Development of a Nafion-free Proton Transport Cellulose Membrane for the Proton Exchange Membrane Fuel Cell

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Introduction

- Fossil fuels—a key cause of global warming
- Proton-Exchange Membrane Fuel Cells (PEMFCs) produce energy by H_2 gas oxidation—the only byproduct is H_2O
- Nafion Membrane:
  - ***High cost***—crosslinking process is a patented secret
  - ***Sensitivity to hydration***
  - ***Lack of durability***—Nafion degradation between 60°C to 80° C reduces conductivity more than 10-fold

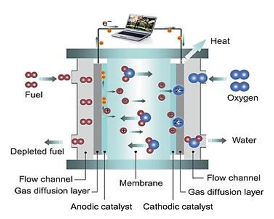

Fig. 1: Proton Exchange Membrane Fuel Cell
(https://www.sciencedirect.com)

Previous Research

- Cellulose filter paper has been found to act as a cost-effective alternative membrane for PEMFC
- Resorcinol bis(diphenyl phosphate) (RDP) has been previously used in membranes as a proton conductor

Fig. 2: Ahlstrom 1.5 micron cellulose filter paper
(https://www.schoolspecialty.com/ahlstrom-qualitative-filter)

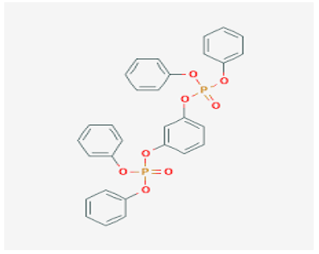

Fig. 3: Structure of RDP
(https://pubchem.ncbi.nlm.nih.gov)

Purpose

- Improve on the performance of cost-efficient cellulose membrane for use in fuel cells
- Eliminate the need for Nafion?
- Resorcinol bis(diphenyl phosphate) (RDP) has been shown to be conducive to protons
- Enhance the cellulose membranes using:
  - 1M Sulfuric Acid
  - 1M Citric Acid
  - 1M Phosphoric Acid

Materials and Methods

- Ahlstrom 1.5 micron filter papers were purchased (7.5 cm diameter) and acidified for 30 min and 24hr in:
  - 1M Sulfuric Acid
  - 1M Citric Acid
  - 1M Phosphoric Acid
- Dried overnight
- RDP added by pipetting 9 drops on the membranes
- Placed in oven at 150°C for 20 minutes
- Each membrane tested at 30°C, 60°C, 80°C, and 90°C in fuel cell testing station

Results

Fig. 4: Applying RDP to membrane

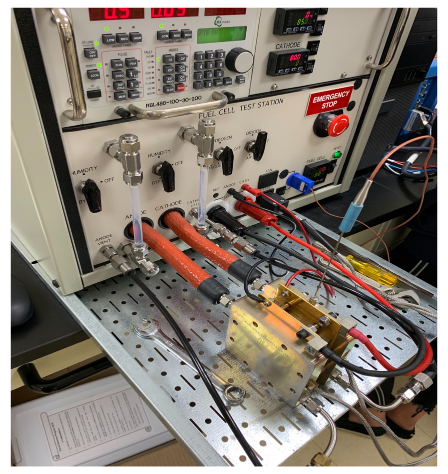

Fig. 5: Hydrogen fuel cell testing station

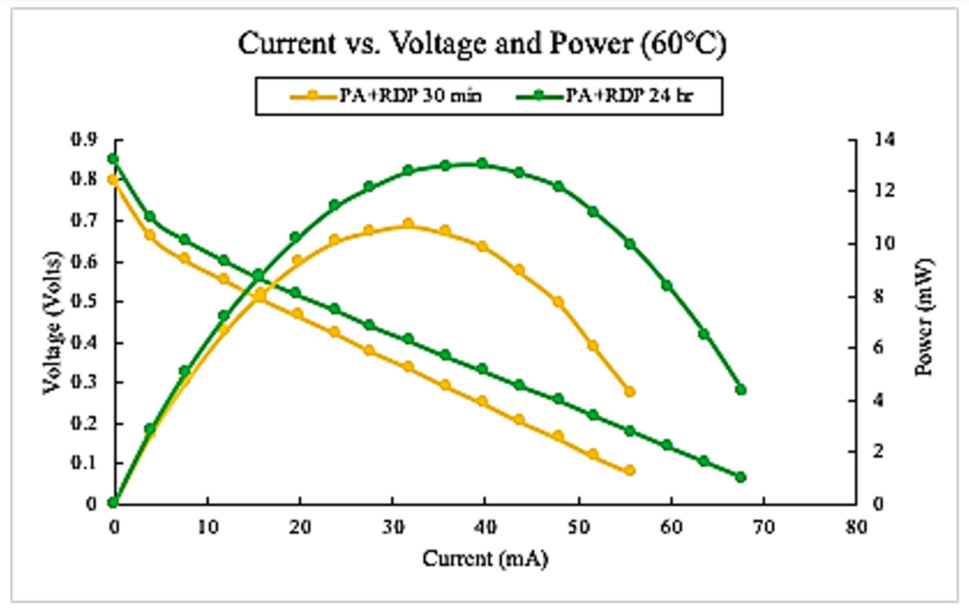

Fig. 6: Polarization curves for phosphoric acid membranes soaked for 30 minutes and 24 hours tested at 60°C.

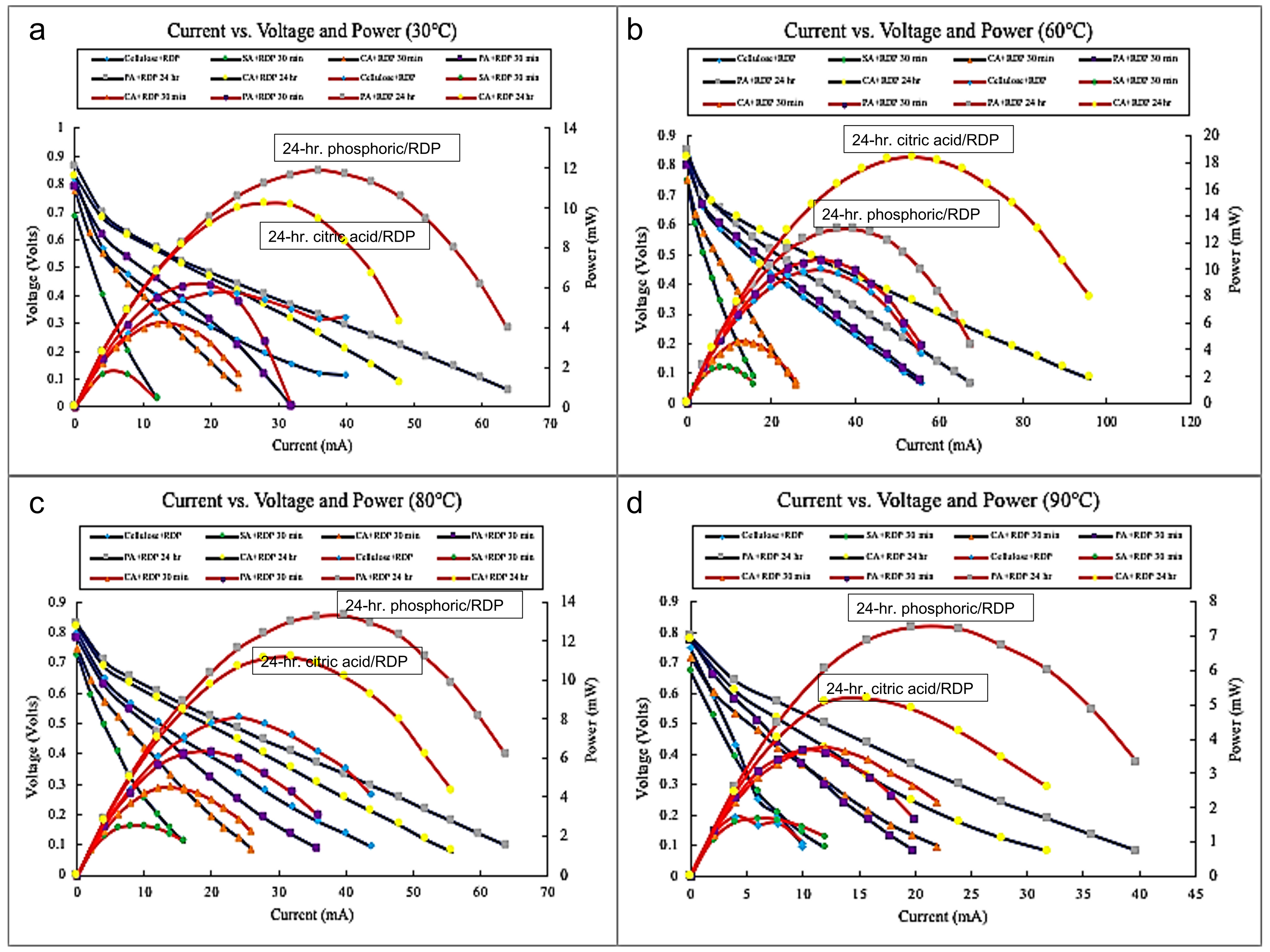

Fig. 7abcd: Polarization curves for each membrane (cellulose+RDP, 30 min sulfuric, citric, and phosphoric acids+RDP, and 24 hr citric and phosphoric acids+RDP) tested at 30, 60, 80, and 90°C

- Control: cellulose+RDP
- Citric acid and phosphoric acid soaked membranes performed similar to or better than the control
- Thus only soaked citric acid and phosphoric acid membranes in 24 hours
- 24-hour soaked citric acid and phosphoric acid membranes performed significantly better than the control

Table 1: Percent increase in power output for 24-hour citric acid+RDP and 24-hour phosphoric acid+RDP, compared to the control at 30, 60, 80, and 90°C

	30°C	60°C	80°C	90°C
CA+RDP 24 hr	77.4%	83.9%	37.9%	199.2%
PA+RDP 24 hr	631.9%	388.2%	422.0%	333.9%

Table 2: Highest power density values for test membranes at 30, 60, 80, and 90°C

	30°C	60°C	80°C	90°C
Cellulose+RDP	5.7618	9.9852	8.112	1.732
SA+RDP 30 min	1.623	2.66	2.542	1.67
CA+RDP 30 min	4.190604	4.5471	4.53468	3.7452
PA+RDP 30 min	6.14394	10.68162	6.367116	3.671
CA+RDP 24 hr	10.22206	18.36194	11.18724	5.1824
PA+RDP 24 hr	11.87844	12.98674	13.26932	7.2468

Table 3: T-Test comparing the 24 hour citric acid+RDP and 24 hour phosphoric acid+RDP membranes to the cellulose+RDP control; $p<0.05$ for most temperatures

	CA+RDP 24 hr	PA+RDP 24 hr
30°C	0.020194361	0.002525708
60°C	0.000664348	0.093079462
80°C	0.090449127	0.007178118
90°C	0.00555784	0.001161151

Results ctd.

- Ion Exchange Capacity (IEC) was measured through the standard titration method
  - Soaked for 24 h in 500 ml of 1M H_2SO_4 solution, then washed in distilled H_2O
  - Immersed in 50 mL of 1M NaCl for 24 h
  - Titrated with 0.01 N NaOH using pH meter
- Calculated using: $$\mathrm{IEC} = \frac{C_{\mathrm{NaOH}} V_{\mathrm{NaOH}}}{W_{\mathrm{dry}}}$$

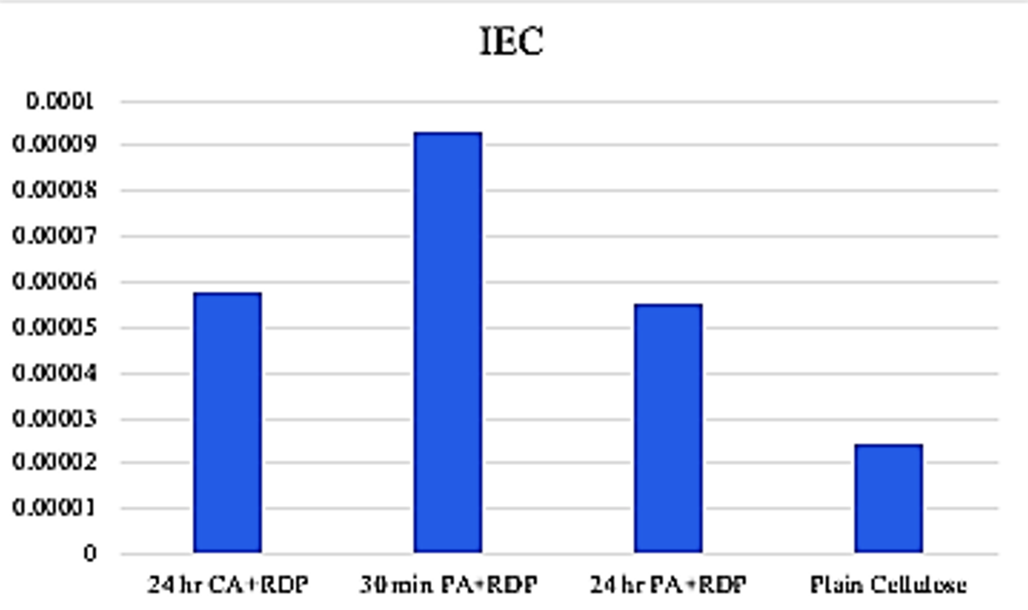

Fig. 8: IEC calculations for 4 membranes tested: citric acid+RDP soaked for 24 hours, phosphoric acid+RDP soaked for 30 minutes, phosphoric acid+RDP soaked for 24 hours, and plain cellulose filter paper

Conclusions

- Cellulose filters provide a scaffold on which materials such as RDP can be applied without having to crosslink
  - *Crosslinking Nafion is a secret patented process*
  - *Stable at higher temperatures*
  - *Stable in uneven hydration conditions*
- Provides a method of creating a new wave of membranes for future use in PEMFCs

Future Work

- Further measure Ion Exchange Capacity
- Characterize membranes using Focused Ion Beam, Raman Spectroscopy and Scanning Electron Microscopy which we can use to compare to untreated cellulose filter paper
- Create new membranes with higher molarity acids

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