate and evaporate, yielding an orange powder.

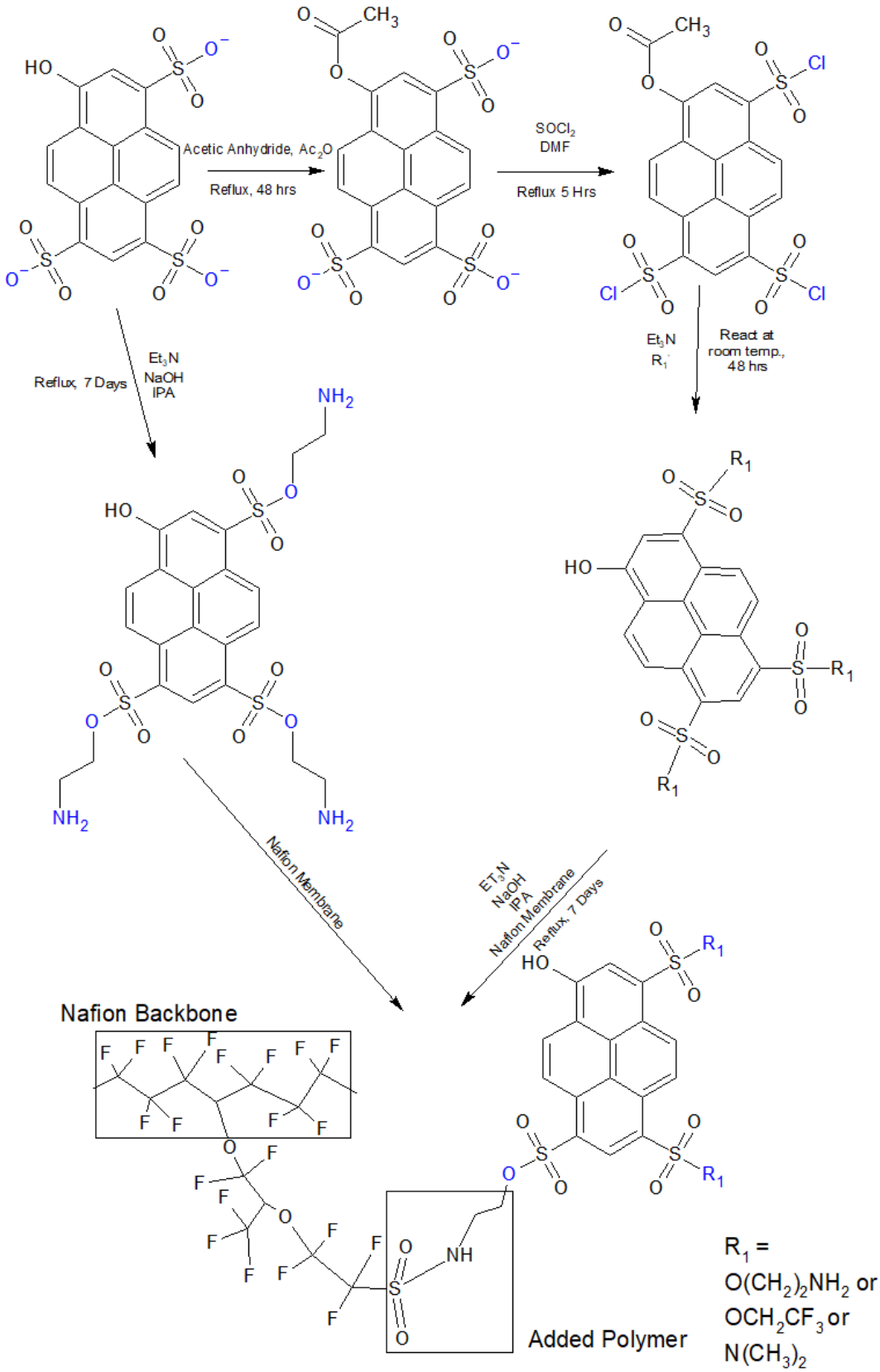
4.2 Modification of Nafion Membrane

(*4a*) Dissolve 3mg of HPTS in 20 ml of isopropyl alcohol. Then add 75 µL of 1M NaOH and 45 µL of triethylamine.
(*4b*) Dissolve 3.53mg of *3a* in 20 ml of isopropyl alcohol. Then add 75 µL of 1M NaOH and 45 µL of triethylamine.
Submerge one nafion membrane cut to a 2x2 cm square in each solution (*4a, 4b*) and sir for 7 days at 90^{o}C
Immerse the membranes in 10 mL of deionized water, 1M H2SO4, 1M NaOH, and deionized water again for 20 minutes each
Store the membrane under 1M NaCl

4.3 Testing Membranes under Light Excitation

Setup the cell by inserting the membrane between two O-rings, putting the two half cells in place and clamping the assembly with a clamp. Fill each side of the cell up with 1M NaCl. Insert the electrodes with the two reference electrodes closest to the membrane. The working electrode is on the side of the cell with the window, attach the red WE potentiostat lead to the platinum electrode on this side, attach the red REF 1 lead to the reference electrode on this side. Connect the blue CE and REF 3 leads together and attach them to the platinum counter electrode. Attach the white REF 2 lead to the reference electrode on the counter electrode side. Line up the laser pointing into the working electrode side.
Perform cyclic voltametry, chronoamperometry and chronopotentiometry on the cell using the potentiostat.

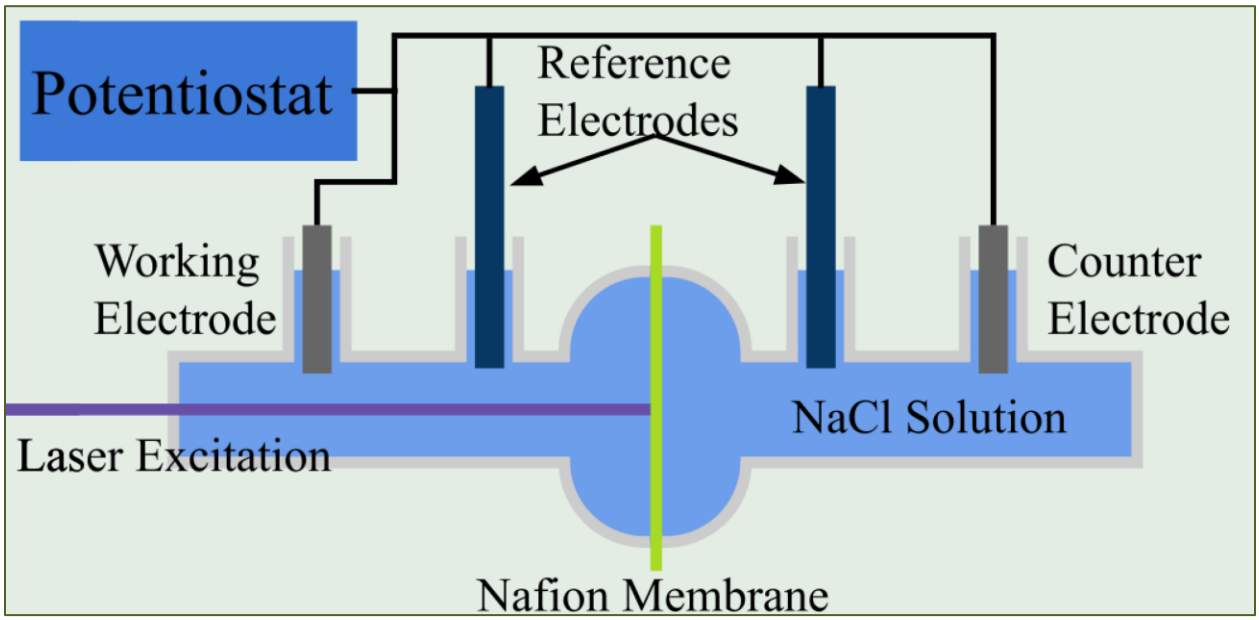
4.4 Reaction Scheme



Reaction scheme of the proposed reactions for this experiment . Depicts two pathways for generating final

membrane product; one for unmodified HPTS and one for the HPTS derivatives (HPTA and Tris(2,2,2-trifluoroethyl) 8-hydroxypyrene-1,3,6-trisulfonate). It also indicates the chemicals used in a reaction and how the reaction was performed.

4.5 Electrochemical Cell Membrane Testing Diagram



This diagram represents the entire cell working together. The laser stimulation pushes cations across the membrane creating a positive charge on the right side of the cell.

5 Results

- Control test was constant and with few fluctuations indicating that the instruments used to measure voltage were precise.
- The HPTS modified membrane reacted to light by transporting cations as indicated by the influx of current as the laser was activated (Graph 1)
- Peak power output was 8.33 x 10-9 watts.
- When factoring in the reverse rate of the membrane and modeling light spread across entire membrane, total power output is 1.00 x 10-8 watts.
- Total 0.0029% efficiency when compared to the power of the laser.
- The HPTS derivative modified membrane reacted to light excitation from the laser much more effectively (Graph 2)
- Peak power output was 4.59 x 10-7 watts.

- When factoring in the reverse rate of the membrane and modeling light spread across entire membrane, total power output is 4.95 x 10-7 watts.
- Total 0.14% efficiency when compared to the power of the laser.
- The power output of the HPTS derivative is nearly 50 times that of the normal HPTS membrane.
- The HPTA modified membrane was less effective than the HPTS derivative but more effective than HPTS (Graph 1)
- Peak power output was 1.94 x 10-8 Watts.
- When factoring in the reverse rate of the membrane and modeling light spread across entire membrane, total power output is 2.11 x 10-8 watts.
- Total 0.0061% efficiency when compared to the power of the laser.

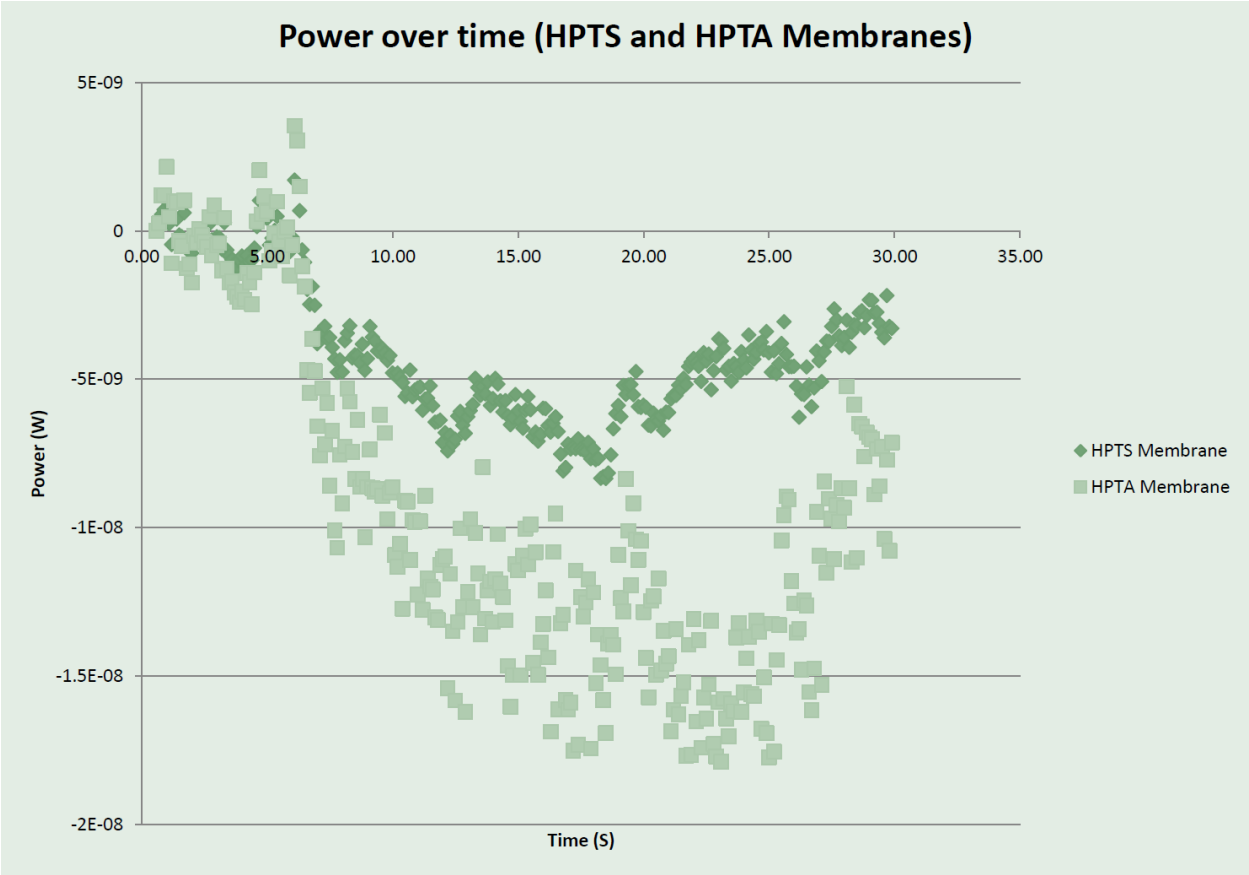
5.2 Tables and Graphs

	HPTS Membrane	HPTS Derivative Membrane	HPTA Membrane	Control
Peak Current (μA)	0.191	8.92	.304	0.0335
Peak Power (nW)	8.33	437	21.1	0.968
CV Ofset (mA)	0.06	0.001	0.03	0.0002
Efficiency (%)	0.0029	0.14	.0061	0.0003

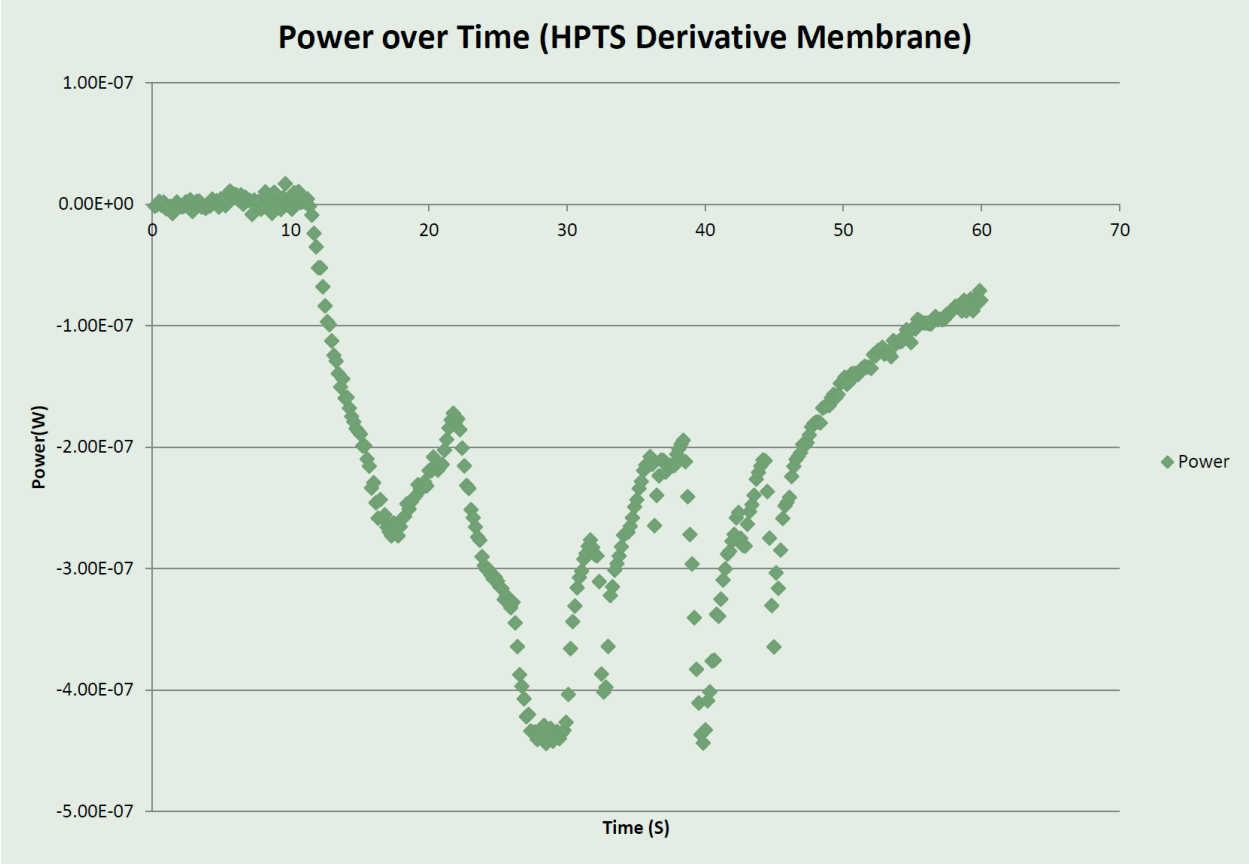
Table 1- The table contains the most important data points for easy data comprehension, these are also illustrated on graphs.

1 square meter panel			
Chemical	Bulk Price	Price per Active Membrane Panel	Price Per Photovoltaic Panel
HPTS	$6.84/g	$2.57	
2,2,2triflouroethyl salt	$16.86/mL	$1.05	
Dichloromethane	$0.53/L	$0.02	
triethylamine	$9.15/L	$0.10	
Acetic anhydride	$13.56/L	$0.06	
THF	$21.50/L	$0.04	
Isopropyl Alcohol	$10.00/L	$1.00	
Total Price		$4.84	$514.50
Price per Watt		$3.45	$3.43
With storage inefficiencies		$3.64	$4.13

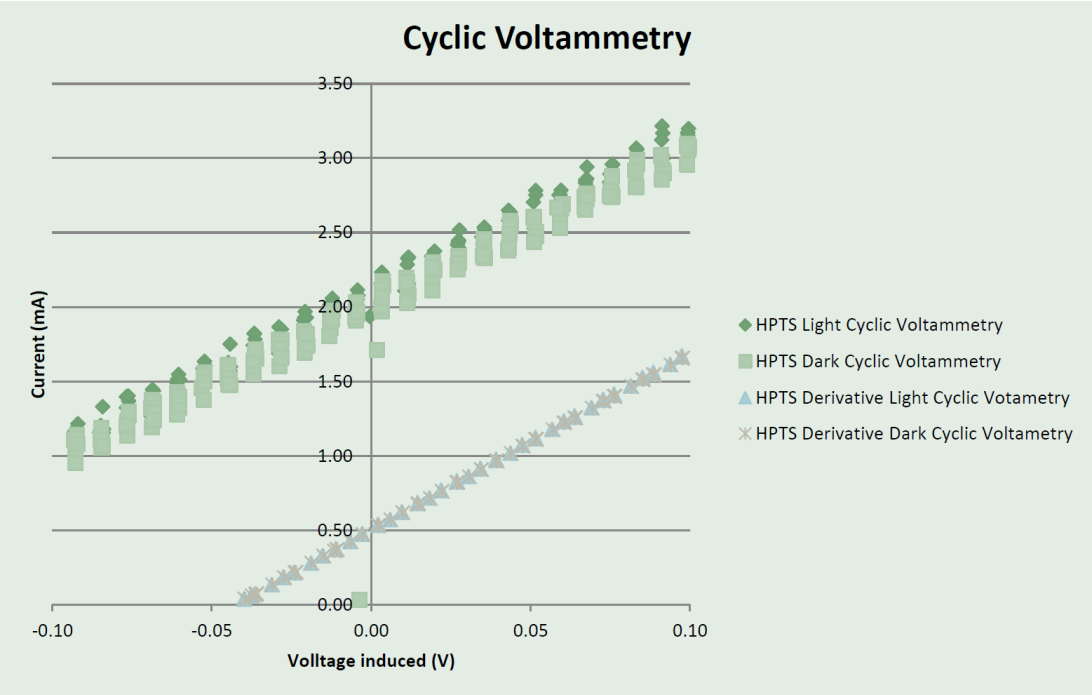
Table 2- Cost analysis for a 1 square meter panel. Because of the very efficient storage that is built into the active membrane cell and the comparatively inefficient storage in photovoltaic technology, the active membrane panel is less expensive than current photovoltaic panels.



Graph 1- *G*raph illustrates the power over time for the regular HPTS membrane and HPTA membrane. There is a clear jump at 5 seconds when the laser is activated.



Graph 2- Power data for the HPTS derivative membrane. It is much more reactive than the other membrane but also more sensitive to light movement and other disturbances.



Graph 3- Cyclic Voltammetry trial, where voltage is induced in the cell and the current is measured, interestingly, the regular HPTS membrane had a stronger reaction to light in this trial than the HPTS derivative.

6 Conclusions

6.1 General Discussion

My hypothesis was not correct, while there was an observable power generation within the cell when the membranes were stimulated, there was no trend observed between the acidity of the photoacid and the efficiency of the membrane. There was however, a strong correlation between the electronegativity of the photoacid and the efficiency of the membrane. Furthermore, the membrane modified with HPTS derivative was much more successful than the HPTS membrane or the HPTA membrane. The control test had very few disruptions, the data is nearly constant. This indicates that the measuring instruments are reliable and precise and helped with further data use and collection.

The Modified membranes were also conductive to cations,. When the HCl was added to the cell, the pH sharply decreased, leading to a quick fall in voltage and then a steady rise in voltage that resulted from cation diffusion and pH balancing between the sides of the cell.

Both modified membranes was also successful at transporting cations after they were produced by light on the membrane. This can be seen in Graph 1 and 2 with sharp increases in current. It is noteworthy that the increase in current on graph one, the HPTS membrane is smaller yet steadier.

6.2 HPTS Modified Membrane Discussion

It was evident that the nafion membrane had been modified with HTPS because of the yellow coloration after it reacted for 7 days. Then the membrane was tested in a cell with a laser to stimulate it and the current increased from approximately 0 to .2 μA immediately after the light was initiated at 5 seconds (Graph 1). This corresponds to a jump in power, from approximately 0 to -8 Nw (negative power still indicates a usable flow of electron, just in the opposite direction as the electrode were set). To this, the reverse rate must also be added to see the entire effect of the light stimulation because after the membrane transfers some cations across the membrane due to the light stimulation, some cations diffuse back without being found in the potential difference and therefore the H^+ concentration change or overall power. To calculate the amount of power that was transferred back without being measured, one must analyze the rate that the pH changed under no stimulation. When the reverse rate is factored in, the total power output of the membrane was calculated at 1.00×10^{-8} watts which is only .0029% efficient.

6.3 HPTS Derivative Modified Membrane Discussion

The membrane modified with an HPTS derivative produce very interesting results. The Electrochemical data demonstrated very promising yet slightly inconsistent data. The generate current, the laser had to be pointed at a very specific area on the membrane. This indicates that the membrane was not fully modified. There is other evidence that would suggest this. The membrane did not demonstrate a color change after the reflux to modify it unlike the HPTS membrane, this shows that there was potentially less of a reaction between the HPTS derivative and nafion than the unmodified HPTS. he reflux was also only able to run for 4.5 days rather than the planned 7 due to time constraints. Another interesting observation is that the reflux solution for the HPTS derivative membrane changed color from pink to a pale yellow. This was perplexing however one theory does offer itself. It was observed that some isopropyl alcohol had boiled off and was not condensed back into solution, this led to the solution being topped off with more isopropyl alcohol. The isopropyl alcohol used was 91% so it is likely that much of the water stayed in the reaction vessel and the concentration of water grew as more of the isopropanol boiled off. The HPTS derivative turns a pale yellow color when dissolved in water, the same collor that was observed. It seems likely that the HPTS derivative dissolved into the water after some time instead of isopropanol and this prevented it from reacting with the other reagents in as much of a capacity, causing less bonding to the membrane. If a higher concentration of isopropyl alcohol is used, and the reflux is preformed for longer, it is very likely that even better results could be observed from the HPTS derivative membrane.

Even with these challenges creating the membrane, the results were very promising. Although the cyclic voltametry showed a smaller deviance between light and dark than the regular HPTS membrane, the HPTS derivative membrane performed much better. This is seen in the nearly 50 times better peak efficiency derived from chronoamperometry even with the inconsistent measurements. Since this is the very first time this species of active membrane has been synthesized it is expected that the efficiency keeps increasing with more reasearch.

6.4 HPTS Modified Membrane Discussion

The HPTA membrane performed only double the efficiency of the HPTS membrane which makes it not very efficient as compared to the HPTS derivative membrane. The synthesis of this membrane, while challenging due to the small quantities, went smoothly and there were no particular observations.

6.5 Errors Analysis

This calculated efficiency may not be entirely accurate due to some potential sources of error in the measuring of the membrane's performance. Some potential minor sources of error included the

distance from each electrode to the membrane(however this error was constant and could easily be corrected in calculations), measurement errors when synthesizing the membrane, contaminating the membrane or glassware slightly just through particles in the air, measurement errors creating standard solutions for use in the cell (NaCl and HCl). The biggest source of error would be the all of the difficulties modifying the HPTS derivative membrane, had this been done again, much better results would be expected. Overall there were very few sources of error in this experiment.

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