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

Introduction

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.

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

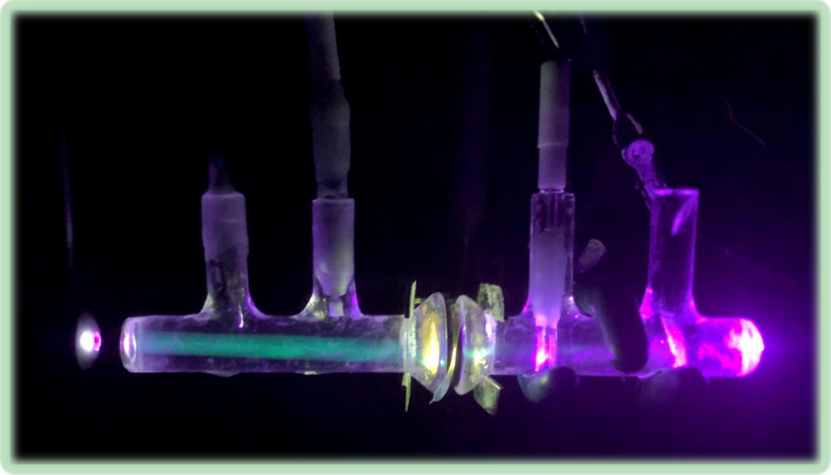


Figure 2- *(photo courtesy of exhibitor)* This image depicts the custom glass cell with the laser activated, the electrodes can be seen with the reference electrodes in the middle. The light beam can be seen and the image creates a much better understanding of the cell.

Background Research

Two main resources inspired the research. With "Observation of Photovoltaic Action from Photoacid-Modified Nafion Due to Light-Driven Ion Transport" (White et al.), a nafion membrane was modified with HPTS, a photoacid to create active transport when stimulated by light. A second paper, "Highly Photostable 'Super'-Photoacids for Ultrasensitive Fluorescence Spectroscopy" (Finkler et al.) details the modification of HPTS to create photoacids with increased activity. By using a new photoacid from the second paper with increased activity and very similar structure to HPTS, a new, more effective membrane can be synthesized.

- Current solar technologies waste approximately 17% of the generated power.
- Lack of efficient storage methods of generated electricity from current solar technology can be addressed by the seamless integration of hydrogen fuel cell technology to store energy generated from the membrane.
- Synthesized active membranes operate in a traditional electrochemical cell, containing electrodes in half cells on either side of the membrane with reduction-oxidation reactions of hydrogen occurring at the electrodes.
- Operating similar to a hydrogen permeable membrane cell; recharging is driven by light stimulation of the membrane rather than traditional electrical input.

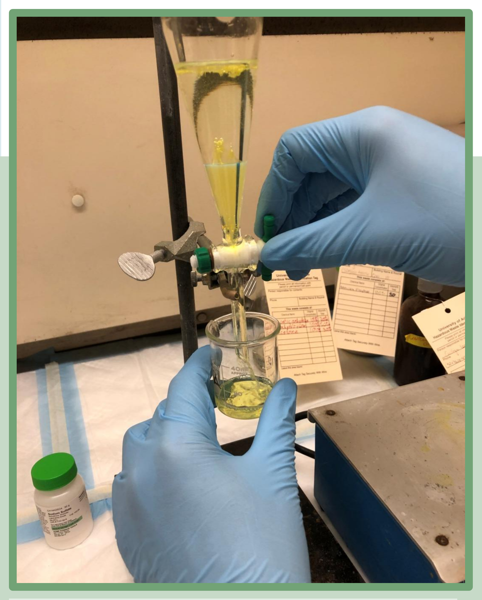


Figure 6- *(photo courtesy of exhibitor)* Separation of the organic phase which contains the modified photoacid

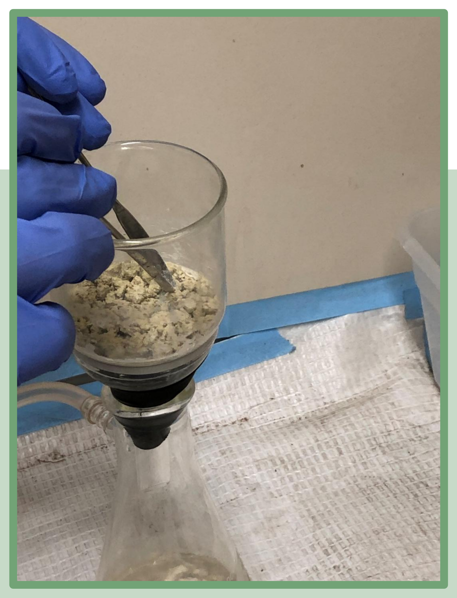


Figure 4- *(photo courtesy of exhibitor)* Intermediary step in the modification of the photoacid; drying under vacuum

Hypothesis

If a photoacid is covalently bonded to a nafion membrane, when the membrane is used in an electrochemical cell and stimulated by light, the membrane will actively transport cations across the membrane to create a potential and pH difference between the two chambers of the electrochemical cell, which can generate electricity. Furthermore, a photoacid with a stronger affinity to dissociate will perform better in such a power-generating cell.

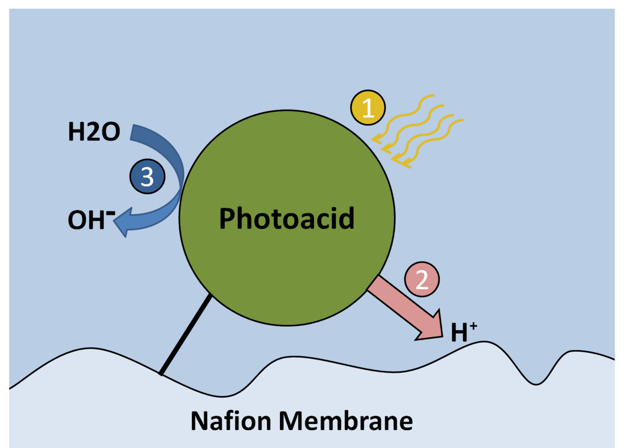
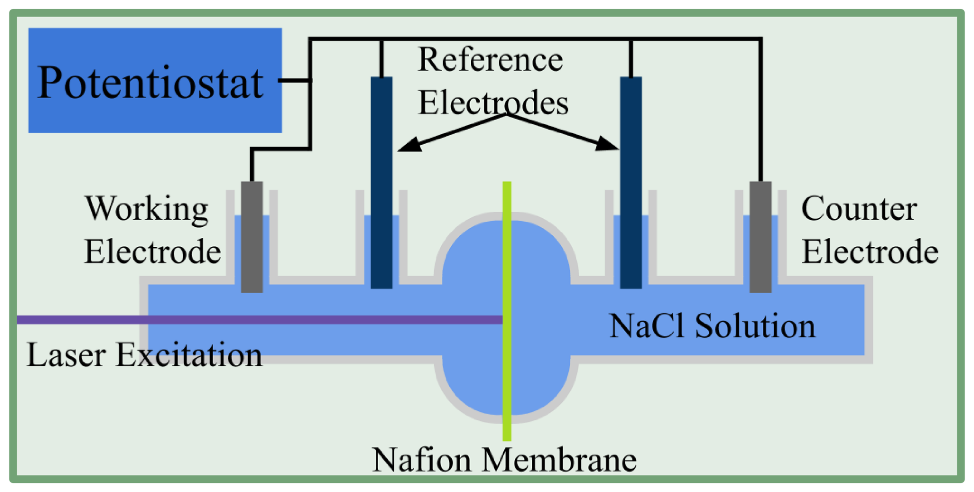


Figure 3- *(Illustration courtesy of exhibitor)* This is a diagram illustrating the course that the photoacid follows when it is bonded to the membrane. First the photoacid is struck by light which causes dissociation and this hydrogen molecule goes through the membrane finally, the photoacid reprotonates with water from the side it is on.

Methods

1. Modify HPTS
   1. Perform recrystallization to purify HPTS
   2. React with thionyl chloride and DMF to yield a chlorine salt of pyranine at reflux for 5 hours
   3. React with trisulfonate salt or DMF and triethylamine in methylene chloride for 48 hours
   4. Dilute with HCl and extract organic phase with seperatory funnel and dry over sodium sulfate and evaporate
2. Modify Membrane
   1. React nafion membrane with ***HPTS***, NaOH and triethylamine in isopropyl alcohol at reflux for 7 days
   2. React nafion membrane with ***modified HPTS***, NaOH and triethylamine in isopropyl alcohol at reflux for 7 days
   3. React nafion membrane with ***HPTA***, NaOH and triethylamine in isopropyl alcohol at reflux for 7 days
   4. Wash the membranes in each of the following: deionized water, 1M H_2SO_4, 1M NaOH, and deionized water again.
   5. Store membrane under 1M NaCl
3. Test the membranes under laser light excitation
   1. Insert the membrane between the two O-rings of the custom cell glassware
   2. Attach the electrodes to the potentiostat
   3. Perform cyclic voltammetry, chronoamperometry and chronopotentiometry on the cell using the potentiostat.

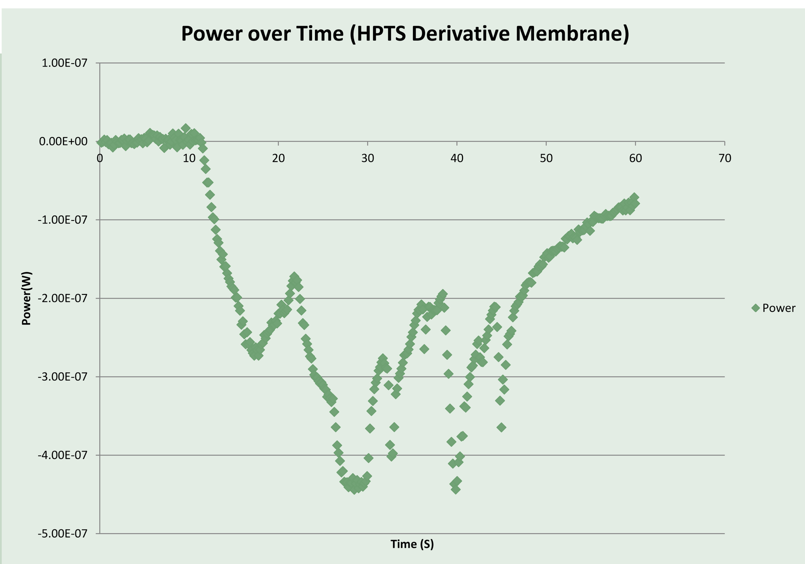
Figure 8- *(Illustration courtesy of exhibitor)* This diagram represents the entire cell working together. The laser stimulation pushes cations across the membrane creating a positive charge on the right side of the cell.



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- *(Exhibitor collected data)* 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 2- *(Exhibitor data)* 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..



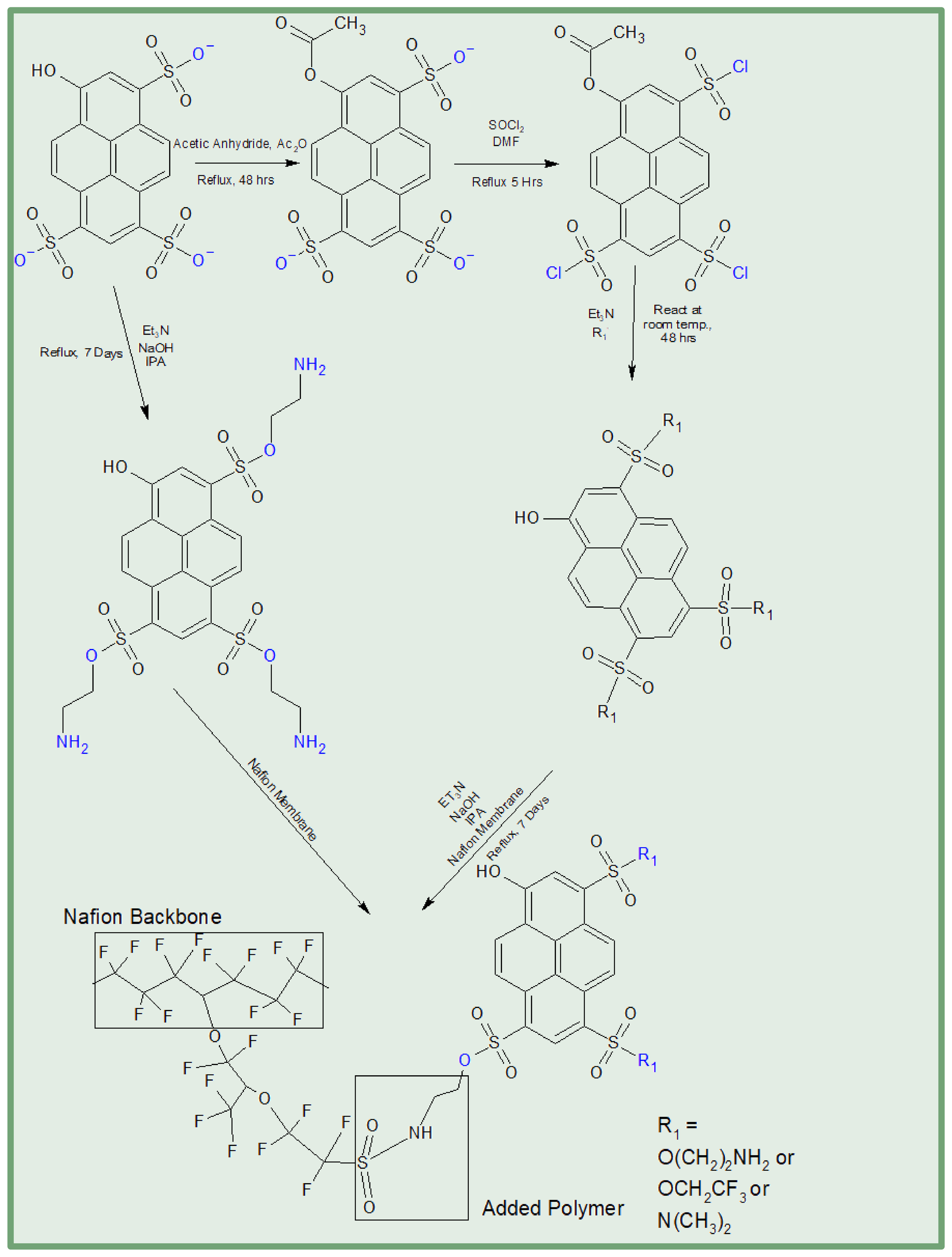
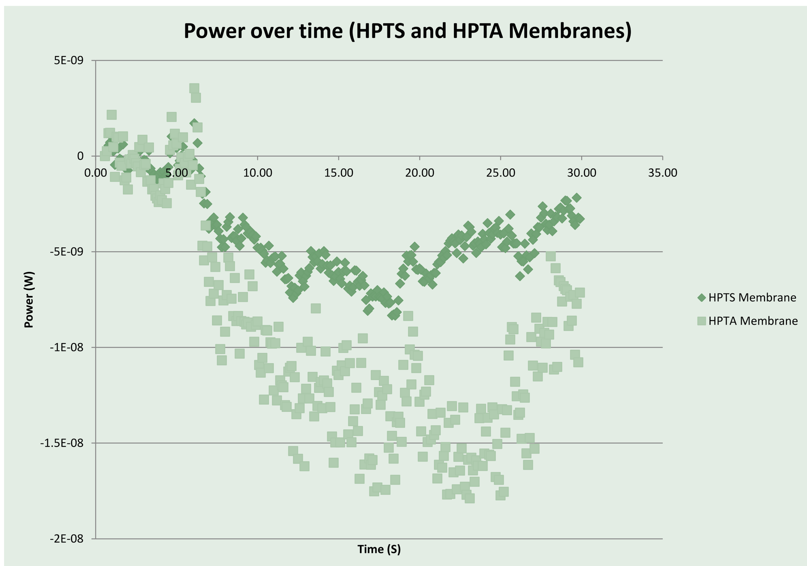


Figure 1- *(courtesy student)* Reaction scheme of the proposed reactions for this experiment . Depicts two pathways for generating final membrane product; one for unmodified HPTS and one for the HPTS derivatives (HPTA and Tris(2,2,2-trifluoroethyl) 8-hydroxypyrene-1,3,6-trisulfonate). It also indicates the chemicals used in a reaction and how the reaction was performed.

	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- *(Student data)* The table contains the most important data points for easy data comprehension, these are also illustrated on graphs.

Graph 1- *(Exhibitor data)* Graph 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.



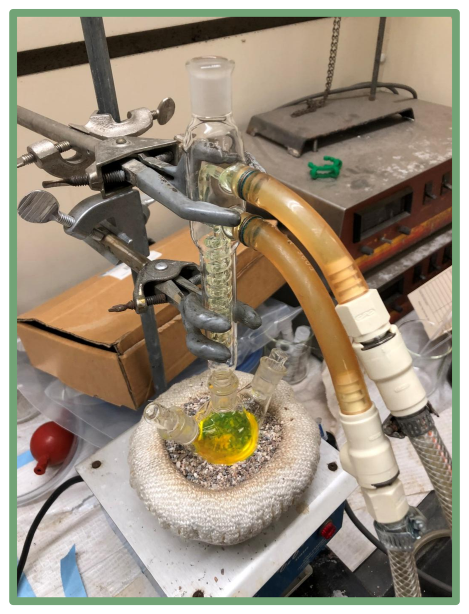


Figure 5- *(photo courtesy of exhibitor)* Reflux of the Nafion Membrane in HPTS. Reflux occurs for 7 days

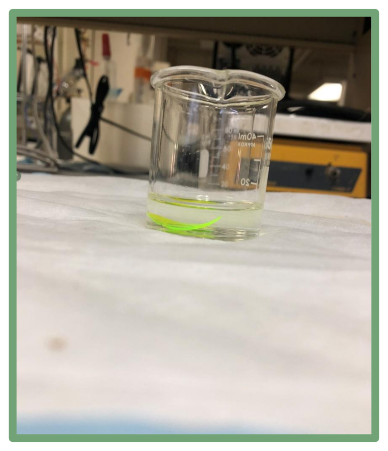
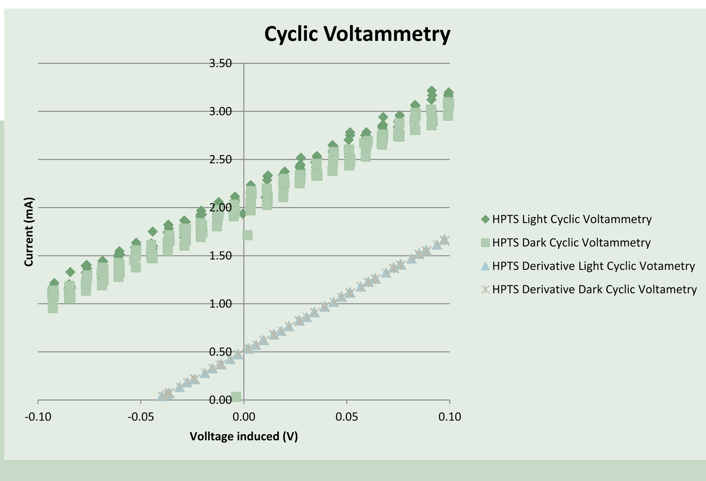


Figure 7- *(photo courtesy of exhibitor)* HPTS modified membrane directly after modification



Graph 3- *(Exhibitor data)* 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.

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.

Discussion

There was an observable power generation within the cell when the membranes were stimulated, upholding the hypothesis. Furthermore, the membrane modified with HPTS derivative was much more successful at current generation than the HPTS membrane. The modified membranes were also conductive to cations. As the HCl was added to the cell, the pH sharply decreased, leading to a quick fall in voltage followed by a steady rise in voltage resulting from cation diffusion and pH balancing between the sides of the cell.

As seen in Graph 1 and 2, there are sharp increases in current, demonstrating both modified membranes are successful at transporting cations after light stimulation.

HPTS modified nafion membrane:
It was evident that the nafion membrane had been modified with HPTS because of the yellow coloration after it reacted for 7 days.

- Laser stimulation produced a current increase from 0 to .2 µA immediately after initiation at 5 seconds (Graph 1)
- Corresponding jump in power from 0 to -8 Nw (negative power indicates a usable flow of electrons)
- Total power output of the membrane was calculated at 1.00 x 10^{-8} watts; only .0029% efficient

HPTS derivative modified nafion membrane:
Although slightly inconsistent, electrochemical data demonstrated very promising results. To generate current, the laser had to be pointed at a very specific area on the membrane, indicating the membrane was not fully modified.

- Nearly 50 times better peak efficiency derived from chronoamperometry
- Cyclic voltammetry showed a smaller deviance between light and dark than the HPTS modified membrane
- It is expected that efficiency will continue to increase with more research

HPTA modified nafion membrane:
This membrane was very similar to the HPTS modified membrane but was slightly less consistent and had approximately twice the efficiency.

Some potential minor sources of error affecting calculated efficiency include electrode to membrane distance (however this error was constant and could easily be corrected in calculations), measurement errors when synthesizing the membrane, contamination of membrane or glassware through particles in the air, and measurement errors in creating standard solutions (NaCl and HCl). Overall, there were very few sources of error in this experiment.

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