High Temperature Polymer Electrolytes for Hydrogen Fuel Cells and Electrochemical Pumps

Gokul Venugopalan

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HIGH TEMPERATURE POLYMER ELECTROLYTES FOR
HYDROGEN FUEL CELLS AND ELECTROCHEMICAL PUMPS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University
and Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Gordon A. and Mary Cain Department of Chemical Engineering

by
Gokul Venugopalan
B.Tech., A. C. Tech, Anna University, Chennai, India, 2017
August 2021
Dedicated to my Amma, Pankajam
Acknowledgments

I would like to express my sincere gratitude to my advisor Dr. Chris Arges, for his support, inspiration, and motivation throughout my graduate studies. It was an excellent opportunity to work on several challenging and exciting research problems that have enabled my development as a scientist in his lab. He has always trusted me and given me the freedom to explore my creativity as a researcher. I am incredibly grateful for his guidance in writing papers and my dissertation. He has also given me several opportunities to present my work at conferences and meetings that have fostered collaborations with other research groups.

I want to thank everyone on my defense committee- Dr. John Flake, Dr. Donghui Zhang, Dr. Manas Gartia, and Dr. Michael Tom for their valuable time and support in shaping this dissertation. I want to thank my collaborators Ardalan Chiachi and Dr. Manas Gartia from the Department of Mechanical Engineering, LSU, for their inputs and guidance in my wide-temperature range supercapacitor project. I am also grateful to my senior colleague, mentor, and dearest sister, Dr. Varada Menon Palakkal, for her patience, guidance, care, and inspiring me throughout my graduate studies. Additionally, this dissertation would not have been possible without my colleagues' help- Matthew Jordan, Deepra Bhattacharya, Subarna Kole, and our undergraduate members – Justin Nijoka and Cameron Ysidron. They have extended their support and worked on several projects. I would also like to thank all employees at the Machine shop, specifically Joe Bell and Nick Lombardo in the Chemical Engineering department, for their work, advice, and suggestions in setting up my experimental setup. My experiments would not have been possible without their help.
I would also like to thank my Baton Rouge family, Trina Akka, Ankita Basu, Bhaswati Gosh, and my friends, Harish, and Arunagiri, who have been a constant encouragement and motivated me towards the completion of this degree. I want to thank Jose Santiago Echevarria, who has encouraged me to push forward with love, constant support, and optimism till the end of my degree. Finally, I want to thank my parents, Venugopalan and Pankajam, my sisters Poornima and Deepika, for being supportive, caring, and believe in me.
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Abstract

Hydrogen fuel cell and separation technologies such as proton exchange membrane fuel cells (PEMFCs) and electrochemical hydrogen pump (ECHP) offer a profound advantage in the transition to a low-carbon economy. An imperative hitch in hydrogen fuel cells and ECHP technology has been the electrocatalyst poisoning by carbon monoxide (CO) and other contaminants in the reactant mixture. By operating, hydrogen fuel cells and ECHPs at high temperatures (>200 °C), the effect of CO adsorption on the electrocatalyst surface could be curtailed. The high-temperature operation of devices necessitates a proton exchange membrane (PEM) to operate under anhydrous conditions.

In this work, a new class of anhydrous high-temperature proton exchange membrane (HT-PEM) based on H$_3$PO$_4$ doped PC-PBI membrane blends were examined, and the optimal blend (50:50 ratio) exhibited remarkably high conductivity in a wide temperature range (-70 °C to 240 °C), while also displaying excellent thermal stability and resiliency to water vapor. The new class of HT-PEM enables the operation of hydrogen fuel cells and ECHPs under a wide temperature range, concurrently promoting a better performance by reducing the ASR. The newly developed HT-PEM yielded high-temperature proton exchange membrane fuel cells (HT-PEMFCs) operating with a peak power density of 680 mW cm$^{-2}$ at 220 °C. For further advancement in performance, the kinetic and mass transport resistances of the liquid H$_3$PO$_4$ electrode ionomer binders needed to be addressed, for which liquid H$_3$PO$_4$ free – phosphonic acid-functionalized high-temperature polymer electrolytes were explored. The thin-film characterization of the newly synthesized polymer electrolytes was carried on using interdigitated electrode (IDE) platforms decorated with nanoscale platinum electrocatalysts.
The enhanced reaction kinetics and gas permeability of liquid H₃PO₄ free binder enabled an excellent ECHP performance of 1 A cm⁻² at 55 mV under pure H₂ anode feed and improved fuel cell performance of >0.9 W cm⁻² of power density with H₂/O₂ at 220 °C. The high-temperature operation of ECHP under varying anode hydrogen-hydrocarbon-contaminant mixtures yielded better tolerance to CO and other contaminants in the anode feed, revealing that the performance was driven by hydrogen concentration rather than the concentration of CO in the anode feed mixtures.
Chapter 1
Introduction

This dissertation aims to investigate the materials design and processing of a new class of anhydrous high-temperature (120 °C to 250 °C) proton conducting polymer electrolytes. These polymer electrolyte materials are used as proton conducting membranes (PEM) and as electrode ionomer binders in high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) and high-temperature polymer electrolyte membrane electrochemical hydrogen pumps (HT-PEM ECHPs). HT-PEMFCs is an electrochemical energy conversion device that converts the chemical energy of hydrogen into clean electrical energy, whereas HT-PEM ECHPs is a stand-alone electrochemical separation device that purifies and/or compresses hydrogen gas.

This dissertation focuses on improving the efficiency, durability, and temperature resiliency of current HT-PEMFCs and ECHPs. It probes molecular mechanics for clean energy production and pure hydrogen separations from petrochemical mixtures that primarily emanate from steam reforming and cracking processes exercising HT-PEMFCs, HT-PEM ECHPs, and interdigitated electrodes (IDE) platform decorated with nanowire platinum catalysts (model electrocatalysts). The term molecular mechanics refers to proton-coupled electron transfer reactions (PCET) in HT-PEM architectures' electrodes. The electrodes' binders hold the electrocatalyst/electrocatalyst supports where simultaneous electro-oxidation of hydrogen and proton migration to and from the electrocatalyst to the HT-PEM separator occurs \(^{1,2}\) (Figure 1.1).

This dissertation's primary goal is to develop a new class of HT-PEM and electrode binders to ameliorate PCET that addresses the overpotential losses in hydrogen fuel cells (HT-PEMFCs) and hydrogen separations (HT-PEM ECHPs).
Figure 1.1 A depiction of the membrane electrode assemblies (MEAs) with platinum group metal (PGM) catalysts and ionomer electrode binders (a) HT-PEMFC: Electro-oxidation of hydrogen to proton and electrons, migration of protons through HT-PEM for a proton-coupled electron transfer reaction (PCET) at the cathode. Electro-reduction of oxygen with the shuttled protons and electrons occurs at the cathode to form water as a by-product. (b) HT-PEM ECHP: Electro-oxidation of hydrogen and selective extraction of the proton from the HT-PEM and shuttled to the cathode for electrochemical reduction and pure hydrogen generation

1.1 Motivation for hydrogen fuel cells and separations

Fossil fuels currently supply most of the world’s energy needs. Meanwhile, the pollution caused by fossil fuels, from climate-damaging greenhouse gases to health-endangering particles, has reached record-high levels\(^3,4\). Due to the ever-increasing demand and consumption of fossil
fuels, greater attention has been provided to developing and implementing alternative fuels such as hydrogen, biofuels, and electrification through solar and wind, as well as a greater interest in energy conversion devices such as fuel cells, solar cells, biomass gasification, and batteries for electric motors.\(^3\)\(^4\)

Renewable energy, primarily solar and wind, is growing faster than all the other energy forms since 2011.\(^3\)\(^4\) In 2019, renewable energy was the largest adopted technology for generating energy as a power capacity of more than 200 gigawatts (GW) was installed. Solar and wind will account for most renewable energy growth as hydroelectric are maxed out (see Figure 1.2)\(^8\). The economic sectors relating to energy production and consumption, such as transport, heating, industrial manufacturing, and electricity generation, account for two-thirds of global CO\(_2\) emissions. Crucial to de-carbonize the energy production and consumption sector is adopting other renewable energy sources (hydrogen fuel cells, batteries, and other electrochemical technologies like hydrogen pumps for separations)\(^3\)\(^4\). By switching to and exploiting multifarious renewable energy sources, we could reduce 90% of the CO\(_2\) emissions needed by 2050 and keeping the global temperature rise below 2 °C.

Fifty years ago, hydrogen was identified as a critical and indispensable element of a decarbonized, sustainable energy system to provide a secure, non-polluting, and cost-effective energy source.\(^5\) Hydrogen plays a vital role in low-carbon future counterbalancing electricity as a zero-carbon energy carrier. Hydrogen enables a more secure energy system with reduced fossil fuel dependence, with the versatility to operate across the transport, heating, industrial, and electricity generation sectors. Hydrogen and fuel cell technologies offer more excellent personal choices in the transition to a low-carbon economy, given their similar performance, operation, and consumer experience to fossil-fuelled technologies.\(^6\)\(^7\)
Through H₂@Scale initiatives by the U.S Department of Energy, as shown in Figure 1.3, blue and green hydrogen is poised to see an expanded role in the U.S. economy. It will make an indelible impact on power production, energy storage, chemical manufacturing, and petroleum refining. Hydrogen plays a vital role in our global society. It is used as a feedstock for making fertilizer (ammonia synthesis via Haber-Bosch), ultra-low sulfur diesel fuel production, bio-fuel upgrading, conversion of petrochemical intermediates and products via hydrogenation, and refining metals. Due to hydrogen's excellent high specific heat capacity and thermal conductivity, 60% of power plants currently use it as a coolant for turbine generators. Purified hydrogen is also used as a fuel source for turbine generators, fuel cell electric vehicles (FCEVs), and stationary power fuel cells. It is now being considered for seasonal and long-term energy storage – e.g., hydrogen batteries and renewed interest in unitized regenerative fuel cells.
Ten million metric tons of hydrogen are currently produced in the United States every year. Over 95% of hydrogen is derived from reformed natural gas, steam cracking, and other fossil fuel processes.\textsuperscript{10-12} The mainstream sourcing of hydrogen from fossil fuels has the consequence of this chemical having a sizeable CO\textsubscript{2} footprint. Electricity—from the grid or renewable sources such as biomass, geothermal, solar, or wind—is currently used to produce hydrogen. In the longer term, solar energy and biomass can be used more directly to generate hydrogen as new technologies make alternative production methods cost-competitive. The other hydrogen production approaches include water splitting, such as electrolysis, photoelectrochemical cells, or solar thermochemical systems. The primary uses of hydrogen today are in the oil refining and ammonia industries. Hydrogen is also used as a coolant in power plants. Other emerging hydrogen applications include fuel cell electric vehicles (FCEVs), metals refining, and synthetic natural gas production.\textsuperscript{9-17}
Hydrogen and fuel cells can enable zero or near-zero emissions in transportation, stationary or remote power, and portable power applications. Proton exchange membrane fuel cell (PEMFC) technology is part of a clean energy technology portfolio because they only emit water when reacting hydrogen (H₂) fuel with oxygen (O₂) from terrestrial air. Furthermore, they convert fuel and oxidants with greater efficiency when compared to traditional heat engines. Fuel cells are generally between 40 and 65% energy efficiency, whereas internal combustion engines are about 25% energy efficient.¹⁸⁻²³ PEMFCs have experienced steady improvement over time in performance, efficiency, cost competitiveness, and stability. PEMFCs provide a lot of benefits over other technologies. For example, high energy density compared to their size, high efficiency due to no energy loss from moving parts, rapid start-up, quiet operation, low operating temperature, and low polluted emission.¹⁸,²⁴

Hydrogen, currently produced from reformed natural gas and other fossil fuel methods, often causes complex mixtures requiring purification. Different purification methods, such as cryogenic separation, pressure swing adsorption, and membrane separation (e.g., palladium membrane), are currently used to yield pure hydrogen. Current hydrogen purification methods require a multi-unit separation process train, require a substantial amount of energy, and are expensive to operate.²⁵⁻³² Also, FCEVs necessitate high-purity hydrogen free from carbon monoxide to poison platinum-based electrocatalysts that compromise stack efficiency.³³ Hydrogen storage and transportation/distribution often require pressurization (e.g., > 87.5 MPa) and adiabatic compression, which is an arduous process.³⁴

The current hydrogen distribution system includes compressed-gas trucks, liquifying hydrogen, and building new hydrogen delivery pipelines. Though these are feasible options, they create several disadvantages. The compressed gas truck could not be used for longer distances

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due to safety concerns and could be used only for more minor demands. The liquefaction process adds a massive cost to transport hydrogen, and constructing new pipelines requires expensive fiber-reinforced polymers. There is the current search going on for converting and using natural gas pipelines to carry a blend of natural gas and hydrogen (up to 20% H₂). By blending natural gas and H₂, the growing demand for hydrogen delivery could be met, but this requires on-site hydrogen purification and compression. Figure 1.4 shows the current hydrogen delivery system and natural gas pipeline interconnection in the United States for hydrogen blending and delivery.39,40

Electrochemical hydrogen pumps (ECHP), as a standalone device, could be a better solution for on-site hydrogen purification and compression, making a cost-effective and direct process. The increased adoption of hydrogen as a coolant in power plants and as a fuel for FCEVs has motivated research in electrochemical hydrogen pumps (ECHP) for pure hydrogen production and compression – especially for attaining blue hydrogen where CO₂ by-products will undergo carbon capture sequestration and utilization (CCSU).11 ECHP provides a single standalone device for pure hydrogen production, separation, and compression, making it a cost-
effective and straightforward process.\textsuperscript{34}

\section*{1.2 Problem statement}

A key challenge in hydrogen fuel cells and ECHP technology has been the poisoning of electrocatalysts by other components in the reactant mixture, e.g., CO adsorption on platinum (Pt), hindering electrochemical hydrogen oxidation to protons that are selectively transported across the PEM. The electrocatalyst poisoning can be managed by increasing the temperature of operation hydrogen fuel cells and ECHPs above 120 °C because that temperature curtails CO adsorption and CO adsorption can be reversed. Operating the devices above 120 °C necessitates a PEM that does not require condensed water for proton conduction.

One of the most widely used proton exchange membranes is Nafion\textsuperscript{®} (Figure 1.5a)\textsuperscript{18,21,42–44}, a perfluorinated membrane invented by DuPont with ether-linked side chains terminate sulfonate cation exchange site and terminal sulfonic acid end groups.\textsuperscript{44–48} Nafion\textsuperscript{®} demonstrates durability in harsh oxidizing and reducing environments. In the anhydrous state, the ionic domains are distributed in a continuous tetrafluoroethylene phase, whereas in the presence of water, these domains swell and form a proton-conducting network. However, Nafion\textsuperscript{®} is still widely more popular due to its lower cost. The main disadvantage of Nafion\textsuperscript{®} is that it requires very high levels of humidity to maintain its ionic conductivity. Figure 1.5b shows the ionic conduction of Nafion\textsuperscript{®} in the presence of moisture. Nafion's need for high humidity levels requires external humidification to maintain its performance in gas-based electrochemical processes like fuel cells. Because of this drawback, a new PEM type of material that can conduct under protons anhydrous conditions while also being thermally, chemically, and mechanically stable is needed.\textsuperscript{18,20,49}

The most advanced HT-PEM relies upon phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) imbibed
polybenzimidazole (PBI). Acid doped PBI provides an edge over Nafion by providing proton conductivity without humidification and being conductive and thermally stable at higher temperatures (100 – 200 °C). PBI interacts with acid via an acid-base interaction. The benzimidazole group present in PBI gets protonated by the phosphoric acid creating an ion-pair interaction. PBI absorbs excess phosphoric acid because of its higher ion exchange capacity (6.5 mequiv g⁻¹) of benzimidazole groups, and the excess phosphoric acid provides high conductivity at higher temperatures. The main disadvantage of PBI is a weak acid-base interaction between the acid group and the protonated benzimidazolium. Due to the weak acid-base interaction, the acid could be leached out in the presence of water at lower temperatures and evaporation of H₃PO₄ at temperatures greater than 160 °C. Figure 1.6a shows the weak acid-base interaction of hydrogen bonding frustration in PBI imbibed with H₃PO₄.⁴²,⁵¹–⁵⁹

![Figure 1.6a](image-url)

**Figure 1.6a** shows the weak acid-base interaction.

Over the past five years, Kim and co-workers⁵⁹,⁶⁰ have examined H₃PO₄ doped polycation (H₃PO₄-PC) membranes (note: PCs are typically used as anion exchange membranes for alkaline fuel cells) as a superior alternative to H₃PO₄-PBI. The H₃PO₄-PC materials foster strong electrostatic interactions between the tethered cation moieties and the phosphate type anions, enabling excellent acid retention across the 50 (C to 220 °C) temperature range.
Additionally, the tethered cation-phosphate anion interactions are more immune to water substitution when the cell is exposed to humidified water at temperatures less than 100 °C.

Compared to H₃PO₄-PBI, the electrostatic interaction between quaternary ammonium groups and phosphate anions in H₃PO₄-PC is 8x more robust than the acid-base interactions between benzimidazole and H₃PO₄, as shown in Figure 1.6b. Hence, the H₃PO₄-PC molecular design mitigates acid leaching in the presence of water and evaporation of H₃PO₄ at temperatures greater than 160 °C. ⁶⁰,⁶¹

![Diagram of ionic conductivity mechanism](image)

**Figure 1.6.** a.) Ionic conductivity mechanism in PBI-H₃PO₄. DFT calculations of interaction energy for b.) acid-base interaction c.) ion-pair interaction ⁶⁰

With H₃PO₄-PC, Kim and co-workers have shown an HT-PEMFC performance with peak power densities as high as 870 mW cm⁻² with oxygen and no humidification. ⁶⁵ However, their data for HT-PEMFC above 200 °C used an H₃PO₄-PC ionomer electrode binder with a ceramic proton-conducting membrane. Hence, polymeric HT-PEMs could provide an edge over ceramic membranes because they can be made thinner leading to a lower area-specific resistance (ASR). A small ASR allows high current density operation with a small ohmic overpotential.

In the case of HT-PEM ECHPs, two types of PEM materials have been primarily investigated: i.) Nafion®, a perfluorosulfonic acid polymer, and ii.) H₃PO₄ doped PBI, high-temperature PEM (HT-PEM). The H₃PO₄ doped PBI for ECHPs has mainly been investigated by
Benicewicz and co-workers\textsuperscript{32,63–65}. However, CO still compromises ECHP performance, and it can also permeate across the PEM and show up in trace quantities of the purified hydrogen on the cathode side. With the industrial interest in operating ECHPs at high temperatures, such as 200 to 240 °C, it is essential to have an HT-PEM that is thermally stable, highly conductive, and less permeable.

The HT-PEM fabricated from H\textsubscript{3}PO\textsubscript{4}-PC by Kim and co-workers has only 80% acid retention at 220 °C, which reduces the long duration operability and device performance at high temperatures. Therefore, a search for H\textsubscript{3}PO\textsubscript{4}-PC with better acid retention, thermal stability, and proton conductivity ensuing in low ASR is required to improve HT-PEMFC and HT-PEM ECHP performance further.

Another critical challenge for high-temperature hydrogen fuel cells and ECHPs is liquid H\textsubscript{3}PO\textsubscript{4} ionomer binders in the electrodes. Ionomer binders strongly influence the performance and stability of numerous electrochemical processes such as fuel cells, water and carbon dioxide electrolyzers, and deionization units.\textsuperscript{1,66–71}

In low-temperature and high-temperature polymer electrolyte membrane (i.e., LT-PEM and HT-PEM) architectures involving hydrogen, the binders hold the electrocatalyst/electrocatalyst supports while also delivering protons to and from the electrocatalyst to the PEM separator for the proton-coupled electron transfer (PCET) reactions.\textsuperscript{1,2} Both PEM separators and ionomer electrode binders require high conductivity and stability under a wide range of conditions (e.g., chemical, electrochemical, and thermal). But there are nuanced differences concerning the properties of PEM separators and electrode binders. PEM separators necessitate low gas permeability for safety and mitigating mixed overpotentials. Ionomer binders require high gas permeability to overcome mass transfer-related resistances and enable high
current density. **Figure 1.7** shows the property requirement differences and similarities for polymer electrolytes employed as a membrane and an electrode ionomer binder.\(^{22,72}\)

Several research has helped understand and develop H\(_3\)PO\(_4\)-PC as ionomer binder materials for high-temperature applications over the past four years.\(^{50,62,73–76}\) Despite several advantages of having strong ion-pair interaction that reduces acid evaporation at high temperatures, the presence of liquid phosphoric acid in the electrodes prevents reactant delivery, leading to higher mass transport resistance, creating kinetic and concentration overpotential losses.\(^7\) Further, the liquid phosphoric acid in the electrodes leads to phosphoric acid anhydrides at high temperatures leading to lower proton conductivity.

![Figure 1.7. Property requirement and differences between polymer electrolytes as membranes and electrode ionomer binders.\(^{66,78}\)](image)

To address the overpotential losses, Los Alamos and the University of Stuttgart adopted an alternative ionomer electrode binder based upon tethered phosphonic acid to the polymer backbone (i.e., poly (tetrafluoroethylene phosphonic acid-\(\text{co-}\)pentafluoro styrene) (PTFSPA)). This binder addressed mass transfer resistances in the electrode layers and achieved a peak power density of 1.7 W cm\(^{-2}\) at 240 °C. **Figure 1.8** shows the transport resistance related to gas
diffusion across ionomer binders (one case with liquid imbibed acid and the other with no liquid acid).

Figure 1.8. Comparison of transport resistance between a.) liquid acid imbibed PC-H$_3$PO$_4$ b.) Phosphonic acid functionalized polymer electrolyte as ionomer binders in electrodes

Another critical challenge is that HT-PEMFCs warrants improved power density, especially with air as the oxidant, while also reducing platinum group metal loadings (e.g., < 6 gPt/vehicle; rated at 90 kW$_{net}$ power). Kim and co-worker's high power density is laudable, but their data used a very high platinum loading of 1.1 mgPt cm$^{-2}$ for the entire MEA$^{65,78}$, which gives rise to the following research problem$^{66,79}$. It is vital to reduce the platinum loadings to reduce the cost of the HT-PEM cell stack. For example, in the case of total fuel cell stack cost, the anode and cathode platinum costs add up to one-third of the entire stack cost. Reducing the cell stack's platinum loading would involve increased voltage losses in anode and cathode, compromising the cell performance. At low Pt loadings, the ionomer binder's effect on electrode reactivity and Pt electrocatalyst interaction is a fundamental material problem to address. Therefore, it is vital to determine the overpotential losses and understand the electrochemical
properties of newly synthesized ionomer binder thin-film materials on Pt electrocatalyst without meddling with porous complexities electrodes.

New materials for fuel cells, ECHPs, and water electrolyzers are characterized in ex-situ experimental setups for assessing their likelihood to improve the electrochemical cell performance. Experimental protocols for ex-situ assessment of bulk membranes (e.g., 4-pt conductivity) and electrocatalyst activity (e.g., rotating disk electrode) are standardized, but there are few precedents and tools to examine the electrochemical properties of thin-film ionomers outside ionic conductivity and without liquid supporting electrolyte. It is worth noting that there is a lack of studies investigating how the properties of thin-film ionomers influence other electrochemical properties, like charge-transfer reaction kinetics and gas permeability, in addition to different types of ionomer chemistries for high temperature hydrogen-based electrochemical systems\textsuperscript{80,81}. These additional properties have a more profound impact on electrochemical device performance when compared to ionic conductivity. For example, ionomers can alter redox reaction rates (e.g., by adsorption of the tethered ion to the catalyst) and gas reactant mass transfer rates to the electrocatalyst surface\textsuperscript{60,61,73,75,82}.

To understand how thin-film ionomers impact other electrochemical properties beyond ionic conductivity, Bhattacharya and co-workers\textsuperscript{83} have developed an IDE platform that features a thin-film ($< 25$ nm) of nanoscale platinum group metal (PGM) electrocatalyst afforded from self-assembled block copolymer templates. The presence of this periodic nanostructure PGM electrocatalyst across the IDE serves as a model electrocatalyst. It helps assess HOR/HER kinetics in a thin-film ionomer (previously Nafion\textsuperscript{®} at room temperature). Model electrocatalysts are essential because of their minimal use of novel PGM catalysts and require a very thin-film of polymer electrolytes, saving the cost spent for material analysis alone.
It is essential to draw a correlation of ex-situ assessment made using model electrocatalyst to electrochemical device performance. ECHPs, used for hydrogen separation and compression in industrial settings, also serves as an in-situ diagnostic tool for hydrogen-based electrochemical systems\textsuperscript{80,81}. HT-PEM ECHPs provide an in-situ assessment of thin-film ionomers' electrochemical properties by visualizing the kinetic parameters (exchange current density, Tafel slope) and permeability of hydrogen. Using model electrocatalyst (PGM catalyst decorated IDEs) and ECHPs, the influence of removing liquid acid from the ionomer binder on HOR/HER kinetics and gas permeability could be studied. No literature has studied the effect of the newly synthesized phosphonated polymer electrolyte (PTFSPA) on HOR/HER kinetics and gas permeability, which drives high-temperature hydrogen-based electrochemical performance systems\textsuperscript{80,81}(HT-PEMFCs, HT-PEM ECHPs). Therefore, using IDEs and HT-PEM ECHP, a deeper understanding between high-temperature thin-film ionomers' electrochemical properties could be achieved.

The last and final research problem is that most HT-PEM ECHP research focuses on membrane development and its relation to ECHP performance. Many of these studies use BASF fuel cell electrodes.\textsuperscript{84} The role of electrode ionomer binder on ECHP performance has not been investigated. Very few studies have been performed in analyzing the hydrogen purity and extraction from traditional reformate mixtures. There are no studies conducted using HT-PEM ECHP analyzing the hydrogen purity and extraction from syngas mixtures, hydrogen mixed with olefins - which is meant to mimic effluents from steam cracking processes. Part of the dissertation focuses on examining reactive-separations in the temperature range of 180 to 220 °C with proton conducting materials that do not require condensed water for proton transport and
are thermally stable contaminant adsorption is reversible and less detrimental to ECHP efficiency for hydrogen separation from petrochemical mixtures.

1.3 Scientific questions, approach, hypotheses, and impact

The dissertation's premise asserts that operating the hydrogen fuel cells and ECHPs above 180 °C will further mitigate adsorption/poisoning of the electrocatalyst by contaminants while co-currently enhancing HOR kinetics and proton migration rates. Hence, higher temperature operation is paramount for advancing device performance and achieving hydrogen separations from the most challenging petrochemical mixtures emanating from steam reforming and cracking processes. It is anticipated that pushing higher temperature operations in fuel cells will manifest cost savings by minimizing or eliminating the radiator and eliminating the humidifier (approximately $1 to 7.5 kW_{\text{net}}^{-1}$ in cost savings). HT-PEMFC operation's effectiveness is primarily governed by high proton conduction, wide temperature and humidity resiliency of HT-PEM, and ionomer binders in the electrodes for augmented PCET. In the case of ECHP, the separation efficiency and performance are primarily governed by the effectiveness of the anode composition and structure. The anode is required to electrochemically oxidize the hydrogen selectively and promote proton charge separation and migration to the HT-PEM without impediment by other components in the gaseous mixture.

Addressing the research problems in HT-PEMFCs and HT-PEM ECHPs necessitates fundamental research that answers the following research questions:

1) Could we synthesize a low resistant, thermally resilient, and mechanically stable HT-PEM to overcome PCs' conductivity shortcomings and the temperature stability limitation of commercially available PBI? Can temperature improve the efficiency of
HT-PEMFC and enable better tolerance to CO in the anode gas mixture without compromising cell efficiency?

2) Could we synthesize liquid H$_3$PO$_4$ free ionomer electrode binders, phosphonic acid functionalized polymer electrolytes and overcome the kinetic and concentration overpotential in HT-PEMFCs and HT-PEM ECHPs? How to characterize the electrochemical properties of newly synthesized electrode binders at high temperatures without dealing with the complexity of porous electrodes in fuel cells and ECHPs?

3) Can temperature and liquid H$_3$PO$_4$ free ionomer electrode binders promote HOR kinetics in the presence of contaminants known to poison platinum group metal (PGM) electrocatalysts in ECHPs?

The approach to answering these research questions relies upon the chemical synthesis of new HT-PEM based on PC-PBI blends and liquid acid-free polymer electrolyte ionomer binders characterized using HT-PEMFC, HT-PEM ECHP, and high-throughput experimental methods (e.g., thin-film studies with interdigitated electrodes (IDES)).

1) Various blends of PC-PBI will be evaluated for their H$_3$PO$_4$ uptake, H$_3$PO$_4$ retention at low temperature in the presence of humidity and high temperatures at anhydrous conditions, thermal stability, and in-plane proton conductivity. These experiments will determine the best PC-PBI blend with low resistance, better thermal resiliency, and mechanical stability at high temperatures. The HT-PEMFC performance with the new HT-PEM will be explored under different anode feed (pure H$_2$ and H$_2$-CO blend), and cathode oxidants (O$_2$, air), and tolerance to CO at high temperatures will also be examined.
2) A new liquid H₃PO₄ free phosphonic acid-functionalized PCs will be synthesized and evaluated for thin-film ionic conductivity, IEC, and thermal stability. These newly synthesized phosphonic acid-functionalized PCs will be tested for their suitability as electrode binders for HT-PEMFC and HT-PEM ECHP operation. Further, investigation on how removal of liquid acid from the ionomer influences HOR/HER kinetics and gas permeability will be carried on using ex-situ model electrocatalysts (IDE platform decorated with nanowire platinum catalysts).

3) The newly developed HT-PEM and phosphonic acid functionalized polymer electrolyte as ionomer binder will be used to contrive MEA for ECHP operation at high temperatures. Using the engineered MEA, ECHP studies will be performed for different anode gas mixtures reciprocating hydrogen spawned from syngas mixtures and steam cracking processes to varying temperatures from 180 °C - 220°C to understand the effect of temperature on anode's impurity tolerance.

The first central hypothesis of this dissertation asserts that the addition of PBI with a PC facilitates higher IEC and acid uptake, resulting in better proton conductivity, water resiliency, mechanical stability, and thermal stability. The HT-PEM with PC-PBI blend will help reduce the ASR and improve performance in HT-PEMFCs and HT-PEM ECHPs, simultaneously increasing CO tolerance in the anode feed mixtures. The second central hypothesis posits that removing liquid phosphoric acid reduces mass transfer resistance by enhancing hydrogen permeability and improves HOR/HER kinetics by reducing phosphate anion poisoning.

The dissertation consists of three primary research objectives listed below to test the hypotheses and to answer the research as mentioned above questions:
**Objective 1:** Develop a high-temperature polymer electrolyte membrane (HT-PEM) with resiliency under a wide temperature and humidity range. The newly developed HT-PEM would enable hydrogen fuel cells (HT-PEMFCs) and hydrogen separations using HT-PEM ECHPs at 200 °C or more significant to generate clean electricity and separate purifying hydrogen from gaseous hydrocarbon mixtures, respectively.

**Objective 2:** (a) Synthesize liquid H$_3$PO$_4$ free ionomers for electrodes to address the kinetic and concentration overpotential caused due to phosphate anion adsorption on the electrocatalyst surface and impeded delivery reactant gas due to the presence of liquid H$_3$PO$_4$. (b) Determine and correlate the electrochemical properties of electrode binders' impact on HOR/HER kinetics and hydrogen diffusivity without meddling with porous electrodes' complexities using ex-situ (IDE platform decorated with nanowire platinum catalysts) and in-situ (HT-PEM ECHP) characterizations.

**Objective 3:** Examine the industrial relevant conditions for HT-PEM ECHP. E.g., the composition of various hydrogen-hydrocarbon-contaminant mixtures and ECHP operating temperature.

Overall, the dissertation's **scientific impact** will enhance the separations community's understanding of how acidity strength, hydrogen bonding, and structural proton diffusion strongly influence thermal resiliency, mechanical strength, and ionic conductivity of H$_3$PO$_4$ imbibed PC-PBI blend HT-PEM. This dissertation will also establish how thin-film ionomers' electrochemical properties (ionic conductivity, HOR/HER kinetics, and gas permeability) impact device-level performance and CO tolerance at high-temperatures by correlating the thin-film ionomers properties to the polarization of single-cell HT-PEMFC and HT-PEM ECHP operation.
1.4 Background

1.4.1 PEMFC

Proton exchange membrane fuel cells (PEMFCs) convert chemical energy to electrical energy. They have been commercialized due to their higher power density, high energy conversion efficiency, fast start-up, low sensitivity to orientation, and environmental friendliness. Figure 1.9 shows the operation of a PEMFC. The anode and cathode compartment in a PEMFC is separated by a solid-state separator called a proton exchange membrane (PEM). The PEM serves as the electrolyte and conducts the protons from the anode to the cathode, separating hydrogen and oxygen gases. During the fuel cell operation, the hydrogen fuel is electrochemically oxidized in the anode catalyst layer to produce protons and electrons. The protons get transported through the membrane to the cathode side, whereas the electrons move through the outer circuit and reach the cathode side. The protons and electrons electrochemically react with oxygen from terrestrial air within the cathode catalyst layer to produce water, generating heat in the electrodes. The reaction between hydrogen and oxygen in a PEMFC generates electricity, water, and heat without polluting by-products. Figure 1.3 shows the electrochemical half-cell reactions that occur in the anode and cathode. The half-cell potential of the anode is 0 V compared to the standard hydrogen electrode (SHE), whereas the half-cell potential of the cathode is 1.23 V compared to SHE, making the overall theoretical cell voltage of 1.23 V.\textsuperscript{23}
The most commonly and commercially available PEMFCs are low-temperature PEMFCs (LT-PEMFCs) (< 100°C). LT-PEMFCs have experienced steady improvement over time in performance, efficiency, cost competitiveness, and stability. However, marketplace success for LT-PEMFCs could be deterred by the high costs associated with ultra-pure H₂ fuel, which is currently ~$5 to 8 GGE⁻¹ (a gallon of gas equivalent) when produced from water electrolysis. Powering fuel cells with H₂ derived steam-reformed methane (SRM) could offer significant cost savings (~$2 GGE⁻¹) that would translate to marketplace competitiveness for LT-PEMFCs. Despite the advantages of H₂ from SRM, it contains pollutants, such as carbon monoxide (CO) and sulfur dioxide (SO₂), that poison electrocatalyst surfaces (< 120 °C), jeopardizing PEMFC performance.
Several challenges arise when commercializing a new technology against a commercialized technology like internal combustion engines. The major challenge in commercializing fuel cell technology is the fuel cell system cost. Figure 1.10 shows the fuel cell system costs, which is around $50 to $55 kW⁻¹ (assuming 0.5M stack units are manufactured annually), and it needs to be reduced to $30 kW⁻¹. Manufacturing about 1,000 stack units annually raises the cost to about $200 kW⁻¹. The platinum group metal (PGM) catalyst in the anode and cathode layer and the PEM forms the costliest part of a fuel cell stack. Another high cost of the fuel cell stack power plant is the ancillary units, such as the humidifier and radiator, that are needed for stack water and heat management. These two units amount to about 15 to 20% of the stack costs, and the radiator is 4x more expensive than the humidifier.

LT-PEMFCs have attained remarkable operational metrics and targets for light-duty fuel cell electric vehicles (LD-FCEVs). Current state-of-the-art 90 to 110 kW stack LD-FCEVs contain 0.25 gPt KW⁻¹ and are stable up to 4,100 hours with a cold start at -20 °C in 30 seconds. The durability and the system cost of the LD-FCEVs need to be improved further to reach the $30 KW⁻¹ target. In general, LT-PEMFCs are fairly mature for LD-FCEVs. Heavy-duty FCEV (HD-FCEV) are less mature and have different requirements as these vehicles are meant to be on-road for a longer time and duration. The larger vehicle size of HD-FCEV necessitates bigger
fuel cell stacks, and thus heat and water management are more challenging. The more extensive power delivery of an HD-FCEV could be achieved by stacking multiple cells in series or parallel, making the cell generate more extensive heat and water as a by-product. Figure 1.11a shows a schematic representation of multiple fuel cells stacked in series to deliver a more significant power requirement. Hence, HD-FCEVs require a larger radiator, humidifier, and better water management for enhanced durability and stability. The power requirement for a truck or bus (HD-FCEVs) can be up to five to six times higher than that of a car (LD-FCEVs). Because of the longer driving duration for shipping goods, HD-FCEVs have more stringent durability requirements (25,000 hours instead of 6,600 hours). Because the driver and fuel costs are the most significant contributor to shipping goods, the fuel cell stack needs to operate at higher fuel efficiency (68% versus 60%).

Interestingly, HD-FCEVs are not as constrained to costs as severely as LD-FCEVs ($80 kW^{-1} versus $35 to $55 kW^{-1}). Hence, the enhanced durability, more significant power requirement, and stability of HD-FCEVs lead to the search for a better fuel cell system that could operate under low/no humidity and better heat rejection to save the cost cell operation performance. Figure 1.11b shows an example of a better heat rejection rate at high temperatures.
Figure 1.11. a.) Fuel cell stacked in series for higher power delivery b.) Depiction of increase in heat rejection rate with temperature

1.4.3 HT-PEMFCs

As stated previously, HT-PEMFCs, which operate in the temperature range of 100 to 250 °C, offer more superficial heat and water management when compared to today’s conventional LT-PEMFC. HT-PEMFCs often use an anhydrous PEM, which does not require constant humidification for cell operation. The elevated temperature operation of HT-PEMFCs reduces the fuel cell stack radiator's size while eliminating any need for feed gas humidification. At high temperatures, low-cost H\textsubscript{2} fuel from SRM can be used because the electrocatalysts are more tolerant to carbon monoxide (CO) contaminant. Hence, cell operation costs could be further reduced using hydrogen produced from steam reformed methane (SMR) as fuel. It is also worth mentioning that higher temperatures promote better redox kinetics in the electrode layers.\textsuperscript{42,85,89} Despite the advantages of HT-PEMFCs, they have not been widely implemented for vehicle applications due to their low power density, high platinum group metal loadings, unsatisfactory stability, and limited temperature range and water tolerance. This fuel cell platform has primarily been relegated to stationary power and niche applications because of these limitations. The
application of HT-PEMFCs has been primarily hindered by the HT-PEM used as a separator and as an ionomer binder in the electrodes.

1.4.4 ECHP

ECHP technology was invented in the 1960s because of the availability of polymer electrolyte membrane (PEM) materials (e.g., Nafion®). General Electric experimented with PEMs for ECHPs, but primarily developed the membranes for fuel cells and chloro-alkali electrolyzers. Hydrogen has seen an expanded role in the manufacturing and power production sectors in the past 15 years. 60% of power plants currently use hydrogen as a coolant for turbine generators because this fluid has high specific heat capacity and thermal conductivity values. The increased adoption of hydrogen as a coolant in power plants and fuel for FCEVs has motivated research activities in ECHP units for hydrogen recycling, recovery, and compression. Hydrogen reuse saves plants money by curtailing the costs associated with purchasing new hydrogen. Although ECHPs can work with non-polymer type electrolytes, such as protonic ceramic conductors, ceramics are not conducive for scalable roll-to-roll manufacturing processes and necessitate high-temperature operation (300 °C and above) for adequate proton conductivity.38

ECHP provides a single standalone device for pure hydrogen production, separation, and compression, making it a cost-effective and straightforward process. Figure 1.12 shows the operation of ECHP. The gas mixture produced from stream reformed methane and cracking is supplied to the anode, where the hydrogen gets selectively oxidized to protons. The generated protons are selectively extracted from the PEM (solid-state separator) and shuttled to the cathode for electrochemical reduction and pure hydrogen generation. Recent developments in high-temperature proton exchange membranes (HT-PEM) have led to a resurgence in ECHP technology.86
HT-PEM ECHP uses an anhydrous PEM, which does not require constant humidification for cell operation. Also, there is industrial interest in improving ECHPs by moving to higher temperatures. Operating the ECHP at higher temperatures, such as 200 to 240 °C, is posited to not only enhance the efficiency of the ECHP unit for hydrogen extraction from the hydrocarbon mixture but it is also may enable the unit to remove hydrogen more effectively from mixtures with larger fractions of contaminants and smaller concentrations of hydrogen (i.e., a dirtier variety). This latter attribute may eliminate additional pre-treatment units that partially enrich the hydrogen in hydrocarbon mixtures and remove contaminants before feeding to an ECHP.

1.4.5 Solid polymer electrolytes

Ion exchange membranes are semi-permeable membranes with polymer structures carrying fixed positive or negative charges that transport specific dissolved ions while blocking other ions or neutral molecules. Polymer membranes containing positively charged groups on their polymer backbone are anion exchange membranes, whereas those containing negatively charged groups on their backbone are cation exchange membranes. Ion exchange membranes ideally display high perm selectivity, lower electrical resistivity, good mechanical and chemical
stability. The use of ion-exchange membranes as solid polymer electrolytes (SPE) in an electrochemical process provides an edge over liquid electrolytes by removing the need for conductive liquid in the cell. SPEs are also safe to handle, have low internal corrosion and are conducive for packaging and manufacturing (e.g., roll-to-roll processes). The electrode reactions in an SPE cell often occur at the membrane electrode interface. SPEs are employed primarily for the electrolysis of pure water, fuel cells (proton exchange membranes), and hydrogen separation and purification. SPEs find additional applications to batteries, sensors, or electrochromic devices.

This dissertation's overall goal investigates a new class of anhydrous high-temperature (120 °C to 250 °C) proton-conducting polymer electrolytes exploited as HT-PEM and as electrode ionomer binders in HT-PEMFCs, and HT-PEM ECHPs. Further, the newly developed HT-PEM's wide-temperature adaptability will be investigated by harnessing it in a solid-state supercapacitor as a wide-temperature range electrochemical charge storage device. Figure 1.13 shows the solid-state electrochemical energy cycle using HT-PEMFCs, HT-PEM ECHPs, and solid-state supercapacitor studied as a part of this dissertation.
Figure 1.13. Solid-state electrochemical energy production, storage, and consumption cycle enabled by the new class of high-temperature polymer electrolytes as membrane separator and electrode binders

1.5 Summary of introduction

The introduction highlighted the overall goal and motivation for renewable energy and hydrogen as an energy carrier in fuel cells and separations. Additionally, this chapter provided a detailed discussion on current research problems in operating fuel cells and ECHPs at high temperatures. The chapter offered scientific questions, approaches, hypotheses, and impact in achieving the overall goal and motivation of this dissertation. The chapter contains background on applying high-temperature polymer electrolytes as HT-PEM and electrode binders in HT-PEMFC and HT-PEM ECHP.
Chapter 2
Electrochemistry Background and Theory

2.1 Significance of ionic conductivity of ion-exchange membranes

Ion-exchange membranes, as electrolyte material, play an essential role in several electrochemical applications in electrochemical energy conversion and storage devices. In the case of fuel cells and electrochemical hydrogen pumps, the electrolyte material, in our case a PEM, necessitates high ionic conductivity, selectively permeate protons, electron insulation while maintaining optimal thermal stability, mechanical stability, etc. The transport of ions in an electrolyte material, in our case a PEM, is provided by the Nernst-Planck flux equation. The equation is used to define the ion fluxes in electrolyte materials, usually dilute liquids, or idealized polymer-based membranes, connected to the influence of electric current and transport/transference number. The transport of ions in an electrolyte is the largest driver of the ohmic resistance component in an electrochemical cell. It is vital to minimize the ohmic resistance by augmenting the ionic conductivity of the PEM.45,46

The electrochemical potential term is defined using the following equation 2.145:

\[
\eta_i = \mu_i + z_i F \phi = \mu_i^0 + \bar{V}_i p + RT \ln a_i + z_i F \phi
\]  

(2.1)

Where \( \eta_i \) is the electrochemical potential associated with the transport of species (i), \( \mu_i \) is the chemical potential of the species (i), \( z_i \) is the valence charge of the species (i), \( F \) is the Faraday's constant, \( \phi \) is the electrical potential, \( \mu_i^0 \) is the chemical potential of species (i), at a chosen standard state, \( \bar{V}_i \) is the partial molar volume of the species (i), \( p \) is the pressure, \( a_i \) is the activity of the species (i).

Differentiating equation 2.1 across the perpendicular direction of the membrane surface and by substituting the activity of the species (i) yields:
\[ \frac{d\eta_i}{dx} = \frac{V_i}{R} \frac{dp}{dx} + RT \frac{d\ln y_i C_i}{dx} + z_i F \frac{d\phi}{dx} \quad (2.2) \]

where \( \gamma_i \) is the activity coefficient of species (i), and x is the thickness of the membrane. The pressure gradient could be neglected due to minimal pressure difference kept across the membranes. For the second term on the left-hand side of equation 2.2, the expression can be redefined as follows:

\[ RT \frac{d\ln y_i C_i}{dx} = RT \frac{d\ln y_i}{dx} C_i + RT \left( \frac{d\ln y_i}{dx} \frac{1}{C_i} \right) \frac{dC_i}{dx} \quad (2.3) \]

After elimination of the pressure term and substituting (2.3) in (2.2), yields

\[ \frac{d\eta_i}{dx} = RT \left( \frac{d\ln y_i}{dx} \frac{1}{C_i} \right) \frac{dC_i}{dx} + z_i F \frac{d\phi}{dx} \quad (2.4) \]

The above equation, (2.4), is used to represent the driving force of species (i) (mobile ion in a membrane) for determining the flux of species (convective and diffusive fluxes).

For any electrolyte, the electrical current passing through it under the influence of an electrical potential gradient is proportional to the concentration of ions in the solution, the stoichiometric coefficients for the ions, the valence of the ions, and its ionic mobility in the medium.

The net flux of species from Faraday's laws of electrolysis can be represented as:

\[ i = \Sigma z_i F N_i \quad (2.5) \]

\( N_i \) is the molar flux, \( N_i = J_i + C_i v_i \), where \( J_i \) denotes the diffusive flux term, and \( C_i v_i \) represents the convective flux term.

The general form for any diffusive flux can be represented as:

\[ J_i = \Sigma L_{ik} X_k \quad (2.6) \]

where \( J_i \) denotes the flux, \( L_{ik} \) is the proportionality constants, \( X_k \) represents the driving forces.

For Fick's first law, \( J_i = D_i C_i d_i \), were the driving force \( d_i \), \( C_i \) is the chemical potential gradient, or the electrochemical potential gradient.
\[ \eta_i = \mu_i + z_i F \varphi \quad (2.7) \]

Where \( \mu_i \) is the chemical potential gradient.

\[ \mu_i = \mu_{i0} + RT \ln a_i = \mu_{i0} + RT \ln Y_i C_i \quad (2.8) \]

Assuming transport in the x-direction alone and no bulk fluid flow/convection (i.e., \( N_i = J_i \))

\[ J_{ix} = D_i C_i \left( \frac{1}{RT} \frac{d \eta_i}{dx} \right) = D_i C_i \left( \frac{d \ln Y_i}{dx} + \frac{1}{C_i} \frac{d C_i}{dx} + \frac{z_i F \varphi}{RT} \frac{d \varphi}{dx} \right) \quad (2.9) \]

Assuming solution ideality and substituting equation 2.8 in 2.4,

\[ i_x = F^2 \sum_i \frac{z_i^2 D_i C_i}{RT} \left[ \frac{RT}{z_i F C_i} \frac{d C_i}{dx} + \frac{d \varphi}{dx} \right] \quad (2.10) \]

Hence, conductivity \( \kappa \) = \( \frac{1}{\rho} = F^2 \sum_i \frac{z_i^2 D_i C_i}{RT} \quad (2.11) \)

2.2 HT-PEMFC electrochemistry

A fuel cell is an electrochemical energy converting device. The hydrogen fuel in the anode undergoes electrochemical oxidation, whereas, in the cathode, oxygen undergoes electrochemical reduction. Both reactions occur simultaneously.\(^{23}\)

At the anode: \[ H_2 \rightarrow 2H^+ + 2e^- \quad (2.12) \]

At the cathode: \[ \frac{1}{2} O_2 + 2e^- + 2H^+ \rightarrow + H_2O \quad (2.13) \]

The reactions often take place at the interface of ionically conductive solid-state electrolyte (PEM) and electrically conductive electrodes.

From Faraday’s law the current density is proportional to the charge transferred and the consumption of reactant per unit area:

\[ i = nFj \quad (2.14) \]

where \( nF \) is the charge transferred (Coulombs mol\(^{-1}\)) and \( j \) is the diffusive flux of the reactant per unit area (mol s\(^{-1}\) cm\(^{-2}\)).

The potential or reversible open cell voltage \( E^0 \) of an electrochemical device is defined as:
\[ E^o = \frac{-\Delta G}{nF} \]  

(2.15)

where \( n \) is number of exchanged electrons (\( n=2 \)), \( F \) is Faraday's constant, \( \Delta G \) is the Gibbs free energy change for the reaction. The theoretical open cell voltage calculated from (2.15) for a fuel cell is 1.23 V.

The theoretical open circuit voltage\(^7\) is calculated as a function of temperature \( T \) and the species partial pressures \( P_i \) as:

\[ E_{oc} = 1.23 - 0.9 \times 10^{-3} (T - 298.15) + \frac{RT}{2F} \ln \left( \frac{P_{H_2}}{\sqrt{P_{O_2}}} \right) \]  

(2.16)

where \( T \) is the temperature of operation, \( P_{H_2} \) and \( P_{O_2} \) is the partial pressure of hydrogen and oxygen. The OCV decreases with increase in temperature.

At a given temperature and pressure, the fuel cell will not generate any current when the circuit is closed, and reactant gases are supplied. It is expected that the open-cell voltage (OCV) is to be at or close to the theoretical cell potential calculated from (2.16). However, practically the open circuit potential is significantly lower than theoretical cell potential, usually less than 1 V. The lower OCV suggests that there are losses in the fuel cell even when no external current is generated. The potential is expected to drop even further under a closed circuit and the current is being generated, due to unavoidable resistances. The different losses that occur in a fuel cell are caused by:

(i) crossover of reactants

(ii) kinetics of electrochemical reactions

(iii) internal electrical and ionic resistance

(iv) difficulties in getting reactants to reaction sites
These above-mentioned voltage losses in fuel cells are termed as polarization and are represented by activation, ohmic, and mass transfer related overpotential values. Polarization is defined as the difference between electrode potential and the equilibrium potential.\textsuperscript{23}

### 2.2.1 Crossover of reactants

Even though a PEM is not electrically conductive and is impermeable to reactant gases, some hydrogen usually diffuses through the PEM from the anode and reaches the cathode. Similarly, some electrons might also find a shortcut through the membranes.\textsuperscript{23} With each hydrogen molecule crossing through the PEM, two electrons are being dragged, and this is called fuel crossover. Each hydrogen that diffuses through PEM reacts with oxygen on the cathode side, resulting in less electron generation, and creating a mixed overpotential in the cathode, reducing the overall cell potential. However, the cross of hydrogen through PEM is low, at very low current density operation of the fuel cell, these losses may have a dramatic effect on cell potential.\textsuperscript{23}

### 2.2.2 Kinetics of electrochemical reactions

Initially, for the electrochemical reaction to happen, a voltage difference from equilibrium is needed. This loss in cell voltage that occurs for the electrochemical reaction to occur is called activation overpotential, and it is associated with sluggish electrode kinetics at the cathode. A higher exchange current density value manifests a lower the activation overpotential ($\eta_{act}$). The exchange current is proportional to the reaction rate coefficient for an electrochemical reaction. Activation overpotentials are present at both the anode and cathode, but the oxygen reduction reaction at the cathode is more sluggish resulting in a higher overpotential.

From the Butler-Volmer equation\textsuperscript{73}, the activation overpotential can be expressed as:

$$\eta_{act} = \frac{RT}{a_{an}F} \ln \left( \frac{i}{i_{an}} \right) + \frac{RT}{a_{cat}F} \ln \left( \frac{i}{i_{cat}} \right)$$  \hspace{1cm} (2.17)
where \( \alpha_{an} \) and \( \alpha_{cat} \) are the anode and cathode transfer coefficients, respectively. \( i_0^{an} \) and \( i_0^{cat} \) is the anode and cathode exchange current density values.

For HT-PEM containing phosphoric acid in the electrode layers, the \( i_0^{an} \) and \( i_0^{cat} \) could be expressed as the following expressions listen, introducing a correction for the phosphoric acid (PA) doping:\(^{73}\):

\[
i_0^{an} = a_C L_C \left( \frac{p_{H_2} H_2^L}{c_{H_2^L}} \right)^{0.5} \exp \left( -\frac{E_{H_2}^C}{R} \left( \frac{1}{T_{an}} - \frac{1}{T_{ref}} \right) \right) i_{0-ref}^{an} \exp \left(-\gamma (1 - m_{io}) \right) \tag{2.18}
\]

\[
i_0^{cat} = a_C L_C \left( \frac{p_{H_2} H_2^L}{c_{H_2^L}} \right)^{0.5} \exp \left( -\frac{E_{O_2}^C}{R} \left( \frac{1}{T_{cat}} - \frac{1}{T_{ref}} \right) \right) i_{0-ref}^{cat} \exp \left(-\gamma (1 - m_{io}) \right) \tag{2.19}
\]

\( m_{io} \), the acid mass fraction is calculated from the IEC (ion exchange capacity of the polymer electrolyte) as:

\[
m_{io} = 0.0902 IEC_{io} + 0.0352 \tag{2.20}
\]

In the above equations, \( \gamma \) is an empirical parameter that helps account for how the H\(_3\)PO\(_4\) content alters the exchange current density values.

Cheddie et al. proposed an empirical expression for calculating Henry's constant for the oxygen in H\(_3\)PO\(_4\).\(^{73}\) In this model, Henry's constant is approximated for oxygen as a function of temperature and H\(_3\)PO\(_4\) mass fraction in the ionomer binder:

\[
H_{O_2}^{CL} = (1.0 \times 10^{-6}) \exp \left( -\frac{900 m_{io}^2 - 150m_{io} + 650}{T} \right) \tag{2.21}
\]

Hydrogen mass transport is not considered a limiting factor. Therefore, for the hydrogen, the Henry's constant is simply assumed to be \( H_{H_2}^{CL} = 4H_{O_2}^{CL} \).

2.2.3 Internal electrical and ionic resistance

Once the current is being drawn from the fuel cell, the electrochemical reaction is driven by the ions' mobility. The resistance to the flow of protons through the PEM and flow of
electrons through the electrodes and fuel cell components give rise to ohmic losses or ohmic overpotential ($\eta_{ohm}$).

$$\eta_{ohm} = iR$$

(2.22)

where $i$ is the current density ($\text{A cm}^{-2}$), and $R$ is total internal area-specific resistance (ASR) and this includes resistances that hail from ion and electron transport as well as contact resistances ($\Omega \text{ cm}^{-2}$). Contact and electronic resistance values are almost negligible. The ionic conduction through PEM and electrode plays a significant role in governing $\eta_{ohm}$. Therefore, $\eta_{ohm}$ could be expressed as a summation of the ionic conductivity resistance of the PEM and ion transport in the electrode layers (fostered by the polymer electrolyte binder).

$$\eta_{ohm} = i \left( \frac{\delta_{mem}}{\kappa_{mem}} + \frac{\delta_{io}}{\kappa_{io}} \right)$$

(2.23)

where $\delta_{mem}$ is the thickness of the PEM, $\kappa_{mem}$ is the ionic conductivity of the PEM, $\delta_{io}$ is the thickness of the ion-conducting electrode binder, and $\kappa_{io}$ is the ionic conductivity of the electrode binder.

### 2.2.4 Mass transport resistance

When the current is being generated at a rapid rate at high current densities, the reactants are rapidly consumed at the electrode by the electrochemical reactions. The voltage losses that occur due to mass transfer limitations of reactants to the electrocatalyst is is called the concentration overpotential ($\eta_c$).

$$\eta_{c,i} = \frac{RT}{F} \ln \left( \frac{C_i|_{surface}}{C_i^{bulk}} \right)$$

(2.24)

where $C_i|_{surface}$ and $C_i^{bulk}$ is the concentration of reactants at the surface and bulk concentration of reactants, respectively.

$$\frac{C_i^{bulk} - C_i|_{surface}}{C_i^{bulk}} = 1 - \frac{i}{i_{lim}}$$

(2.25)
\[ \eta_{c,t} = \frac{RT}{F} \ln \left(1 - \frac{i}{i_{lim}}\right) \quad (2.26) \]

The oxygen diffusivity in the catalyst layer containing H$_3$PO$_4$ for high-temperature polymer electrolytes is approximated from the H$_3$PO$_4$ mass fraction in the ionomer binder as$^{73}$:

\[ D_{O_2}^{CL} = (1.0 \times 10^{-6}) \exp \left( -\frac{4500 m_{io}^2 - 4000 m_{io} + 4010}{T} \right) \quad (2.27) \]

For the hydrogen diffusivity, it is assumed to be \( D_{H_2}^{CL} = 2D_{O_2}^{CL} \)

The total cell voltage is calculated as:

\[ E(i) = E_{oc} - \eta_{act} - \eta_{con} - \eta_{ohm} \quad (2.28) \]

Here \( \eta \) represents the cell overpotentials.

**Figure 2.1** shows the fuel cell polarization curve with four types of losses in the fuel cell. Activation losses are by far enormous losses at any current density. Activation and concentration overpotential occur at both anode and cathode.
2.3 HT-PEM ECHP

In an electrochemical hydrogen pump, hydrogen or hydrogen mixtures are supplied in the anode compartment, where they are oxidized to protons and electrons within the catalyst layer of the electrode. The protons are then driven through the PEM to the cathode, while the electrons pass through the external circuit to the cathode due to the voltage applied in the cell. The protons and electrons combine in the cathode to form pure hydrogen. The overall chemical reactions are:

At the anode: \[ H_2 \rightarrow 2H^+ + 2e^- \] (2.29)

At the cathode: \[ 2H^+ + 2e^- \rightarrow H_2 \] (2.30)

The cell voltage between the anode and cathode is given by (2.31)
\[ E(i) = E_{\text{Nernst}} + \eta_{\text{act}} + \eta_{\text{ohm}} + \eta_{\text{conc}} \]

(2.31)

where the Nernst potential is given by the Nernst equation:

\[ E_{\text{Nernst}} = E^0 - \frac{RT}{2F} \ln \frac{p_{\text{cathode}}}{p_{\text{anode}}} \]

(2.32)

\( E^0 \) is the standard potential of a hydrogen reaction, \( R \) is the gas constant, \( T \) is temperature, \( F \) is the Faraday’s constant, \( p_{\text{cathode}} \), and \( p_{\text{anode}} \) is the partial pressure of hydrogen in the anode cathode, respectively.

The activation overpotential is the sum of polarization overpotentials in the anode, and the cathode. Butler-Volmer equation gives the activation overpotential and at low overpotentials,

\[ \eta_{\text{act}} = \frac{iRT}{i_0(\alpha_a + \alpha_c)nF} \]

(2.33)

\( i_0 \) (A cm\(^{-2}\)) is the exchange current density, where \( i \) is the current density, \( \alpha_a \) and \( \alpha_c \) is the anodic and cathodic transfer coefficients, respectively. \( \eta \) (mV) is the overpotential.

Ohm’s law gives the ohmic overpotential:

\[ \eta_{\text{ohm}} = iR \]

(2.34)

where \( R \) is the resistance of the PEM.

The concentration overpotential occurs when the reactants are rapidly consumed at the electrode by the electrochemical reactions and concentration gradients are established, and is defined by:

\[ \eta_{\text{conc}} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_{\text{lim}}} \right) \]

(2.35)

2.4 Conclusions

The theoretical concepts and electrochemical background discussed in Chapter 2 were used in the dissertation for the following purposes:
(i) To understand the ionic transport within the ion-exchange membranes (e.g., PEM) to understand PEM properties and conduct a systematic study on their influence on HT-PEMFC and HT-PEM ECHP performance.

(ii) To understand the sources of resistances in the HT-PEMFC and HT-PEM ECHP

(iii) The need to develop new ionomer binders for HT-PEMFC and HT-PEM ECHP that eliminate H_3PO_4 and show improved reaction kinetics and mass transport.

(iv) To study the anode and cathode kinetics by measuring the exchange current density and Tafel slope for new high-temperature polymer electrolytes for HT-PEMFC and HT-PEM ECHP, aiding in improving device performance.
Chapter 3
Experimental Methods

3.1. Introduction

This chapter discusses the experimental methods used to carry out the research disseminated in this dissertation. The chapter includes the procedure for material synthesis and characterization of HT-PEMs and electrode ionomer binders and the fabrication and testing of membrane electrode assemblies in fuel cell/electrolyzer hardware.

3.2 For HT-PEMFC study

3.2.1 Synthesis of CMPSf

CMPSf was prepared by Friedel-Crafts reaction as reported by Arges et al. 92, but with a slight modification to the procedure, as shown in Figure 3.1. 10 g of Udel® poly(arylene ether) sulfone (PSf) was dissolved in 500 mL of chloroform (CHCl₃). The reaction was carried out in a round bottom flask equipped with a magnetic stirrer and a reflex condenser. After the PSf dissolved, 6.8 g of paraformaldehyde was added, followed by 30 mL of chlorotrimethylsilane. The bulb flask was blanketed with nitrogen and sealed with a rubber septum. 525 μL of SnCl₄, the Lewis acid catalyst, was added slowly to the bulb flask using a syringe punctured through the septum.

The extent of chloromethylation was monitored during the reaction until the desired degree of functionalization (DF) value of chloromethyl groups per repeat unit was achieved. The DF value was monitored by ¹H NMR during the reaction. The reaction solutions, either collected at the end of the reaction or withdrawn during the reaction, were cooled to room temperature and poured into methanol (5:1 volume ratio of methanol to reaction solution) to precipitate the polymer out of solution. The precipitated polymer was collected by vacuum filtration and vacuum dried. The CMPSf was purified further by dissolving it in CHCl₃ (5 wt%), followed by
precipitating in methanol and vacuum filtering and drying the solid using the aforementioned procedure.

![Synthesis scheme for QPPSf]

**Figure 3.1.** Synthesis schemes for QPPSf

### 3.2.2 Preparation of blended and non-blended membranes

CMPSf was dissolved in DMAc to attain a 5 wt % solution. Similarly, a 5 wt% solution of PBI in DMAc was prepared. PBI was added to CMPSf at different volume ratios to achieve a desired CMPSf-PBI blend composition. The ratios examined were 0, 30, 40, 50, 60, and 100%. 0% refers to PBI only, and 100% refers to CMPSf only. The solutions were sonicated for ten minutes and drop cast on a glass plate on a leveled surface in an oven at 120 °C for 6 hours. After peeling off the membranes from the glass plate, the blended membranes that featured CMPSf were then immersed in pyridine solution (1M in reagent alcohol) at 40 °C for 16 hours to
convert the chloromethylated groups in PSf to quaternary benzyl pyridinium chloride groups. Then, the resultant membranes were washed excessively with DI water to removed unreacted pyridine and were blot dried. The thickness of the dry membranes ranged from 40 – 68 μm. The acid doping of PBI and QPPSf-PBI blended membranes was done by immersing membranes in 85 wt% phosphoric acid (H₃PO₄) at 120 ºC for 6 hours. QPPSf was doped with 85 wt% phosphoric acid (H₃PO₄) at 25 ºC because immersion of this membrane in this acid at 120 ºC for 1 hour dissolved the membrane. After acid doping, the membranes were then blot dried for removing the excess acid from the surface.

3.2.3 Physical characterization of PC-PBI blend membranes

Scanning electron microscope images were obtained by Quanta 3D DualBeam FEG FIBSEM with working distance of 10.2 mm and accelerating voltage of 5 kV. Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy were performed by Thermo Nicolet Nexus 670 ATR-FTIR (total # of scans = 64) and Renishaw inVia confocal Raman microscope, respectively. Laser 532 nm was used for Raman spectroscopy of samples in the range of 500-3000 cm⁻¹ and exposure time of 10 s.

3.2.4 H₃PO₄ uptake and amount per base moiety and calculation of QPPSf IEC

The H₃PO₄ uptake of QPPSf, PBI, and their blends were observed by measuring their weight change before, and after immersing in 85wt% H₃PO₄. The total H₃PO₄ uptake by the membrane was calculated using equation 1:

\[
\text{H}_3\text{PO}_4 \text{ uptake} = \frac{W_2 - W_1}{W_1} \quad (3.1)
\]

Where \( W_1 \) and \( W_2 \) are the weight of the polymer membrane before and after doping.

Where \( W_{\text{dry}} \) is the dry weight of the acid doped membranes.
The IEC of the pristine QPPSf membrane (i.e., not H₃PO₄ doped and not blended) was determined using $^1$H NMR spectroscopy. First, the degree of functionalization (DF) of CMPSf was calculated using $^1$H NMR:

$$DF = \frac{2 \times \text{Area}_{CH₂Cl \text{ substitution} (\delta)}}{\text{Area}_{PSf \text{ substitution} (\delta)}}$$

(3.2)

Conversion of chloromethylated sites to cation sites:

$$Conversion = \frac{\text{Area}_{cation \text{ substitution} (\delta)}}{\text{Ratio} \times DF \times \text{Area}_{PSf \text{ substitution} (\delta)}}$$

(3.3)

$$Ratio = \frac{\# \text{ of protons for cation substitution}}{\# \text{ of protons for PSf substitution}}$$

(3.4)

Determining theoretical IEC of polycations

$$IEC \left( \frac{\text{mmol}}{g} \right) = \frac{DF \times 1000}{(MW_{PSf,\text{monomer}} + DF \times MW_{cation})} \times Conversion$$

(3.5)

$$MW_{cation} = (MW_{cation \text{ free base conjugate}} + MW_{counteranion} + MW_{CH₂} - 1)$$

The IEC of the non-H₃PO₄ doped membrane blends (QPPSf-PBI) were determined by performing a weighted average between the known IEC of QPPSf and the known IEC of PBI. The IEC of the non-H₃PO₄ doped membranes represents the IEC (base moiety basis).

Number of H₃PO₄ per base moiety (nH₃PO₄ B⁻¹) was found by:

$$nH₃PO₄ B⁻¹ = \frac{X \times 1000}{IEC_B \times M_w}$$

(3.6)

3.2.5 $κ_{H⁺}$ and cycling measurements

In-plane $κ_{H⁺}$ measurements were carried out in a 4-point platinum probe with PTFE housing (Bekktech conductivity cell) and using galvanostatic electrochemical impedance spectroscopy (EIS) using a Gamry 3000 AE8 channel potentiostat over frequency range of 1 MHz to 1 Hz with a current perturbation of 0.1 mA. The $κ_{H⁺}$ measurements were carried out in a temperature-controlled gravity oven in the temperature range of 100 – 250 °C. The cross-
sectional area of the membrane samples was 1 x 3 cm². The $\kappa_{H^+}$ of the membrane samples was calculated using equation 7:

$$\kappa_{H^+} = \frac{L}{R \times D \times W}$$ (3.7)

where $L$ (cm) is the distance between the electrodes, $R$ (Ω) is the resistance of the membrane, $D$ (cm) is the thickness of the membrane and $W$ (cm) is the width of the membrane.

3.2.6 Assessment of thermal stability

Thermal stability of the membranes PBI, QPPSf and QPPSf-PBI 50:50 were assessed via five different methods. The first method examined thermal stability cycling by placing the membrane sample in the Bekktech conductivity cell in the gravity oven followed by ramping up the temperature from 100 – 250 °C. Individual temperature points were held while performing an EIS measurement. After carrying out the EIS at 250 °C, the oven was cooled to 100 °C then reheated to 250 °C using the same ramp up and temperature hold (during EIS measurement) protocol. The results from the EIS were used to compute the $\kappa_{H^+}$. The goal was to perform three cycles to assess conductivity losses for PBI, QPPSf and 50:50 QPPSf-PBI membrane. However, the PBI and QPPSf did not survive the first heating cycle.

The $\kappa_{H^+}$ was also measured in a temperature-controlled oven (-70 to 220 °C). Three different thermal cycles performed for three individual membrane samples. During each cycle, the conductivity was measured from -70 to 220 °C at different points. The membranes were equilibrated at 25 °C before proceeding to the next cycle (-70 to 220 °C).

The second thermal stability assessment monitored changes in $\kappa_{H^+}$ of 50:50 QPPSf-PBI at 220 °C for 96 hours. This sample was only evaluated because PBI and QPPSf were shown to be unstable once the temperature of 200 °C was attained.
The third stability assessment examined the changes in membrane weight for all the membrane samples when holding the samples at 220 °C for 48 hours in a gravity oven. The change in membrane weight before and after the temperature hold was gravimetrically determined.

The fourth stability test investigated the membranes’ tolerance to humidity at 80 °C/40% RH. The changes in the membrane weight before the test and after the test was determined gravimetrically. For the test, the membrane sample was first placed in a Bekktech 4-point conductivity cell, which was then loaded into a Fuel Cell Technologies hardware setup plumbed to 850 E Scribner Fuel Cell Test Stand to control temperature and humidity of the membrane sample.

The fifth and final thermal stability assessment performed TGA of 50:50 QPPSf-PBI with and without doping with H₃PO₄ under nitrogen using Pyris 1 TGA (TA instruments). The samples were initially heated to 100 °C and equilibrated at that temperature for 10 minutes. Then, the samples’ temperature was heated up to 700 °C at the rate of 10 °C min⁻¹. The change in weight of the sample was monitored during the heating from 100 °C to 700°C.

The phase transition in H₃PO₄ 50:50 QPPSf-PBI membrane was recorded using DSC Q-10 (TA instruments) under nitrogen at heating rate of 10 °C min⁻¹ from 60 °C to -40 °C.

3.2.7 Mechanical properties

The stress-strain curves of the membranes doped with H₃PO₄ were measured using an INSTRON 3365. The strain rate during the test was 2 mm min⁻¹. The measurements were carried out at 25 °C and 220 °C in an ambient environment (~50% relative humidity). The time between doping the acid with membranes and performing the tensile test were short enough to negate the humidity effect on the membranes.
3.2.8 Preparation of GDEs

Catalyst inks were first prepared by mixing 0.2 g carbon supported catalyst (37% Pt on high surface area carbon, Tanaka Kikinzoku International) with 1.715 g of QPPSf ionomer solution dissolved in approximately 5.5 g of reagent alcohol. The schematic representation of fabrication of GDEs in shown in Figure 3.2. This catalyst ink gave the best fuel cell performance. The prepared ink was stirred for 10 minutes and sonicated for 30 minutes. The GDE was prepared by painting the ink on a carbon-based gas diffusion layers (GDL) with an aerosolized spray gun (nitrogen gas). The active area of the resultant GDE was 5 cm². The catalyst loading was determined gravimetrically by weighing the GDL prior to spray deposition and after depositing the catalyst layer and drying the electrode. The catalyst loading was maintained as 0.5 mgPt cm⁻² for each GDE (one used as the anode and the other as the cathode). The weight fraction of the ionomer in the electrode layer was 30 wt.%. The GDEs were then immersed in 85wt% H₃PO₄ for 10 minutes. The short immersion time was done to prevent excess H₃PO₄ uptake in the electrodes that cause poor mass transfer in the GDE layers. An alternative catalyst ink was prepared in identical fashion except that CMPSf and PBI were used a 50:50 weight ratio of 1.715 g total and the solvent was DMAc. After painting the catalyst ink on to the GDLs with this formulation, the resultant GDEs were immersed in pyridine solution (1 M in reagent alcohol) to convert the chloromethylated groups in PSf to quaternary benzyl pyridinium chloride groups. Then the electrodes were immersed in H₃PO₄ for acid uptake using the same procedure.
3.2.9 MEA assembly and fuel cell testing

For the fuel cell tests, a MEA was prepared by placing the acid doped QPPSf-PBI 50:50 blended membrane between two identical GDE’s that were housed with PTFE gaskets. The MEA was then sandwiched between graphite serpentine flow fields and gold current collectors in Fuel Cell Technologies Hardware setup (5 cm² geometric area). The assembled single cell was plumbed to an 850 E Scribner Associates, Inc. Fuel Cell test station. Then, a homemade fiberglass housing was placed over the fuel cell hardware for insulation followed by heating the cell to 220 °C (note: the insulation is required to stabilize the cell temperature). Then, dry nitrogen was passed on the anode and cathode side (note: the humidifier was by-passed for both gas feeds). Then, non-humidified H₂/O₂, H₂-CO/O₂, or H₂/air were passed into the fuel cell at a minimum flow rate of 0.2 l SLPM at a stoichiometric ratio of 1.2x and 2x for the anode and cathode, respectively. 60 kPa of back pressure was applied to both the anode and cathode (i.e.,
161 kPa(abs). The polarization curves were collected every 0.05 V by holding the voltage for 1 minute. The EIS was performed in the fuel cell test stand over frequency range of 1 kHz to 0.1 Hz with a current perturbation of 0.1 mA.

Stability tests were performed by continuous supply of dry H\textsubscript{2}/O\textsubscript{2} for 2 hours, followed by H\textsubscript{2}-CO/O\textsubscript{2} for 6 hours, and then 18 hours of dry H\textsubscript{2}/O\textsubscript{2}. The cell voltage was held to 0.4 V (T = 220 °C) during the 24-hour stability assessment. The polarization curves with dry H\textsubscript{2}/O\textsubscript{2} were recorded before and after the stability tests.

3.3 For high temperature thin-film ionomer electrode binder study

3.3.1 Synthesis of PTFSPA (poly (tetrafluoro styrene phosphonic acid-co-pentafluorostyrene))

The addition of phosphonic acid to poly(pentafluorostyrene) (PPFS) was carried out by following the procedure by Atanasov et al.\textsuperscript{93} 1 g PPFS (200 kDA M\textsubscript{w}) (5.2 mmol) was dissolved in DMAc (4 g) at room temperature in a round bottom flask equipped with magnetic stirrer, reflux condenser and an oil bath. The temperature was increased to 170 °C and tris(trimethylsilyl) phosphate (TSP; 1.07 g, 3.6 mmol) was added dropwise, and the reaction was carried out for 16 hours. The resulting polymer solution was poured into DI water and the white solid was precipitated. The white solid polymer was refluxed in DI water for 30 minutes, by changing fresh water every 10 minutes, followed by boiling in 2 wt.% phosphoric acid solution and washing with DI water till a neutral pH was obtained. The PTFSPA white solid was dried in vacuum oven overnight. The phosphonic acid tethered groups were confirmed via \textsuperscript{31}P NMR. A 70% degree of phosphonation was assumed based on the ratio of TSP added to PPFS repeat unit.\textsuperscript{66,79} The resulting PTFSPA was dissolved in DMSO to make an ionomer solution (5 wt.%).
3.3.2 Synthesis of poly(vinylbenzyl phosphonic acid) (PVBPA)

The addition of phosphonic acid to poly(vinyl benzyl chloride) (PVBCl) was carried out similar to Nedal et al.\textsuperscript{94} PVBCl (5 g) was dissolved in NMP (90 ml). Diethyl carbitol (30 mL) and triethyl phosphite (15 mL) were added to the polymer solution. The reaction temperature was increased to 140 °C for 6 – 8 hours and cooled back to room temperature. The reaction was terminated by precipitating in DI water with continuous vigorous stirring. The resulted phosphite tethered polymer was dried until a constant weight was achieved. The phosphonic acid was generated by refluxing the phosphite tethered polymer in aqueous hydrochloric acid. The hydrolysis reaction was carried out for 6 hours. The resulting polymer was filtered and washed with DI water until a neutral pH was achieved. The retained PVBPA was dried overnight in vacuum oven until a constant weight was achieved. Figure 3.3 shows the synthesis schemes for PTFSPA and PVBPA.

IEC of PTFSPA and PVBPA was determined using a base titration. A sample of PTFSPA and PVBPA was immersed in 1 M sodium chloride (NaCl) for 24 hours for exchanging the protons for sodium ions. This solution was titrated against 0.1 M sodium hydroxide (NaOH) solution until equivalence point observed using potassium permanganate indicator. The IEC of PTFSPA and PVBPA was calculated using equation 3.

\[
\text{IEC} \left( \frac{\text{mmol}}{\text{g}} \right) = \frac{V_{\text{NaOH}} \times N_{\text{NaOH}}}{w_{\text{dry}}} \tag{3.8}
\]

\(w_{\text{dry}}\) is the weight of dry PTFSPA.

The IEC of PTFSPA and PVBPA was using the base titration method was 2.5 mmol g\textsuperscript{-1} and 1.8 mmol g\textsuperscript{-1} respectively.
3.3.3 Thermal stability assessment

The thermal stability of PTFSPA, PVBPA, and QPPSf-H₃PO₄ was determined using a Pyris 1 TGA (TA instruments) instrument under nitrogen. The samples were initially heated to 100 °C and equilibrated at that temperature for 10 minutes. Then, the temperature was heated up to 700 °C at the rate of 10 °C min⁻¹. The change in weight of the sample was monitored during the heating from 100 °C to 700 °C.

3.3.4 Ionic conductivity (κ) of thin-films

Thin-film in-plane ionic conductivity was measured on the IDEs using the procedure by Arges et al. Thin-films of QPPSf, PPVB, and PTFSPA were deposited on the IDEs by spin coating a 1 wt.% solution at 4000 rpm for 45 seconds. The IDE with thin-films of polymer electrolytes were then heated at 120 °C in nitrogen atmosphere to remove the excess solvents.
from the samples. H$_3$PO$_4$ was imbibed into the QPPSf thin-films by placing a drop of 85 wt.% H$_3$PO$_4$ on the thin-films for 10 minutes. Complete hydrolysis and activation of PTFSPA and PVBPA thin-films were ensured by adding a drop of 5 wt.% H$_3$PO$_4$ on the thin-films for 10 minutes. The excess acid for all thin-film samples was removed by blot drying the IDEs carefully without rupturing the thin-film coated on the IDEs. The electrode pads of the IDE substrate were scraped away using a cotton Q-tip to make electrical connections. The thickness of the thin-films (t) was calculated using ellipsometry by coating a thin-film of ionomers on a bare Si wafer. The thickness of QPPSf-H$_3$PO$_4$ films ranged from 12-15 nm, PTFSPA and PVBPA films ranged from 10-12 nm. The thin-film resistance of QPPSf H$_3$PO$_4$ and PTFSPA was determined using electrochemical impedance spectroscopy (EIS). The frequency range was set to 100,000 to 1 Hz with an oscillatory amplitude of 0.0001 mA as described in our previous work.\textsuperscript{73,96} Equation 3.9 and IDE dimensions given below were used to calculate in-plane ionic conductivity of the thin-films.

\[
\kappa = \frac{1}{R} \cdot \frac{d}{l \cdot (N-1) \cdot t}
\]  

(3.9)

\(\kappa\): in-plane ionic conductivity

\(R\): in-plane ionic resistance

\(d\): spacing between teeth on IDE (100 μm)

\(l\): length of teeth on IDE (4500 μm)

\(t\): Ionomer film thickness on IDE substrate

\(n\): number of teeth on IDE substrate (22)
3.3.5 Manufacturing of IDEs with nanoscale Pt

The method to manufacturer IDEs is based upon the work by Arges et al. The procedure for block copolymer (BCP) self-assembly on IDEs was adopted from Arges et al. Poly(styrene-block-2-vinyl pyridine) (PS₄₀₋₅₋₄₄k) forming lamellae was self-assembled on gold current collector IDEs. First, a non-preferential layer was grafted to the IDE by spin coating (4500 rpm for 45 sec) 1 wt% of mono-hydroxy terminated poly (styrene-random-2-vinyl pyridine) (OH-PS-r-P2VP, 60% styrene weight fraction) in toluene on the IDE followed by grafting to the polymer to the surface by exposing the sample to 200 °C for 10 minutes under nitrogen. Unreacted OH-PS-r-P2VP was removed by immersion and sonication in toluene (3x cycles). Then, 1.5 wt% of PS₄₀₋₅₋₄₄k in toluene was spin coated on the IDE with a non-preferential layer at 4000 rpm for 45 second. The BCP on the IDE was solvent annealed with acetone vapor in a flow chamber, where the microphase separation and formation of perpendicular lamellae occurred. A Menshutkin rection was performed for methylating the pyridine moiety in the BCP film by exposing the substrate to iodomethane for 4 hours. Next, the IDE sample with methylated BCP film (poly(styrene-block-2-vinyl pyridine/n-methyl pyridinium iodide) (PS-b-P2VP/NMP⁺ I⁻)) was immersed in 10 mM hexachloroplatinate (H₂PtCl₆ in DI water) to exchange the iodide counterions to chloroplatinate ([MCl₆]²⁻). The chloroplatinate exchanged BCPs were then converted to platinum oxide by exposing it to oxygen plasma (Oxford Plasma Lab System 100 RIE tool). After the exposure to oxygen plasma for 7.5 minutes, the platinum oxide nanowires were exposed to argon plasma for 15 seconds to convert the platinum oxide into metallic platinum. At the end of the process, periodic and dense 20 nm diameter platinum nanowires with a 20 nm thickness were covered across the IDE chip. The platinum nanowires do not short the cell because the wire structures terminate within a few
microns in length and the distance between teeth electrodes in the IDE is 100 μm. The loading of nanostructured Pt was calculated by dissolving the platinum nanowires in aqua regia (mixture of 7.5 ml of 37% HCl and 2.5 ml of 69%) using a microwave digestor and quantifying the platinum ions in solutions (after dilution) via Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) (Perkin Elmer Optima 8x00).

3.3.6 HOR/HER on IDEs using chronoamperometry

HOR/HER studies with IDEs were carried out in a custom-built stainless-steel chamber that can be sealed, and that has heating capabilities. This chamber has inlets and outlets for gas feeds and electrical connections. Figure 3.4 provides a picture of the chamber. After purging the chamber with dry nitrogen gas for 15 minutes at 1 SLPM, the flow of dry nitrogen to the chamber was stopped, and a continuous flow of dry hydrogen was fed to the chamber at 1 SLPM. A Gamry Reference 3000 Potentiostat/Galvanostat was used for obtaining the polarization curves for HOR/HER on IDEs containing nanoscale platinum and with different thin-film ionomers. Chronoamperometry experiments were performed to generate the polarization curves. These experiments used 0.05 V potential steps and held the voltage for 30 seconds at each step to attain a steady-state current value. The chronoamperometry experiments were conducted from 0 V to 0.7 V.
Figure 3.4. Custom-built flow chamber for performing HOR/HER studies on IDEs.

3.3.7 Exchange current density analysis

The linear region of the polarization curve (i.e., low current density regime) was used for calculating the exchange current density as described by Neyerlin et al.\textsuperscript{81} The linearized Butler-Volmer equation is appropriate for reactions that have low overpotentials such as HOR/HER under acid conditions.

\[
i = \frac{i_0(\alpha_a + \alpha_c)\eta F}{RT}
\] (3.10)

\(i_0\) (A cm\(^{-2}\)) is the exchange current density, \(\alpha_a\) and \(\alpha_c\) is the anodic and cathodic transfer coefficients, respectively. \(\eta\) (mV) is the overpotential. It is assumed that \(\alpha_a\) and \(\alpha_c = 1\).

3.3.8 Hydrogen permeability

The limiting current form the LSV is used in calculating the hydrogen diffusion coefficient \(D_{H2}\). The calculation of \(D_{H2}\) was performed using the following equation\textsuperscript{100}:

\[
P_{H2} = D_{H2}H
\] (3.11)

\[
i_{lim} = nF \left(\frac{P_{H2}}{\delta}\right)^{c_{H2}}
\] (3.12)
\(i_{lim}\) is the limiting current density obtained from the polarization curves. \(\delta\) is the thickness of thin-film calculated using ellipsometry. \(C_{\text{H}_2}\) is the concentration of \(\text{H}_2\). \(D_{\text{H}_2}\) is the diffusivity of \(\text{H}_2\). It is assumed that the thin-film is exposed to constant concentration of hydrogen. In other words, the hydrogen is not depleted at the gas-film boundary layer interface. This was ensured by having high flowrate of hydrogen (1 SLPM) to the humidity chamber. \(P_{\text{H}_2}\) was calculated for different thin-films at different temperature range.

3.4 For HT-PEM ECHP

3.4.1 Preparation of GDEs and MEA fabrication

The catalyst inks for fabrication of gas diffusion electrodes (GDEs) were prepared by mixing 0.2 g of platinum electrocatalyst supported on high surface area graphitic carbon (37\% Pt/C, Tanaka Kikinzoku International) with 1.715 g of ionomer solution diluted with approximated 5.5 g of isopropyl alcohol (IPA). The prepared inks were sonicated for 30 minutes for dispersing the particles in the ink. The gas diffusion layers (GDLs) were then painted with the prepared catalyst inks using an aerosolized spray gun (nitrogen gas) to make GDEs. The active area of the resultant GDE was 5 cm\(^2\). The catalyst loading was measured gravimetrically by measuring the weight change before and after painting and drying. The catalyst loading was maintained at 0.5 mgPt cm\(^{-2}\) (or 1 mgPt cm\(^{-2}\)) for each GDE (one used as the anode and the other as the cathode). The weight fraction of the ionomer in the electrode layer was 30 wt.\%. PTFSPA and QPPSf ionomers were used in the fabrication of the GDEs. The QPPSf GDEs were then immersed in 85wt\% \(\text{H}_3\text{PO}_4\) for 10 minutes to imbibe acid into the electrodes. The MEAs were prepared by sandwiching the prepared GDEs with 50:50 QPPSf-PBI \(\text{H}_3\text{PO}_4\) HT-PEM in a Fuel Cell Technologies Hardware setup (5 cm\(^2\) geometric area). The assembled cell was plumbed to an 850 E Scribner Associates, Inc. Fuel Cell test station for HT-ECHP studies.
3.4.2 HT-ECHP studies with MEAs

ECHP tests were conducted using 850 E Scribner Associates, Inc. Fuel Cell test station. Before testing, the cell was heated to 120 °C under nitrogen on both anode and cathode. The cell was heated further to 180 °C under pure hydrogen on the anode and no sweep gas at the cathode. The polarization curves were obtained for 160 °C, 180 °C, 200 °C, and 220 °C by performing chronoamperometry with 0.05 V potential step by holding the voltage for 30 seconds at each step to reach steady-state current from 0 V-0.7 V. Additionally, different anode gas mixtures were used, including pure hydrogen, 75% H2 – 25% CO, premixed reformate gas (30% H2, 3% CO with N2 balance), premixed syngas mixture (25% H2, 40% CO, 25% CO2, 5% CH4, 5% N2), premixed steam reforming methane – water gas shift (SMR-WGS) reactor mixture (78% H2, 18.5% CO2, 2.9% CH4, 20 PPM CO). All the HT-PEM ECHP tests were performed under atmospheric conditions without any backpressure.

3.5 For wide-temperature range solid-state supercapacitor study

3.5.1 Fabrication of rGO electrodes

High quality water-dispersed graphene oxide (GO) was purchased from Graphenea Inc., Cambridge, MA with GO concentration of 4 mg mL⁻¹ and monolayer content of >95 %. For proper exfoliation of the GO, water-dispersed GO was sonicated for 30 minutes in a sonication bath. Afterwards, the GO solution was drop-cast on the surface of a Teflon® sheet and dried at room temperature overnight. The reason for using Teflon® sheet is to prevent the adherence of reduced graphene oxide (rGO) to the temporary substrate. Neewer PRO i-TTL xenon camera flash was employed for reduction of GO to rGO under ambient conditions. Gentec QE25ELPS-MB-INT-D0 light energy meter was used to measure the energy of camera flash which was in the range of 0.1-2 J cm⁻². A small explosion sound was heard after flashing the GO and the produced rGO
easily detached from the Teflon® surface afterwards. Color change from brown to black was indicated successful GO to rGO conversion. Sandwich type devices were made by packing the electrodes and membrane by means of temperature resistant Kapton® tape. Copper tape was used for collecting and passing charge from electrodes.

### 3.5.2 Electrochemical characterization

Electrochemical tests were performed on sandwich type devices made of rGO flash reduced electrodes and QPPSf-PBI electrolyte. GAMRY 1010E potentiostat was employed to perform the galvanostatic charge discharge (GCD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Kryo 560-16 controlled rate freezer was used to cool down the temperature from 25 to -70 °C. VWR standard oven was employed to test the device at high temperatures (up to 220 °C). Before all the temperature dependent tests, the device was held at the desired temperature for 10 min to reach the temperature equilibrium. EIS experiments were performed in the range of 100 kHz to 1 Hz. From CV curves, areal capacitance was calculated from equation 2:

\[ C_v = \frac{\int i \cdot dV}{v \cdot \Delta V} \quad (3.13) \]

In which, \( \Delta V \) is the potential window (V), \( i \) is the current density (A cm\(^{-2}\)) and \( v \) is the area of the active material (cm\(^2\)). From GCD plots, areal capacitance was measured by using the following equation:

\[ C_v = \frac{-i dt}{v \cdot dV} \quad (3.14) \]

In which, \( t \) is value of discharge time. Power (P) density values obtained by equation 4 and 5:

\[ P = \frac{E \times 3600}{\Delta t} \quad (3.15) \]
Chapter 4
Low-Resistant and Thermally Stable High-Temperature Polymer Electrolyte Membrane (HT-PEM) for Proton Exchange Membrane Fuel Cells (PEMFCs)

4.1 Introduction

HT-PEMFCs based on anhydrous HT-PEM provides several advantages over the LT-PEM. HT-PEM enable the operation of fuel cell above 120 °C. At elevated temperatures, low-cost H₂ fuel from SRM can be used because the electrocatalysts are more tolerant to CO and SO₂ pollutants.¹⁰¹,¹⁰² Furthermore, higher cell temperature enhances HT-PEMFC efficiency through better heat rejection from the cell caused by larger temperature gradients. The better heat rejection shrinks the sizeable radiator currently used in LT-PEMFC stacks for automotive applications.

With H₃PO₄-PC as electrode binder and a ceramic proton-conducting membrane (i.e., only a partial polymeric membrane electrode assembly was used), Kim and co-workers have shown peak power densities as high as 870 mW cm⁻² with oxygen and no humidification.⁶²,⁷⁶ To overcome PCs' conductivity shortcomings and the temperature stability limitation of PBI, we have prepared a new class of anhydrous proton conducting membranes based upon PC-PBI polymer blends doped with H₃PO₄.


Using the optimal blend of 50:50 PC-PBI, a fuel cell demonstration was carried out at the challenging temperature of 220 °C with an all-polymeric membrane electrode assembly (MEA). Therefore, the motivation for new HT-PEM for HT-PEMFCs was to comprehend how HT-PEM properties influence the performance parameters of HT-PEMFC operation, i.e., fuel cell polarization, stability, and operation.

4.2 Results and discussion

4.2.1 Preparation of H₃PO₄ doped 50:50 QPPSf-PBI membranes

In search of a better PC, initially, different AEMs (i.e., polycations) were tested for their suitability as HT-PEM. Three different AEMs, quaternary pyridinium polysulfone (QPPSf), quaternary ammonium poly (2,6-dimethyl 1,4-phenylene oxide), perfluorinated AEM from NREL were converted to PCs by immersing them in H₃PO₄ for two hours at room temperature. Figure 4.1 shows the in-plane proton conductivity at high temperatures and IEC values of different H₃PO₄ doped PCs and PBI. HT-PEM with other PC chemistries imbibed with H₃PO₄ demonstrated substantially smaller κ⁺⁺ values than commercially available H₃PO₄-PBI. The κ⁺⁺ values of PCs were attributed to the low IEC compared to PBI. It was inferred that the PCs had lower acid uptake and fewer ionic charges that are needed for promoting ionic conductivity. Though PCs showcase better acid retention than PBI, it is vital to increase PCs' acid uptake to improve κ⁺⁺ values. To improve the acid uptake and κ⁺⁺ of PCs, a new HT-PEM based on PC-PBI blend was prepared. From Figure 5.1, H₃PO₄-QPPSf had the closest κ⁺⁺ to that of H₃PO₄-PBI; hence, QPPSf was chosen to blend with PBI to fabricate the new HT-PEM.
**Figure 4.1.** a.) In-plane $\kappa_{H^+}$ and IEC$_B$ values for different H$_3$PO$_4$ doped PCs and PBI. b.) The chemical structures for PBI and PCs

**Figure 4.2** depicts the method to prepare the PC-PBI blends that resulted in mechanically robust, free-standing membranes. The scheme illustrates a pathway to yield stable solutions of chloromethylated Udel® polysulfone (CMPSf)-PBI, of varying ratios that can be further processed into free-standing membranes. The chloromethyl groups in CMPSf are converted into quaternary benzyl pyridinium cations (QPPSf) with a chloride counterion by immersing the membrane into 1 M pyridine reagent alcohol. It is important to note that blending 5wt% QPPSf in DMAc with 5wt% PBI, at any ratio, during membrane preparation immediately resulted in gelation.

Quaternary benzyl pyridinium cationic moieties was selected over quaternary benzyl trimethylammonium (or other alkyl ammoniums) because its aromatic structure has greater oxidative stability. The polyaromatic backbone and aromatic cation were employed to withstand the high-temperature environment of the cell with concentrated oxygen. During fuel cell operation, reactive oxygen species are generated at the cathode, and these species spur polymer degradation (with the worst-case scenario being at elevated temperatures, dry
conditions, and OCV). Different blends of PC-PBI membranes were prepared to identify the composition that would yield the best $\kappa_{H^+}$, while also satisfying stability constraints at temperatures above 200 °C and in the presence of water vapor. Furthermore, the all-polymer notation for this report's remainder infers that the materials have been imbibed with H$_3$PO$_4$ (unless otherwise noted).

**Figure 4.2.** Scheme to prepare QPPSf-PBI membrane blends that provide anhydrous, high-temperature proton conduction

### 4.2.2 Physical properties of QPPSf-PBI membranes

Raman spectroscopy (Figure 4.3a) and ATR-FTIR (Figure 4.3b) were used to identify the different chemical moieties in the H$_3$PO$_4$-QPPSf-PBI membrane and the non-acid doped QPPSf-PBI membrane. The peak at 1539 cm$^{-1}$ in the Raman spectra in the non-acid doped QPPSf-PBI membrane was ascribed to the imidazole group present in PBI. The peak at 1610 cm$^{-1}$ corresponded to the C-N$^+$ stretching in the pyridinium moiety. The FTIR peak at 2924 cm$^{-1}$ was attributed to the methylene group that tethered the cation to the poly (arylene ether
sulfone) backbone and the methyl groups in the isopropyl moiety in the poly (arylene ether sulfone) backbone. The FTIR peak at 1487 cm\(^{-1}\) came from the C-H stretching the arylene rings and the pyridinium cation.\(^{43-44}\) After immersing the membrane in H\(_3\)PO\(_4\), the ridge at 1539 cm\(^{-1}\) in the Raman spectra shifted to 1570 cm\(^{-1}\) because the H\(_3\)PO\(_4\) protonated the imidazole PBI to yield imidazolium.\(^{43-44}\) A broad FTIR peak in the range 2400-3000 cm\(^{-1}\) for the acid-doped in the QPPSf-PBI membrane was ascribed to the N-H stretching in the protonated PBI. Furthermore, a significant vibration at 956 cm\(^{-1}\) in the FTIR was observed and was attributed to the P=O in H\(_3\)PO\(_4\).\(^{43-44}\)

![Figure 4.3](image)

**Figure 4.3.** a.) Raman spectra of QPPSf-PBI with and without H\(_3\)PO\(_4\). b.) ATR-FTIR spectra of QPPSf-PBI with and without H\(_3\)PO\(_4\). Both Raman and FTIR spectra show the charged ionic moieties (e.g., pyridinium, imidazolium, and H\(_3\)PO\(_4\)) in the membranes.

### 4.2.3 H\(_3\)PO\(_4\) uptake and per base moiety and IEC values

**Table 4.1** reports the H\(_3\)PO\(_4\) uptake, H\(_3\)PO\(_4\) per base moiety (nH\(_3\)PO\(_4\) B\(^{-1}\)) in the membrane, and the ion-exchange capacity (IEC) values for PBI, QPPSf, and blends of QPPSf-PBI on a base moiety basis (IEC). The IEC of QPPSf in the chloride counterion form is 1.7 mequiv g\(^{-1}\) and for PBI (i.e., benzimidazole) is 6.5 mequiv g\(^{-1}\).\(^{57,60}\) IEC for the blend membranes
was found using weighted averages of the individual IEC values of PBI and QPPSf. The IEC of 50:50 QPPSf-PBI blend was 4.1 mequiv g⁻¹, and 60:40 QPPSf-PBI blend was 3.6 mequiv g⁻¹, the lowest IEC values among the blend membranes.

**Table 4.1.** Physical and mechanical properties of H₃PO₄ doped PBI, QPPSf, and QPPSf-PBI blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₃PO₄ uptake (%)</th>
<th>IEC (mequiv g⁻¹)</th>
<th>nH₃PO₄ B⁻¹</th>
<th>Ultimate tensile strength (MPa)ᵃ</th>
<th>Elongation at break (%)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBI</td>
<td>295</td>
<td>6.5</td>
<td>9.4</td>
<td>8.2</td>
<td>33</td>
</tr>
<tr>
<td>QPPSf</td>
<td>180</td>
<td>1.7</td>
<td>9.3</td>
<td>2.0</td>
<td>28</td>
</tr>
<tr>
<td>50:50 QPPSf-PBI</td>
<td>220</td>
<td>4.1</td>
<td>7.9</td>
<td>11.9</td>
<td>25</td>
</tr>
<tr>
<td>30:70 QPPSf-PBI</td>
<td>264</td>
<td>5.0</td>
<td>5.9</td>
<td>4.6</td>
<td>27</td>
</tr>
<tr>
<td>40:60 QPPSf-PBI</td>
<td>235</td>
<td>4.6</td>
<td>6.6</td>
<td>8.4</td>
<td>33</td>
</tr>
<tr>
<td>60:40 QPPSf-PBI</td>
<td>254</td>
<td>3.6</td>
<td>6.8</td>
<td>10.2</td>
<td>28</td>
</tr>
</tbody>
</table>

ᵃMeasurements conducted at ambient conditions: 25 °C and ~50% relative humidity

The H₃PO₄ uptake of QPPSf was 180%, whereas, for PBI, it was 295%. The higher acid uptake of PBI was because of the higher IEC compared to QPPSf. The 50:50 QPPSf-PBI blend had the lowest acid uptake among the blended membranes. The 50:50 QPPSf-PBI blend had an H₃PO₄ uptake of 220%, and this corresponded to a 7.9 H₃PO₄ B⁻¹, which was smaller than PBI (9.4 H₃PO₄ B⁻¹) and QPPSf (9.3 H₃PO₄ B⁻¹). The 50:50 QPPSf-PBI blend had a smaller nH₃PO₄ B⁻¹ value because its IEC was 2.4x higher than pristine QPPSf, but its H₃PO₄ uptake concerning QPPS was only 1.2x greater. The high value of the nH₃PO₄ B⁻¹ for PBI was due to its large acid uptake. The lower acid uptake and higher nH₃PO₄ B⁻¹ of 50:50 QPPSf-PBI blend made it the best blend ratio.

### 4.2.4 Mechanical properties

**Table 4.1** also reports the tensile strength and elongation at break of the 50:50 QPPSf-PBI, QPPSf, and PBI. **Figure 4.4a** and **Table 4.4b** show and report the results from tensile test
measurements of the other QPPSf-PBI polymer blends at 25 °C. 50:50 QPPSf-PBI had the highest mechanical strength among all the different blends. However, the tensile test measurement of 50:50 QPPSf-PBI membrane at 220 °C (see Figure 4.4b) showed a substantial loss in mechanical strength of the membrane (from 11.9 MPa to 2 MPa). The excellent mechanical strength of the 50:50 QPPSf-PBI blend at 25 °C may be due to the phase separation of the different polymers at the micron-size level observed via electron microscopy (see Figure 4.5). The phase separation seen in the electron micrograph partially explains why the blended membranes have slight cloudiness.

**Figure 4.4.** Stress-strain curves of PBI, QPPSf, and QPPSf-PBI membranes a.) at 25 °C and ~50% relative humidity. b.) 220 °C
The tensile properties of the membranes will depend on the amount of phosphoric acid present in the membranes and other factors such as temperature and humidity. The variation of ultimate tensile strength with acid uptake (%) of the membranes is shown in Figure 4.6. The mechanical strength of the 50:50 QPPSf-PBI was the highest, which may be attributed to the lower acid uptake of this membrane variant. Improving the toughness of the membrane is vital for HT-PEMFCs because it can better tolerate backpressure applied to the anode and/or the cathode without concern of puncturing the membrane that would lead to catastrophic cell behavior (e.g., mixed overpotentials).

**Figure 4.5.** Electron micrograph of 50:50 QPPSf-PBI with chloroplatinate anions
4.2.5 Thermal stability, water resiliency, and acid retention

To understand the acid retention properties of QPPSf, PBI, and QPPSf-PBI blends, the PCs' weight loss was studied at two different testing conditions. First, the weight loss of PCs was 220 °C/0% RH up to 48 hours. Additionally, the best blend membrane 50:50 QPPSf-PBI, QPPSf, and PBI were studied for the water resiliency at 80°C/40% RH up to 48 hours.

Figure 4.7a reports the weight loss of the PBI, QPPSf, and 50:50 QPPSf-PBI at 220 °C up to 48 hours. PBI lost 36% of its weight during that time within the first two hours, whereas QPPSf and 50:50 QPPSf-PBI lost 15% and 7% of their initial weight, respectively. At the end of the 48 hour test, PBI and QPPSf suffered 40% and 17% weight loss, while 50:50 QPPSf-PBI lost only lost 8% of its initial weight. The high acid loss of PBI was due to the excess free acid imbibed into its system because of its larger IEC whilst having only two basic sites per repeat unit of the polymer. Figure 4.7b reports the weight loss of the other QPPSf-PBI polymer blends at 220 °C/0% RH for 48 hours, and this Figure conveys that the other polymer blends only lose
17% to 20% of their initial weight during the thermal stability test. This result indicates that the different polymer blend membranes yield similar thermal stability to the QPPSf variant and do not give the same level of stability as the 50:50 QPPSf-PBI variant.

Finally, 50:50 QPPSf-PBI has assessed under the condition of 80 °C and 40% relative humidity (RH) by placing it in a BekkTech conductivity cell (4-point platinum probe with PTFE housing) situated in fuel cell hardware under humidity control (see Figure 4.7c). This condition was assessed because the 50:50 QPPSf-PBI should be flexible for fuel cell conditions at elevated temperatures and dry conditions (220 °C and 0% RH) and lower temperatures with moderate humidity (e.g., 80 °C and 40% RH). At the lower temperature condition with humidity, it is well-known that water can supplant H$_3$PO$_4$ resulting in an $\kappa$ drop due to the loss of electrolyte. Figure 4.7c shows that 50:50 QPPSf-PBI retained 93% of its weight over 48 hours at 80 °C and 40% RH, while PBI only retained 65% of its weight (i.e., a 35% weight loss). QPPSf retained 82% of its weight. The excellent stability at 80 °C/40% RH for 50:50 QPPSf-PBI signifies a synergistic effect between PBI and the PC that assists H$_3$PO$_4$ retention in the presence of water vapor. Overall, 50:50 QPPSf-PBI shows excellent thermal stability (up to 220 °C) and resilience in the presence of water vapor (80 °C and 40% RH) making it a promising candidate for HT-PEMFCs that can operate robustly under a wide-range of temperatures and levels of humidification.
Figure 4.7. a.) Percentage weight loss of membranes at 220°C / 0% RH. b.) Percentage weight loss of QPPSf-PBI membrane blends at different ratios at 220 °C/0% RH. c.) Percentage weight loss of membranes at 80°C/ 40% RH

Figure 4.8a shows the TGA curves for an undoped and H₃PO₄ doped 50:50 QPPSf-PBI and pristine QPPSf membranes to identify the optimal polymer's thermal stability limitations blend and to verify weight loss results observed in Figure 4.7a. The pristine 50:50 QPPSf-PBI exhibited two regions of weight loss: i.) between 220 – 275 °C due to the quaternary benzyl pyridinium group degradation, and ii.) ≥ 450 °C - which was attributed to the degradation of the polymer backbones. The pristine QPPSf, however, showed quaternary benzyl pyridinium degradation starting at 200 °C. Marwani et al. have been demonstrated that pristine PBI is stable
up to 300 °C\textsuperscript{106,107}. Figure 4.8b shows the TGA of the H\textsubscript{3}PO\textsubscript{4} doped 50:50 QPPSf-PBI membrane, and this TGA curve showed four regions of weight loss: i.) the first stage between 100 – 160 °C was due to evaporation of residual water; ii.) the second region between 160 – 250 °C was due to some H\textsubscript{3}PO\textsubscript{4} evaporation in addition to conversion of H\textsubscript{3}PO\textsubscript{4} to triphosphoric acid, pyrophosphoric, or polyphosphoric acid that releases water;\textsuperscript{108} and iii.) the third and fourth stages between 300 - 450 °C and 450 – 700 °C are due to polymer backbone degradation, respectively (determined from the TGA trace of the undoped 50:50 QPPSf-PBI membrane). Overall, the TGA for the H\textsubscript{3}PO\textsubscript{4} doped 50:50 QPPSf-PBI membrane showed about 7% weight loss up to 250 °C, showcasing that the HT-PEMs are stable up to 250 °C (mostly due to excess H\textsubscript{3}PO\textsubscript{4} evaporation and some water evaporation).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_8}
\caption{TGA of a.) undoped QPPSf and 50:50 QPPSf-PBI and b.) undoped 50:50 QPPSf-PBI and H\textsubscript{3}PO\textsubscript{4} doped QPPSf-PBI}
\end{figure}

To further investigate if the quaternary benzyl pyridinium groups in the 50:50 QPPSf-PBI blend and QPPSf membranes without acid were stable at 220 °C, both pristine QPPSf and 50:50 QPPSf-PBI membrane samples were exposed to 220 °C for 48 hours. After this thermal treatment, the membranes were imbibed with H\textsubscript{3}PO\textsubscript{4}, and the in-plane $\kappa_{H^+}$ was measured at 25
°C, 50 °C, and 100 °C. The in-plane $\kappa_{H^+}$ values of these membranes after thermal treatment were compared against existing data sets of the membranes not exposed to 220 °C for 48 hours. 

**Figure 4.9** demonstrates that the 50:50 QPPSf-PBI blend had much better thermal stability over QPPSf by itself. The TGA data and weight loss data support that the 50:50 QPPSf-PBI membrane blend could be stable at the fuel cell operating temperature of 220 °C. But this temperature may cause slow degradation of quaternary benzyl pyridinium over time.

![Graph](image1)

**Figure 4.9.** a.) Weight loss of pristine QPPSf and 50:50 QPPSf-PBI at 220 °C b.) In-plane $\kappa_{H^+}$ of H$_3$PO$_4$ doped pristine QPPSf and 50:50 QPPSf-PBI and H$_3$PO$_4$ doped QPPSf and 50:50 QPPSf-PBI after heat treatment at 220 °C for 48 hours

### 4.2.6 $\kappa_{H^+}$ Conductivity and Microwave Dielectric Spectroscopy

Proton conductivity ($\kappa_{H^+}$) is a critical HT-PEM property for the HT-PEMFCs because the ohmic overpotential is linearly proportional to the area specific resistance (ASR) for any fuel cell device. The ASR is inversely proportional to the proton conductivity (i.e., $\text{ASR} = \text{membrane thickness}/\kappa_{H^+}$). At high current densities, a high ASR can severely compromise HT-PEMFC efficiency.

**Figure 4.10a** shows the anhydrous $\kappa_{H^+}$ of PBI, QPPSf, and 50:50 QPPSf-PBI from 25 °C to 240 °C. **Figure 4.10b** presents the anhydrous $\kappa_{H^+}$ of the other QPPSf-PBI blends. A very high
κ_{H^+} value, 0.3 S cm^{-1}, was attained with the 50:50 QPPSf-PBI at 240 °C. Conversely, a commercially available PBI membrane displayed about half the κ_{H^+} (0.1 S cm^{-1}) at 180 °C compared to the 50:50 QPPSf-PBI blend. Additionally, the PBI membrane experienced a drop in κ_{H^+} at temperatures above 180 °C and eventual complete loss in κ_{H^+} when held at temperatures above 180 °C for a few minutes. Similarly, QPPSf membrane gave a maximum κ_{H^+} of 0.09 S cm^{-1} at 200 °C (less than half of the 50:50 QPPSf-PBI blend); and like PBI, QPPSf’s κ_{H^+} severely deteriorated when increasing the temperature to 200 °C. It is essential to point out that QPPSf swelled quite a bit during the H_3PO_4 imbibing step, which occurred at 25 °C. Immersion of the QPPSf in 85 wt% H_3PO_4 at 120 °C for one hour resulted in membrane dissolution. Plus, the QPPSf had a significant mass uptake of 180% after immersing in 85 wt% H_3PO_4 at 25 °C. Although a lower IEC of QPPSf may curtail swelling when doping it with H_3PO_4, it will have the undesired consequence of lower κ_{H^+} values because of the smaller concentration of fixed ionic groups polymer backbone.

To ensure that the κ_{H^+} values were not inflated due to residual H_3PO_4 being present at the membrane surface, the in-plane and through-plane κ_{H^+} of the 50:50 QPPSf-PBI was compared (see Figure 4.11a), alongside of measuring the area specific resistance (ASR) during HT-PEMFC operation under pure H_2/O_2 (see Figure 4.11b). The through-plane κ_{H^+} is about 20% lower than in-plane κ_{H^+} due to contact resistances at the electrode-electrolyte interface\textsuperscript{109}. The membrane may also have some anisotropy when it comes to proton conduction. Figure 4.11b shows that 50:50 QPPSf-PBI exhibited very low ASR at high temperatures, showcasing that it can withstand high current densities without compromising HT-PEMFC efficiency.
Figure 4.10. a.) In-plane proton conductivity ($\kappa_{H^+}$) for PBI, QPPSf, and 50:50 QPPSf-PBI (Note: the error bars are tiny in the traces.) b.) dielectric constant ($\varepsilon'$) for these samples as a function of microwave frequency.
Figure 4.11. a.) Comparison of in-plane and through-plane $\kappa_{H^+}$ for 50:50 QPPSf-PBI membrane b.) Variation of ASR with temperature measured during HT-PEMFC operation under pure H$_2$/O$_2$ (ASR = membrane thickness/$\kappa_{H^+}$)

Figure 4.12 shows the activation enthalpy calculation plot for QPPSf, PBI, and 50:50 QPPSf-PBI membranes. The activation enthalpy and pre-exponential values are reported in Table 4.2. It was observed that 50:50 QPPSf-PBI had the highest activation enthalpy compared to PBI and QPPSf. This might be due to the increased network frustration of protons in the blended membrane and phosphoric acid condensation to pyrophosphoric acid at higher temperatures.
Figure 4.12. Arrhenius plot of ion conduction for PBI, QPPSf, and 50:50 QPPSf-PBI membranes to attain activation enthalpy values and pre-exponential values.

Table 4.2. Pre-exponential and activation enthalpy values of PBI, QPPSf, and 50:50 QPPSf-PBI membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-exponential ($\kappa_0$) (mS cm$^{-1}$)</th>
<th>Activation enthalpy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50:50 QPPSf-PBI</td>
<td>912</td>
<td>14.8</td>
</tr>
<tr>
<td>PBI</td>
<td>229</td>
<td>6.3</td>
</tr>
<tr>
<td>QPPSf</td>
<td>128</td>
<td>12.0</td>
</tr>
</tbody>
</table>

To better understand the proton conductivity properties of the different membranes, the dielectric constant ($\varepsilon'$) of the membranes was measured using microwave dielectric spectroscopy. Chang *et al.* used microwave dielectric spectroscopy to examine the interplay of water content, $\varepsilon'$, and ion sorption in hydrated polymers. They reported that a fully hydrated PFSA (Nafion®) had an $\varepsilon'$ near 20, and this value was approximately a quarter of the value for water. Figure 4.13a reports the $\varepsilon'$ response of the membranes as a function of frequency. Our analysis focused on the low-frequency regime of Figure 4.13a as the ion dipoles in this frequency range are in phase with the microwave signal. The dielectric constant $\varepsilon'$, for PBI was nearly a factor of two more significant than that of QPPSf. Blending PBI into QPPSf at 50 to
70% caused an increase in the $\varepsilon'$ values and the $\varepsilon'$ of those materials were close to that of PBI. The measured $\varepsilon'$ was taken to be proportional to the concentration of mobile ion dipoles in the polymer host, which is a proxy for the quantity of nomadic $\text{H}_3\text{PO}_4$ groups present. **Figure 4.13b** shows that the $\varepsilon'$ values increase when the membranes contain more $\text{H}_3\text{PO}_4$. Larger populations of mobile $\text{H}_3\text{PO}_4$ in the membrane will help enable higher $\kappa_{\text{H}^+}$ values.

**Figure 4.13.** a.) Dielectric constant ($\varepsilon'$) for these samples as a function of microwave frequency. b.) Variation of dielectric constant with acid uptake for QPPSf, PBI, and QPPSf-PBI blends

Hydrogen bonding, structural proton diffusion, and condensation of $\text{H}_3\text{PO}_4$ to pyrophosphoric acid strongly influence $\kappa_{\text{H}^+}$ in $\text{H}_3\text{PO}_4$ electrolytes at higher temperatures.\textsuperscript{56,111} Plus, residual water present in the $\text{H}_3\text{PO}_4$ doped membranes can compromise $\kappa_{\text{H}^+}$.\textsuperscript{112} It is important to note that PBI is a strong Brønsted base and $\text{H}_3\text{PO}_4$ protonates the nitrogen in benzimidazole leading to a reduction in hydrogen bond frustration and a lower $\kappa_{\text{H}^+}$ in comparison to neat phosphoric acid.\textsuperscript{56,101} In a PC host, the tethered cation cannot accept a proton; thus, hydrogen bond frustration is higher for PC doped with $\text{H}_3\text{PO}_4$ than PBI doped with $\text{H}_3\text{PO}_4$. It would seem that $\text{H}_3\text{PO}_4$ doped PCs are better suited for promoting $\kappa_{\text{H}^+}$ because they foster more hydrogen bonding frustration, but it is essential to consider that most anion exchange membranes
which are used for these materials HT-PEMs when doped with H₃PO₄ have lower IEC values when compared to PBI. Therefore, they tend to have smaller acid uptake values. The reduction in acid uptake prevents large κₜH⁺ values despite more significant hydrogen bonding frustration by the polycation. Recall that ionic conductivity scales linearly with the concentration of ionic charge carriers. By blending PC with PBI, a compromise was struck as the PC promotes more significant hydrogen bond frustration, while the PBI yields greater H₃PO₄ uptake. The 50:50 QPPSf-PBI had the highest nH₃PO₄ B⁻¹ value (12.6) of all the membrane samples, and this attribute is partially responsible for the high κₜH⁺ value observed.

**Figure 4.14** shows the mechanism of κₜH⁺ in QPPSf-PBI membrane blends. The model drawn was inspired by Dippel et al.¹¹³. Because of iso-neutrality constraints, H₂PO₄⁻ pairs with the pyridinium cation in QPPSf, leaving behind a free proton that can shuttle along with the excess H₃PO₄ network through the Grotthuss mechanism. However, the Brønsted base in PBI interacts with the proton in H₃PO₄, forming an acid-base interaction leaving no free protons behind. This not only reduces the structural diffusion of protons but also reduces the condensation of phosphoric acid. This is one reason why PBI doped H₃PO₄ cannot achieve the same κₜH⁺ as neat H₃PO₄ (i.e., less hydrogen bonding frustration and poorer structural diffusion).

Furthermore, higher temperatures above 200 °C lead to condensation of H₃PO₄ to pyrophosphoric acid.¹¹² In the case of the QPPSf-PBI blend, increased hydrogen network frustration and pyrophosphoric acid formation at elevated temperatures are believed to be the reasons why high κₜH⁺ values are attained at temperatures above 180 °C. The rate of H₃PO₄ condensation to pyrophosphoric acid may occur faster than the evaporation of excess H₃PO₄ in the polymer host. Hence, the acid electrolyte is retained in the polymer blend matrix for promoting κₜH⁺ and why the blended material can stabilize at temperatures of 200 °C.
A well-known challenge in HT-PEMFCs relates to their thermal stability and acid retention when operating the cell above 180 °C. Moving to higher cell temperatures can improve the redox kinetics in the HT-PEMFC while also creating a larger temperature gradient between the cell and the external environment for heat rejection. Yan and co-workers reported an impressive alkaline anion exchange membrane fuel cell performance of 920 mW cm$^{-2}$ with H$_2$-clean air by pushing the cell temperature from the conventional 80 °C to 90 °C. Figure 4.15a shows the loss in $\kappa_{H^+}$ for PBI, QPPSf, and 50:50 QPPSf-PBI membranes during three thermal
cycles in the temperature range of 100 to 250 °C. For the first cycle, the temperature was ramped to 250 °C. At the end of that cycle, the temperature was returned to 100 °C followed by ramping it back up to 250 °C. 50:50 QPPSf-PBI experienced a 20% drop in $\kappa_{H^+}$ after the first cycle and retention of $\kappa_{H^+}$ into the third cycle. PBI and QPPSf, on the other hand, ceased $\kappa_{H^+}$ after the first thermal cycle. To further assess the thermal stability of the 50:50 QPPSf-PBI membrane, $\kappa_{H^+}$ was monitored at 220 °C and 0% RH, a challenging condition, over 96 hours (see Figure 4.15b). Similar to Figure 4.15a, Figure 4.15b shows a 20% drop in $\kappa_{H^+}$ over 20 hours followed by stable $\kappa_{H^+}$ of 0.24 S cm$^{-1}$ over the next 76 hours. At the challenging 220 °C temperature, it appears that there is some excess H$_3$PO$_4$ evaporation from the 50:50 QPPSf-PBI host. After that minor acid loss, this membrane blend stabilizes while still providing a high $\kappa_{H^+}$ of 240 mS cm$^{-1}$.

![Figure 4.15a](image1.png)

**Figure 4.15.** a.) In-plane $\kappa_{H^+}$ for PBI, QPPSf, and PBI – QPPSf (50:50) blend during temperature cycling from 100 – 250 °C and 0% RH. For each cycle, the temperature was brought back to 100 °C and increased up to 250 °C. b.) In-plane $\kappa_{H^+}$ for QPPSf-PBI 50:50 for 96 hours.

An important PEM property is its ability to foster adequate proton conductivity across a wide temperature range. **Figure 4.16a** presents the proton conductivity of the QPPSf-PBI 50:50 from -70 to 220 °C. For the temperature range between 25 to 220 °C, the $\kappa_{H^+}$ increase was
commensurate with rising temperature values. As the temperature increases, the structural diffusion of protons in the hydrogen-bonded network becomes greater. Surprisingly, the QPPSf-PBI 50:50 displayed higher conductivity at -20 °C versus 25 °C. The ionic conductivity measurements were performed under ambient laboratory settings, and it is known that residual water in H₃PO₄ disrupts the hydrogen-bonded network hindering facile ionic conductivity. Therefore, cooling the environment down to -20 °C reduced/eliminated the partial pressure of water in the environment, resulting in an increase in the QPPSf-PBI 50:50’s κH⁺ compared to the value at 25 °C. It is worth noting that pure H₃PO₄ is solid at room temperature. Still, this acid imbibed into the polycation-PBI host depresses its freezing point enabling κH⁺ as high as 50 mS cm⁻¹ at -20 °C. Reducing the temperature from -20 to -70 °C severely compromises κH⁺. The reduction in κH⁺ below -20 °C could be realized from the differential scanning calorimetry (DSC) for QPPSf-PBI 50:50 (Figure 4.16b). Figure 4.16b shows two peaks, one at 0 °C and the other at -15 °C. The former peak could be corroborated by reducing the partial pressure of water in the environment. In contrast, the last peak was observed due to complete immobilization of phosphate anion due to crystallization.

The proton conductivity at -70 °C is 0.01 mS cm⁻¹. Although this value is at least a 4-order magnitude reduction of the maximum κH⁺ observed, the value of 0.01 mS cm⁻¹ for conductivity still rivals some lithium salt containing polymer electrolytes for lithium-ion batteries. It will be shown later that the supercapacitor device can still operate at the extreme low temperature of -70 °C with the QPPSf-PBI 50:50 despite the high ohmic penalty. Finally, it is essential to note that this proton exchange membrane displayed repeatable conductivity values (n=3 repeat traces plotted in Figure 4.16a) when evaluating the temperature across the range of -70 to 220 °C. During each cycle, the temperature was ramped up from room temperature to 220
°C and cooled to -70 °C and ramped up to 220 °C. Individual temperature points were held while performing EIS measurements. In-plane proton conductivity loss and the membranes' stability in the temperature range were assessed by performing cycling tests.

**Figure 4.16** a.) In-plane $\kappa_{H^+}$ of the $\text{H}_3\text{PO}_4$ imbibed QPPSf-PBI membrane in the temperature range of -70 to 220 °C. b.) DSC of $\text{H}_3\text{PO}_4$-QPPSf-PBI. Two peaks were observed at 0 °C and -15 °C. The peak at 0 °C was due to residual water freezing within the sample. The other peak was due to the freezing of $\text{H}_3\text{PO}_4$ in the sample.

To determine if CMPSf and PBI could crosslink, the prepared 50:50 CMPSf-PBI membrane blend was immersed in DMAc, DMSO, NMP, and DMF. The 50:50 CMPSf-PBI blend dissolved in each of the solvents (5 wt%; see **Figure 4.17**). Furthermore, the $\text{H}_3\text{PO}_4$ doped 50:50 CMPSf-PBI $\kappa_{H^+}$ and thermal stability were compared against QPPSf-PBI (Figure 4.18). The 50:50 QPPSf-PBI displayed better acid retention and higher $\kappa_{H^+}$ compared to 50:50 CMPSf-PBI because it contained pyridinium moieties that promoted acid retention. The retention of acid improved $\kappa_{H^+}$ – in particular at higher temperatures. If the 50:50 CMPSf-PBI were crosslinked, which could occur by the chloromethyl groups reacting with benzimidazole,\textsuperscript{51} it would contain tethered benzimidazolium cation moieties that would retain acid and promote $\kappa_{H^+}$ like 50:50 QPPSf-PBI. The fact that CMPSf-PBI was soluble in the solvents mentioned above and has low
acid retention and $\kappa_{H^+}$ when doped with $H_3PO_4$ signified that CMPSf and PBI were not crosslinked.

![Figure 4.17. Solubility test for CMPSf-PBI in different organic solvents](image)

**Figure 4.17.** Solubility test for CMPSf-PBI in different organic solvents

**Figure 4.18.** a.) Percentage weight loss of 50:50 CMPSf-PBI and 50:50 QPPSf-PBI for 48 hours at 220 °C. b.) In-plane $\kappa_{H^+}$ of 50:50 CMPSf-PBI and 50:50 QPPSf-PBI

From **Figures 4.15a, 4.15b, and Figures 4.16a**, it is self-evident that the 50:50 QPPSf-PBI displayed reasonably good thermal stability at 220 °C in terms of acid retention and $\kappa_{H^+}$ up to two days. The excellent acid retention and $\kappa_{H^+}$ at 220 °C for 48 hours was attributed to the cationic group in the PC anchoring the phosphate type anions preventing $H_3PO_4$ evaporation, which occurs in PBI membranes. Additionally, there appears to be a combined effect between
PBI and QPPSf that prevents excess swelling of the membrane when incorporating H₃PO₄, resulting in enhanced thermal stability and improves kH⁺. Recall that the QPPSf by itself swelled quite a bit when comprising H₃PO₄. Taking this membrane variant above 200 °C resulted in further swelling and eventual dissolution. We speculate that the synergistic effect of PBI with the QPPSf PC arises from the mixture of different cation-anion pairs and acid-base pairs in the H₃PO₄ network across the polymer host. The cation-anion teams facilitate H₃PO₄ retention at high temperatures and more significant hydrogen bonding frustration – an essential property for structural proton diffusion. The presence of PBI aids in greater H₃PO₄ uptake and a higher ε’ for the membrane. Another consideration for the excellent acid retention of 50:50 QPPSf-PBI is due to the condensation of H₃PO₄ to pyrophosphoric acid at 220 °C.¹¹² These high molecular weight acids are less volatile and cannot evaporate at 220 °C.

Regarding the below room temperature proton conductivity, there is no literature available on H₃PO₄ doped polycations and sparse reports on H₃PO₄-PBI. As previously stated, pure H₃PO₄ is solid at room temperature. Mixing this acid with the polycation-PBI polymer host disrupts the hydrogen-bonded network in H₃PO₄, preventing it from becoming stable at low temperatures. With this effect, it is possible to maintain structure proton diffusion within the membrane and proton conductivity at depressed temperatures.

### 4.2.8 HT-PEMFC performance, stability, and CO tolerance

Using the newly fabricated HT-PEM as membrane separator, 50:50 QPPSf-PBI, the HT-PEMFC performance was evaluated. The electrodes in the membrane electrode assembly (MEA) contain ionomer binder, which usually is similar to that of the membrane separator. By using 50:50 QPPSf-PBI as electrode binder and membrane separator, the HT-PEMFC performance was evaluated. Figure 4.19 shows the polarization curve using 50:50 QPPSf-PBI as membrane
and ionomer binder in fabricating the MEA. Due to the large acid uptake in the electrodes, significant mass transfer resistance hindered the reactant gas delivery to the electrocatalyst surface. Thus, a peak power density of 60 mW cm\(^{-2}\) was only attained. To further improve the fuel cell performance, QPPSf was used as electrode binder, while 50:50 QPPSf-PBI was used as the membrane separator. Figure 4.19 shows a polarization curve using a 50:50 QPPSf-PBI membrane and ionomer binder in the GDEs compared to a 50:50 QPPSf-PBI membrane and a QPPSf ionomer binder only in the GDE. Due to lower acid uptake of QPPSf, compared to that of 50:50 QPPSf-PBI (see Table 4.1), three-fold better performance of HT-PEMFC was at the same temperature obtained. Hence, removing PBI from the electrode reduces the electrodes' mass transfer resistance because there is less H\(_3\)PO\(_4\) present that obfuscates reactant gas delivery.

![Figure 4.19](image)

**Figure 4.19.** Fuel cell performance of 50:50 QPPSf-PBI membrane with 50:50 QPPSf-PBI (black) and QPPSf (red) as the ionomer binders. The catalyst loading for the MEAs was 0.5 mg\(\text{Pt}\) cm\(^{-2}\). The cell was operated at 180 °C with 0 kPa backpressure for dry \(\text{H}_2/\text{O}_2\)

**Figure 4.20** gives the HT-PEMFC polarization curve at 220 °C and 60 kPa of back pressure with 50:50 QPPSf-PBI membrane featuring GDEs that use a QPPSf ionomer binder and
platinum (Pt) nanoparticle electrocatalyst decorated on higher surface area carbon (0.5 mg Pt cm$^{-2}$). The polarization behavior was examined initially for dry H$_2$/O$_2$ and H$_2$/air. The peak power density values for H$_2$/O$_2$ were 687 mW cm$^{-2}$ and for H$_2$/air, it was 250 mW cm$^{-2}$. The H$_2$/O$_2$ values were competitive with the 2016 and 2018 Los Alamos National Laboratory peer-reviewed reports that showed 870 mW cm$^{-2}$ at 240 °C with a ceramic membrane and PC binder and 800 mW cm$^{-2}$ at 180 °C with a PC membrane and binder (note: both of these demonstrations were with H$_2$/O$_2$).

![Figure 4.20. Fuel cell polarization curve with H$_2$/O$_2$ and H$_2$-CO/O$_2$ with 50:50 QPPSf-PBI membrane with QPPSf GDEs (0.5 mg$_{Pt}$ cm$^{-2}$) 220 °C/0% RH with 60 kPa of back pressure on both the anode and cathode.](image)

Using electrochemical impedance spectroscopy (EIS; see Figure 4.21a), the high-frequency resistance (HFR) was 0.08 to 0.015 Ω·cm$^2$ at 220 °C, as shown in Table 5.3, signaling that the 50:50 QPPSf-PBI membrane can withstand a high current density with a small ohmic overpotential. For example, 20 mV ohmic overpotential would occur if the cell were operated near 2 A cm$^{-2}$, which was near the peak power density for this H$_2$/O$_2$ demonstration. However,
the peak power density occurred near 0.3 to 0.35 V showing about 600 mV of polarization.

**Figure 4.21a** demonstrates a 0.05 Ω-cm$^2$ to 0.075 Ω-cm$^2$ charge-transfer resistance when operating the cell at different current density values. These values are substantially higher than the HFR (due to ohmic resistances) in the cell and highlight that the HT-PEMFC’s performance is primarily reaction kinetics limited. A drawback to H$_3$PO$_4$ doped polymers for HT-PEMFCs is phosphate type anion adsorption to electrocatalyst surfaces that block sites for reactant adsorption and hindering reaction kinetics.$^{116,117}$ From **Figure 4.21b**, a higher charge-transfer resistance was observed when the cell was operated at 220 °C with H$_2$/air, while the HFR remained similar to that of H$_2$/O$_2$. The considerable charge-transfer resistance was correlated to the lower availability of oxygen and sluggish reaction kinetics of electrodes in the presence of air. **Table 4.3** shows the comparison of HFR and charge-transfer resistance under oxygen and air as oxidants and H$_2$ as fuel.

![Figure 4.21](image)

**Figure 4.21.** Nyquist plots of 50:50 QPPSf-PBI membrane with QPPSf electrodes at 220 °C/0% RH for a.) H$_2$/O$_2$ b.) H$_2$/air
Table 4.3. Sources of resistance deduced from Nyquist plots of 50:50 QPPSf-PBI membrane with QPPSf electrodes at 220 °C/0% RH for different oxidants

<table>
<thead>
<tr>
<th>Cell voltage (V)</th>
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<th></th>
<th>Oxygen</th>
<th></th>
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</thead>
<tbody>
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<td>R_{HF}</td>
<td>R_{ct}</td>
<td>R_{HF}</td>
<td>R_{ct}</td>
</tr>
<tr>
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<td>0.115</td>
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<td>0.008</td>
<td>0.040</td>
<td>0.008</td>
<td>0.11</td>
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Figure 4.22a directly compares the fuel cell performance of an HT-PEMFC with different membrane separators: 50:50 QPPSf-PBI, PBI, and QPPSf membranes. This comparison was carried out at 180 °C and 0 kPa back pressure to ensure the membranes were stable for attaining polarization curves. Figure 4.22a clearly shows that the 50:50 QPPSf-PBI membrane blend gave superior performance over the other membrane separators. It is essential to note the MEAs for the 50:50 QPPSf-PBI and QPPSf demonstrations used QPPSf ionomer as the electrode binder. The PBI demonstration used PBI as the electrode ionomer binder. The 2.5x higher power density for the 50:50 QPPSf-PBI blend membrane separator was attributed to its higher ionic conductivity resulting in a lower ohmic drop. The higher ionic conductivity was substantiated by, the lower HFR of 50:50 QPPSf-PBI membrane observed in Figure 4.22b from EIS experiments during the HT-PEMFC tests (note: the membrane thicknesses for each of these fuel cell runs ranged from 36 μm to 42 μm, and hence it is the conductivity of the membrane and not membrane thickness for influencing the HFR).
Figure 4.22. a.) Fuel cell performance b.) Nyquist plots of 50:50 QPPSf membrane with QPPSf ionomer binder, PBI membrane with PBI ionomer binder, and QPPSf membrane with QPPSf ionomer binder at 180 °C with 0 kPa backpressure for dry H₂/O₂.

Figure 4.23a depicts the HT-PEMFC performance at different temperatures. Figure 4.23b shows the polarization curves are iR corrected and show that the redox kinetics are increasing when moving the cell to higher temperatures, which is another reason justifying higher temperature operation. Our future plans to improve the performance of HT-PEMFCs with the 50:50 QPPSf-PBI membrane will pursue tethered phosphonic acid groups to polymer backbones for the electrode ionomer binder used in electrode layers, studied in Chapter 5. Tethering the phosphonate groups to the polymer chain is anticipated reduce phosphate type anion adsorption to the electrocatalyst surface. Plus, Eliminating H₃PO₄ into the electrode that is anticipated to enhance the reactant mass transfer.
Figure 4.23. a.) Polarization curves for QPPSf-PBI 50:50 membrane with QPPSf ionomer binder at different temperatures and no back pressure applied. b.) iR-corrected polarization curves for QPPSf-PBI 50:50 membrane with QPPSf ionomer binder to varying temperatures with HFR values at each temperature are mentioned at the end of each turn.

As previously mentioned, HT-PEMFCs can tolerate CO in the H₂ fuel stream and thus enables the use of low-cost H₂ fuel. Hence, an HT-PEMFC demonstration was carried out with a blend of 75% H₂ and 25% CO as the fuel (see Figure 4.20). This fuel composition reflects a from methanol reforming. The peak power density for H₂-CO/O₂ was 440 mW cm⁻². Figure 4.24 compares the Nyquist plots for H₂/O₂ and H₂-CO/O₂. It is clear from this Figure that the charge-transfer kinetics increase by almost a factor of 2, resulting in the near 35% drop in fuel cell performance. CO present in the fuel stream dilutes the hydrogen reactant in addition to blocking the platinum catalyst surface. It is important to note that the HFR for the H₂-CO/O₂ was about the same (10 to 15 mΩ-cm²) as H₂/O₂, indicating that the CO did not impact the membrane’s resistance.
Figure 4.24. Nyquist plots of 50:50 QPPSf-PBI membrane with QPPSf electrodes at 220 °C/0% RH for H\textsubscript{2}/O\textsubscript{2} (closed circle) and H\textsubscript{2}-CO/O\textsubscript{2} (open circle)

A 24 hour stability evaluation was performed for the HT-PEMFC with a 0.4 V voltage hold and monitoring cell current density at 220 °C and 0% RH (see Figure 4.25). During the stability assessment, the cell was initially operated on H\textsubscript{2}/O\textsubscript{2} for 2 hours, switched to H\textsubscript{2}-CO/O\textsubscript{2} for 6 hours, and then switched back to H\textsubscript{2}/O\textsubscript{2} for 16 hours. Because of dynamic shifts in the cell, the HT-PEMFC current density always dropped quickly when changing the fuel type, but then the cell was stable for several hours, showing no decay in the current density at 0.4 V. More importantly, the cell recovered its initial current density when switching back to H\textsubscript{2}/O\textsubscript{2}, indicating that the adsorbed CO on the electrocatalyst surface could be desorbed when pure H\textsubscript{2} was present in the anode.
Figure 4.25 24 hour stability test for 50:50 QPPSf-PBI membrane with QPPSf GDEs under H₂/O₂ and H₂-CO/O₂ at 220 °C/0% RH.

At the end of 24 hour stability test, which featured exposure to CO, the polarization curve for H₂/O₂ was collected, and it was within 95% of the original polarization curve composed with H₂/O₂) (see Figure 4.26a). A drop in OCV was observed after the stability test. To understand the OCV drop, the hydrogen crossover at 220 °C was measured before and after the stability (see Figure 4.26b). The difference in hydrogen crossover before and after the stability test was about 0.5 mA cm⁻² indicating mixed overpotentials could not be why the drop in the OCV. The decline in OCV after the 24 hour stability assessment may be due to some residual carbon monoxide still being present in the HT-PEMFC and may be due to the leaching of phosphate/H₃PO₄ leaching into the electrodes.
Figure 4.26. a.) Fuel cell performance analysis after 24 hours of 50:50 QPPSf-PBI membrane with QPPSf ionomer binder at 220 °C with 60 kPa backpressure for dry H₂/O₂ b.) Linear sweep voltammogram of 50:50 QPPSf-PBI membrane with QPPSf GDEs (0.5 mgPt cm⁻²) at 220 °C/0% RH under H₂/N₂ to measure H₂ crossover. The H₂ crossover flux rate was 1.56 x 10⁻⁸ moles cm⁻² s⁻¹ and 1.72 x 10⁻⁸ moles cm⁻² s⁻¹ at 0 hour and 24 hours respectively.

Furthermore, a more comprehensive stability assessment was performed for the HT-PEMFC under a different protocol. As reported by Li et al., the cell was operated at a constant current at 0.2 A cm⁻² and no back pressure was applied. We evaluated the HT-PEMFC stability at different temperatures over 116 hours. Before discussing these results, it is essential to note that the HT-PEMFC with the 50:50 QPPSf-PBI membrane blend failed at 32 hours at 0.2 A cm⁻² at 220 °C and 60 kPa of backpressure. Because of this failure related to the blended membrane breaking, it was decided to reassess stability at lower temperatures and no back pressures. Figure 4.27 shows that the 50:50 QPPSf-PBI membrane blend was stable for 48 hours at 180 °C followed by 36 hours of stability at 200 °C. Then, the cell temperature was raised to 220 °C, and the cell failed after an additional 32 hours – which was similar to the time it took for the cell to fall in the previous stability assessment. From our tensile test results, we observed that the 50:50 QPPSf-PBI membrane blend experienced a significant drop in mechanical strength when increasing the temperature to 220 °C. Our future work will look to overcome the membrane mechanical integrity failure mode for improving HT-PEMFC stability.
Along with stability, the repeatability of 50:50 QPPSf-PBI membrane with QPPSf ionomer binder was also tested at 220 °C under H\textsubscript{2}/O\textsubscript{2} and 0 kPa backpressure. Three independent MEAs were prepared with this configuration and evaluated with H\textsubscript{2}/O\textsubscript{2} for repeatability, as shown in Figure 4.28.

**Figure 4.27.** Cell voltage (vs) time at 0.2 A cm\textsuperscript{-2} for 50:50 QPPSf-PBI membrane with QPPSf ionomer binder at 180 °C, 200 °C and 220 °C under H\textsubscript{2}/O\textsubscript{2} and 0 kPa backpressure.

**Figure 4.28.** Average n=3 MEAs (independently prepared) fuel cell polarization curves with 50:50 QPPSf-PBI membrane with QPPSf ionomer binder in the electrode layers. The catalyst loading for the MEAs was 0.5 mg\textsubscript{Pt} cm\textsuperscript{-2}. Test conditions were H\textsubscript{2}/O\textsubscript{2} at 220 °C/0% RH with 60 kPa backpressure. Error bars represent the standard error.
4.3 Conclusions

In summary, these experiments highlight the following salient points: i.) the 50:50 QPPSf-PBI can sustain a high current density with low polarization, and HT-PEMFC performance is currently limited by reaction kinetics (and potentially gas reactant transport) caused by H₃PO₄ in the electrode layers, ii.) the HT-PEMFC can operate with reasonable power density when changing the anode feed composition to 75% H₂ and 25% CO (indicating reformate or syngas can power the cell potentially), iii.) the QPPSf ionomer binder and 50:50 QPPSf: PBI PEM are stable within the cell at 220 °C for 24 hours with oxygen as the oxidant, and iv.) the cell can recover its original performance when switching from H₂-CO fuel back to H₂ energy, showing that the CO adsorption effect is reversible.
Chapter 5
Correlation of In-Situ and Ex-Situ Electrochemical Properties of High-Temperature Polymer Electrolyte Thin – Films

5.1 Introduction

Ionomer binders strongly influence the performance and stability of numerous electrochemical processes such as fuel cells\textsuperscript{1-4}, water\textsuperscript{5} and carbon dioxide electrolyzers\textsuperscript{6}, and deionization units\textsuperscript{7,8}. It is worth noting that there is a lack of studies investigating how the properties of other thin-film ionomers influence electrochemical properties, such as charge-transfer reaction kinetics as well as gas permeability, in addition to other types of ionomer chemistries for hydrogen-based electrochemical systems. These other properties have a more profound impact on electrochemical device performance when compared to ionic conductivity\textsuperscript{20}. For example, ionomers can alter redox reaction rates (e.g., by adsorption of the tethered ion to the catalyst)\textsuperscript{21,22} and gas reactant mass transfer rates to the electrocatalyst surface\textsuperscript{11,20,23,24}.

In this work, we study how two different high-temperature ionomers thin-films influence hydrogen oxidation/evolution reaction (HOR/HER) kinetics and hydrogen gas permeability on interdigitated electrodes (IDEs). Our work is motivated by our previous reports and others, showing that ion-pair HT-PEMs operate over a more comprehensive temperature range and have greater humidity tolerance when compared to the conventional benchmark based upon phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) imbibed polybenzimidazole. In HT-PEM fuel cell studies, we observed significant kinetic and mass transfer resistances that hail from the presence of liquid H\textsubscript{3}PO\textsubscript{4} in the electrode layers. To address these resistances, Los Alamos and the University of Stuttgart adopted an alternative ionomer electrode binder based upon tethered phosphonic acid to the polymer backbone (i.e., poly(tetrafluorostyrene phosphonic acid-\textit{co}-pentafluorostyrene)
This binder addressed mass transfer resistances in the electrode layers and achieved a peak power density of 1.7 W cm$^{-2}$ at 240 °C. Drawing inspiration from this group, the effect of liquid acid removal from the ionomer thin-films influence on HOR/HER kinetics and gas permeability was investigated. The thin-films' properties were then correlated to the polarization of a single-cell electrochemical hydrogen pump (ECHP).

5.2 Results and discussions

5.2.1 Preparation and characterization of phosphonated polymers

QPPSf $\text{H}_3\text{PO}_4$, PVBPA, and PTFSPA were studied as thin film to assess their viability as electrode binders. The synthesis of QPPSf $\text{H}_3\text{PO}_4$, PVBPA, and PTFSPA polymer electrolytes are described in Chapter 3. QPPSf was synthesized and characterized using the procedure mentioned in Venugopalan et al. $^{74,75}$, PTFSPA and PVBPA were synthesized following the recipe from Atanasov et al. $^{66,79,93}$ and Zaidi et al. $^{94}$. The structural characterization of PTFSPA and PVBPA was carried out using $^{31}$P NMR (Figure 5.1). In the $^{31}$P NMR of PTFSPA, a peak at -2.4 PPM was attributed to the phosphonic acid group in PTFSPA. The peak at 0 ppm corresponds to the phosphoric acid internal standard. In the $^{31}$P NMR of PVBPA, a peak at 4.0 PPM could be attributed to the phosphonic acid group in PTFSPA. The peak at 0 ppm corresponds to the phosphoric acid internal standard.

One of the essential properties of a polymer electrolyte is the ion-exchange capacity (IEC), which yields the number of exchangeable ions per gram of the membrane. The IEC of QPPSf was theoretically calculated using the procedure described in Chapter 3. The IEC Of QPPSf in chloride counterion form was 1.7 mequiv g$^{-1}$. The number of $\text{H}_3\text{PO}_4$ per base in QPPSf $\text{H}_3\text{PO}_4$ was calculated to be 9.4 from our previous work. $^{118}$ The IEC of PTFSPA and PVBPA
was determined using the acid-base titration. The IEC of PTFSPA and PVBPA was estimated to be 2.5 mequiv g\(^{-1}\) and 1.75 mequiv g\(^{-1}\), respectively.

**Figure 5.1.** \(^{31}\)P NMR to identify the phosphonic acid moieties in a.) PTFSPA b.) PVBPA

TGA enables us to identify the thermal limitations of the polymer electrolytes. **Figure 5.2** presents the TGA of QPPSf H\(_3\)PO\(_4\), PVBPA, and PTFSPA. PTFSPA showed thermal stability up to 340 °C, whereas QPPSf H\(_3\)PO\(_4\) and PVBPA showed quaternary benzyl pyridinium and phosphonic acid functional group degradation starting 220 °C - 240 °C. The TGA showed that PTFSPA was very stable at high temperatures (180 °C – 240 °C), whereas QPPSf H\(_3\)PO\(_4\) showed 7% weight loss below 250 °C. The thermal stability indicates that PTFSPA is a good candidate for ionomer binder material HT-PEM fuel cells and ECHPs.
Figure 5.2. TGA of PTFSPA, PVBPA and QPPSf H₃PO₄. PTFSPA does not undergo thermal decomposition until 340 °C

5.2.2 Ionic conductivity (κ₊) of thin-films

Before performing hydrogen pump experiments using thin polymer electrolytes coated on Pt nanostructured IDEs, in-plane proton conductivity of polymer electrolytes thin-film was studied. Though a very high ionomer binder's very high conductivity is not needed for an efficient operation at higher temperatures, optimal proton conduction is required for efficient proton-coupled electron transfer reactions. Very few studies have been performed to understand the ionic conductivity of polymer electrolytes in thin-films. Most of the reviews are conducted for bulk polymer membranes. The ionic conductivity of thin-film polymer electrolytes can deviate from the bulk membrane properties. It is essential to understand and study the thin-film proton conductivity to understand the ionic conduction in the porous electrode layers, consisting of a thin layer of ionomer film covered over platinum electrocatalyst (see Figure 1.1).
Interdigitated electrodes with gold current collectors were used to study the thin-film in-plane conductivity of polymer electrolytes at high temperatures. Unlike Nafion, the polymer electrolytes used in this study do not require humidification for ionic conduction. Hence, thin-film in-plane proton conductivity at high temperatures could be studied. A home-built humidity and temperature-controlled chamber were used to measure the in-plane proton conductivity using IDEs.

Figure 5.3 shows the in-plane proton conductivity of PTFSPA and QPPSf H₃PO₄ thin-films on IDEs. The film's thickness was measured via ellipsometry and was observed to be 10-12 nm. The thin-film proton conductivity of PTFPSA rapidly increased from 0.045 S cm⁻¹ to 0.084 S cm⁻¹ as the temperature was increased from 100 °C to 240 °C. The conductivity of QPPSf H₃PO₄ increased from 0.45 S cm⁻¹ to 0.08 S cm⁻¹ from 100 °C to 220 °C. QPPSf has slightly better conductivity than PTFSPA at high temperatures, but PTFSPA does not require H₃PO₄ for ionic conductivity, and this should help promote reaction kinetics and gas reactant transport. The better ionic conduction for PTFSPA over PVBPA was attributed to the electron-withdrawing fluorine moieties in the styrene ring, increasing the acidity of the phosphonic acid-functionalized groups. PVBPA had the lowest ionic conductivity compared to other two polymer electrolytes, so it was not studied further.
The ability of PTFSPA to provide adequate ionic conductivity without liquid acid across a wide temperature range makes it a good candidate for HT-PEM fuel cells and ECHPs. It was anticipated that the removal of liquid H$_3$PO$_4$ would enhance mass transfer in the electrodes in the said devices and improve redox kinetics. H$_3$PO$_4$ is known to have a detrimental effect on oxygen reduction reaction (ORR) kinetics because of phosphate anion adsorption to the platinum catalyst surface$^{42}$. 

Stable proton conductivity at elevated temperatures is essential for HT-PEMFC commercialization. To assess PTFSPA thermal stability, the material was kept at 220 °C for 100 hours, and the changes in in-plane proton conductivity of the polymer electrolyte before and after the thermal exposure was measured. Figure 5.4 shows the in-plane proton conductivity comparison for PTFSPA before and after thermal exposure. PTFSPA retained more than 96% of
its initial after 100 hours at 220 °C. TGA and the conductivity stability assessment demonstrate that PTFSPA is resilient and an excellent material choice for a fuel cell binder.

![Graph showing conductivity vs. temperature for PTFSPA before and after thermal treatment.](image)

**Figure 5.4.** In-plane proton conductivity of PTFSPA before and after thermal treatment at 220 °C for 100 hours.

### 5.2.3 Ex-situ electrochemical properties of polymer electrolyte thin-films

To understand how thin-film ionomers impact other electrochemical properties beyond ionic conductivity, Bhattacharya *et al.*\(^8^3\) developed an interdigitated electrode (IDE) platform that features a thin-film (≤30 nm) of nanoscale platinum group metal (PGM) electrocatalyst afforded from self-assembled block copolymer templates (**Figure 5.5**). Here, we extended this platform to assess the electrochemical properties (HOR/HER kinetics, ionic conductivity, and hydrogen permeability) for two different types of thin-film high-temperature (HT-) ionomers, QPPSf H\(_3\)PO\(_4\), and PTFSPA.
After the ionic conductivity experiments were completed, the nitrogen gas was switched to dry hydrogen (i.e., 0% RH). Chronoamperometry experiments were performed from 0 V to 0.7 V at temperatures of 160 °C, 180 °C, and 200 °C on the IDEs. Temperatures above 200 °C were not pursued due to instability of the IDE platform for extended periods at that temperature. The presence of this periodic nanostructure PGM electrocatalyst across the IDE is useful for assessing HOR/HER kinetics in the presence of a thin-film ionomer (previously Nafion® at room temperature). Here, this platform was extended to assess the electrochemical properties (HOR/HER kinetics, ionic conductivity, and hydrogen permeability) for two different types of thin-film high-temperature (HT-) ionomers.

![Figure 5.5](image.png)

**Figure 5.5** a.) IDE platform with high-density platinum nanowires (~20 nm diameter and 20 nm in thickness). b) IDE platform is placed in a sealed, temperature-controlled chamber for HOR/HER measurements

**Figure 5.6** plots the iR-corrected polarization curves with IDEs featuring the two different high-temperature ionomers as a function of temperature. In this plot, the PTFSPA thin-film displayed larger current responses in the linear regime, as well as larger limiting currents, over the QPPPSf-H₃PO₄ thin-film. Notably, the PTFSPA showed larger increases in current density across the voltage range as a function of temperature when referenced against QPPPSf-H₃PO₄.
To quantify the improvements in HOR/HER with thin-film PTFSPA over QPPSf-H$_3$PO$_4$, we first analyzed the limiting current density values of the iR-corrected polarization curves. The limiting current corresponds to limitations from mass transfer resistances that arrive from gas permeability across the thin-film ionomer. Gas permeability ($P_{H_2}$) is a product of the species diffusion coefficient ($D_{H_2}$) multiplied by its solubility coefficient (e.g., Henry’s constant – $H_{H_2}$ in this case) in the polymer electrolyte thin-film (equation 2.11). By knowing the limiting current density values and the film thickness values, temperature, and concentration of hydrogen in the environmental chamber, we estimated the gas permeability values using equation 2.12 for the two different thin-film high-temperature polymer electrolytes as a function of temperature (Figure 5.7). The hydrogen gas permeability values were 6x greater or more for the PTFSPA ionomer over the QPPSf-H$_3$PO$_4$ thin-film polymer electrolyte.
The hydrogen permeability values as a function of temperature for the two different thin-film ionomers extracted from the limiting current values in the polarization curves

Next, we analyzed the iR-corrected polarization curves' linear regime to assess how the different thin-film ionomers affect HOR/HER kinetics. The iR-corrected potential values in the linear regime, which also corresponds to low current density values, are under mixed-control (i.e., reaction kinetics and mass transfer resistances dictate the current response). Here, the mass transfer resistance was assumed to be bot severe but do recognize that it’s not negligible because of the thin-film ionomer coating. Because HOR/HER kinetics is facile under acidic media with platinum electrocatalysts, the linearized version of the Butler-Volmer equation was used to attain the exchange current density values \( i_0 \) (a proxy for the reaction rate coefficient)\(^\text{43} \). We assumed the transfer coefficients summed to 1 in equation \textit{2.13}. The \( i_0 \) values include both HOR and HER contributions, and these individual reaction rates cannot be decoupled with the IDE platform. Therefore, the \( i_0 \) values reported from the IDE electroanalytical platform are relativistic, and their utility lies in comparing how ionomer materials affect HOR/HER kinetics and gas permeability. Figure \textit{5.8} compares the \( i_0 \) value for the two different high-temperature
thin-film ionomers as a function of temperature. At 160 °C, the $i_0$ value for the PTFSPA film was a little over 2x more excellent for HOR/HER when compared to QPPSf H$_3$PO$_4$. Increasing the temperature to 200 °C resulted in a more extensive enhancement for $i_0$ for PTFSPA, while the improvement $i_0$ for QPPSf H$_3$PO$_4$ was marginal. The presence of H$_3$PO$_4$ in the thin-film ionomer is catastrophic to HOR/HER kinetics because of phosphate anion species adsorption to the PGM catalyst. Surface blockage by phosphate species prevents enhancement in reaction kinetics when raising the temperature.

![Figure 5.8](image)

**Figure 5.8.** Exchange current density values ($i_0$) as a function of temperature for the two different thin-film ionomers extracted from the linear regime in the polarization curves, respectively

### 5.2.4 In-situ electrochemical properties of polymer electrolyte thin-films

After identifying that the PTFSPA thin-film ionomer is more effective at promoting hydrogen permeability and HOR/HER kinetics, membrane electrode assemblies (MEAs) were fabricated for single-cell ECHP studies. The MEAs consisted of QPPSf PBI H$_3$PO$_4$ HT-PEM separators and Pt/C gas diffusion electrodes (GDEs) that used QPPSf H$_3$PO (termed MEA 1) and PTFSPA (termed MEA 2) as electrode binders. **Figure 5.9a** presents the iR-corrected single-cell
ECHP polarization curves for the MEAs that featured the different electrode binders at different temperatures (160 to 220 °C). There are two salient features in Figure 5.9a: i.) the MEA with a PTFSPA electrode binder outperformed the MEA with a QPPSf H₃PO₄ electrode binder and ii.) as the cell temperature increased, the polarization decreased more with PTFSPA as the electrode binder. In contrast, the polarization remained about the same with QPPSf H₃PO₄ as the electrode binder.

Figure 5.9b presents the Nyquist plots from electrochemical impedance spectra taken at no applied potential during ECHP experiments. The charge-transfer resistance (i.e., the semi-circle diameter) was 0.04 Ω-cm² or less with PTFSPA as the electrode binder, while the charge-transfer resistance for QPPSf H₃PO₄ was > 0.25 Ω-cm² (i.e., at least 6x greater). The charge-transfer resistance values reflect how detrimental liquid H₃PO₄ is to HOR/HER kinetics and ECHP performance.

In the next set of analyses, the linear-regime and limiting current density values of the polarization curves were analyzed for extracting the $i_0$ and hydrogen permeability values for single-cell ECHPs. The $P_{H_2}$ and the $i_0$ values as a function of temperature are plotted in Figures 5.10a and Figure 5.10b. Similar to the observations from IDE studies, the $P_{H_2}$ and $i_0$ values were larger for the MEAs containing PTFSPA as the binder over QPPSf H₃PO₄ as electrode binder (e.g., 6x for $P_{H_2}$ and 2-3x greater for $i_0$).
Figure 5.9 a.) Single-cell ECHP iR-corrected polarization behavior with the same HT-PEM and Pt/C loadings (0.5 mgPt cm$^{-2}$) but with different types of electrode binders. b.) Nyquist plots from ECHP experiments with the MEAs featuring different electrode binders as a temperature function.
Figure 5.10. a.) The hydrogen permeability ($P_{H_2}$) values and b.) exchange current density values ($i_0$) as a function of temperature for the two different MEAs. These values were extracted from the limiting currents and the linear regime in the polarization curves from Figure 5.9a.

5.2.5 Correlation of in-situ and ex-situ electrochemical properties of polymer electrolyte thin-films

Figures 5.11 and 5.12 provide the IDE and MEA polarization curves with platinum loading normalized current values. The correlation between $P_{H_2}$ and the platinum loading
normalized exchange current density values \((i_{0,m})\) attained from studies with IDEs and single-cell MEA ECHPs from Figure 5.11 and 5.12 is conveyed in Figures 5.13a and 5.13b. A commensurate linear relationship was observed for the \(P_{H_2}\) and \(i_{0,m}\) values between the two different platforms indicating that the IDEs are useful for probing how potential new ionomer binders may affect ECHP electrode performance. The IDE platform uses >100x less platinum than an MEA and far less ionomer material. Several IDE platforms can be loaded into a single environmental chamber and studied using a multi-channel potentiostat, making it an excellent high-throughput tool for studying the electrochemical properties of thin-film ionomers used electrode binders.

Figure 5.11. Mass specific current polarization curves for HOR/HER on IDEs with different thin-film ionomers as a function of temperature.
Figure 5.12. Mass specific current polarization curves for the ECHP at 180 °C, 200 °C, and 220 °C.

Figure 5.13. Correlation between the a.) permeability values ($P_{H_2}$) and b.) exchange current density values ($i_{0,m}$; normalized to platinum loadings) in single-cell MEA ECHPs and IDEs.

A notable difference between HT-PEM and LT-PEM ECHP studies in the literature is the electrodes' platinum loading. LT-PEM ECHPs use about 0.5 mg Pt cm$^{-2}$ to 0.8 mg Pt cm$^{-2}$ in the MEA while HT-PEMs typically use 2 mg Pt cm$^{-2}$ studies. Because the PTFSPA is a good electrode binder, our studies were initially done with 1 mg Pt cm$^{-2}$ in the MEA (Figure 5.9a).
Figure 5.14. Single-cell ECHP iR-corrected polarization behavior using PTFSPA as the electrode binder and 1 $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$ for each electrode. The MEA used the QPPSf-PBI $\text{H}_3\text{PO}_4$ PEM

Table 5.1. Performance comparison of various single-cell HT-PEM ECHPs with the same Pt loading in electrodes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Electrode binder &amp; electrocatalyst used</th>
<th>Anode/cathode catalyst loading (mg$_{\text{Pt}}$ cm$^{-2}$)</th>
<th>Temperature (°C) / RH (%)</th>
<th>Cell voltage (V) at 1 A cm$^{-2}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fumatech PBI</td>
<td>PBI with Pt/C</td>
<td>-</td>
<td>160 °C/0%</td>
<td>1.40</td>
<td>119</td>
</tr>
<tr>
<td>Para-PBI</td>
<td>BASF electrodes that contain Pt*</td>
<td>1.0/1.0</td>
<td>160 °C/1.6%</td>
<td>0.10</td>
<td>32</td>
</tr>
<tr>
<td>Para-PBI</td>
<td>BASF electrodes that contain Pt*</td>
<td>1.0/1.0</td>
<td>200 °C/1.6%</td>
<td>0.12</td>
<td>32</td>
</tr>
<tr>
<td>50:50 QPPSf PBI $\text{H}_3\text{PO}_4$</td>
<td>PTFSPA</td>
<td>1.0/1.0</td>
<td>160 °C/0%</td>
<td>0.11</td>
<td>This work</td>
</tr>
<tr>
<td>50:50 QPPSf PBI $\text{H}_3\text{PO}_4$</td>
<td>PTFSPA</td>
<td>1.0/1.0</td>
<td>200 °C/0%</td>
<td>0.075</td>
<td>This work</td>
</tr>
<tr>
<td>50:50 QPPSf PBI $\text{H}_3\text{PO}_4$</td>
<td>PTFSPA</td>
<td>1.0/1.0</td>
<td>220 °C/0%</td>
<td>0.055</td>
<td>This work</td>
</tr>
</tbody>
</table>

* Exact composition of this electrode is unknown

For a fair comparison with existing data on HT-PEM ECHPs in the literature, another MEA was fabricated with 2 $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$ in the MEA (equal loading on each electrode) with PTFSPA binder. The ECHP polarization curve of this MEA is given in Figure 5.14, and its performance is comparable to some of the best performance values reported by LT-PEM ECHPs;
however, the platinum loading is substantially higher (2x to 3x), and the cell temperature is much higher (220 °C versus 35 to 80 °C). Table 5.1 shows the comparison of various single-cell HT-PEM ECHPs with the same Pt loading in the electrodes. The PTFSPA electrode binder with 50:50 QPPSf-PBI HT-PEM outperformed the current state-of-the-art HT-PEM ECHP performance.

5.3 Conclusions

In summary, we show here that PTFSPA is a more effective electrode binder for ECHPs over QPPSf-H$_3$PO$_4$ binders because it does not contain liquid acid known to obfuscate hydrogen gas permeability and hinder reaction kinetics due to phosphate anion adsorption on the electrocatalyst surface. Using the IDE platform decorated with nanowire platinum catalysts for HOR/HER studies, we unequivocally demonstrate that the measured thin-film polymer electrolyte electrochemical properties correlate to single-cell ECHP polarization behavior. IDE platforms are useful for high-throughput assessments of potential new ionomer materials for use as electrode binders. Finally, implementing PTFSPA materials as electrode binders in HT-PEM ECHPs results in excellent performance (1 A cm$^{-2}$ at 55 mV; see Table 5.1 for comparison of values).
Chapter 6
A Versatile Electrochemical Pump for Hydrogen Separations

6.1 Introduction

The contaminants (e.g., CO) in the hydrocarbon mixture present significant performance challenges for ECHP separation units because they poison or deactivate the catalysts needed for hydrogen oxidation in the anode. Reactivity of electrocatalyst is critical because it generates protons that are selectively extracted from the HT-PEM and shuttled to the cathode for electrochemical reduction and the generation of pure hydrogen. The HT-PEM mitigates crossover of the other hydrocarbon and contaminant species from the anode to the cathode. Higher temperature operation of the ECHP assists in overcoming catalyst poisoning and deactivation. It also promotes hydrogen oxidation and reduction reaction (HOR/HER) kinetics.  

This project investigates a new class of high-temperature polymer electrolytes employed as ionomer binders in the electrodes for electrochemical hydrogen pumps (ECHP) operated at 180 °C or greater for separating and purifying hydrogen from gaseous hydrocarbon mixtures. The liquid acid free phosphonated ionomer (PTFSPA) was utilized as electrode binder candidates for HT-PEMCHPs because of their excellent proton conductivity, HOR/HER kinetics, and hydrogen diffusivity (see Chapter 5). The new HT-PEMs based upon ion-pair interactions (discussed in Chapter 4) that display excellent thermal stability (> 48 hours @ 220 °C) and proton conductivity (> 0.25 S cm\(^{-1}\) @ 220 °C) were employed as membrane separators in the ECHP operation.

In this project, industrial relevant mixtures for the ECHP (e.g., syngas, cracking, and reformate mixtures) was examined by investigating the performance of HT-PEM ECHP with
new phosphonated polymer electrode binders in purifying hydrogen.

6.2 Results and discussion

6.2.1 HT-PEM ECHP operation and electrode fabrication

Figure 6.1 shows the schematic representation of an electrochemical hydrogen pump using HT-PEM for producing pure hydrogen from gas mixtures. The gas mixtures represent effluents from stream reformed methane and crackers, and this gas mixture is supplied to the anode, where the hydrogen gets selectively oxidized to protons on the catalyst surface. The generated protons are selectively extracted from the PEM and shuttled to the cathode for electrochemical reduction and pure hydrogen generation. 50:50 QPPSf-PBI H$_3$PO$_4$ (PC-PBI) membrane was used as the HT-PEM for in single-cell HT-ECHPs. The PC-PBI H$_3$PO$_4$ membrane has a high in-plane proton conductivity of 240 mS cm$^{-1}$, good thermal cyclability, and ultimate tensile strength of 11.9 MPa at 25% elongation at break. The excellent conductivity, thermal stability, and toughness made it a good material for the HT-ECHP. The single-cell MEA for the ECHP used PTFSPA as the electrode binder. As shown previously, the use of PTFSPA reduced mass transport resistance and enhanced the HOR/HER kinetics in ECHPs with pure hydrogen at the higher temperature.

The voltage is provided from the external power source required to operate ECHP. Opposite of fuel cells, lower voltage applied to the ECHP signals less energy needed for a given hydrogen separation. At a lower current density regime, a direct relationship between current and cell voltage could be observed. At a lower current density regime, the hydrogen reaction kinetics on the anode plays a significant role, after which the cell resistance drives the cell. A limiting current could be observed in the high current density regime due to mass transport resistance.
**Figure 6.1.** A depiction of the membrane electrode assembly (MEAs) with platinum electrocatalyst and phosphonic acid ionomer electrode binder

### 6.2.3 HT-PEM ECHP performance with hydrogen gas mixtures

From Chapter 5, **Figure 5.15**, showed the performance of HT-PEM ECHP with PTFSPA electrode binder and QPPSf-PBI 50:50 membrane at high temperatures (160 °C to 220 °C) using pure H₂ in the anode feed stream. Employing PTFSPA materials as electrode binders in HT-PEM ECHPs results in excellent performance with just 55 mV requirement for 1 A cm⁻² at 220 °C.

The main advantage of HT-PEM ECHP is its predicted ability to operate in the presence of contaminants. Inlet feed gases with different CO, CO₂, and CH₄ concentrations were supplied in the anode to test the cell's tolerance to variations in the inlet feed stream. The four gas mixtures were syngas (25% H₂, 40% CO, 15% CO₂, 15% CH₄, and 5% N₂), reformate gas (30% H₂, 3% CO with N₂ balance), syngas water-gas shift reactor mixture (WGS) (76% H₂, 20% CO₂, 5% CH₄, and 20 PPM CO), and H₂-CO blend (75% H₂, and 25% CO). The polarization curves for each anode gas mixtures were evaluated at different temperatures 160 °C, 180 °C, 200 °C, and 220 °C, respectively, for further investigation on the temperature effects. The tolerance to
CO was improved by increasing the operating temperature of ECHP. At higher temperatures, CO has a smaller propensity to adsorb to the Pt electrocatalysts.\textsuperscript{121}

As clearly seen from Figure 6.2 (a-d), there is a noticeable temperature effect on Pt tolerance on CO, which predominantly governs the cell performance, especially while using dilute hydrogen sources with large amounts of CO (see Figure 6.2a and 6.2b). The effect of anode inlet gas mixture composition on HT-PEM ECHP performance can be observed by comparing Figure 6.2 (a-d). The amount of cell voltage applied to purify and oxidize hydrogen on the anode increased substantially when the feed stream contained higher catalyst impurities concentrations. For instance, at 220 °C, at 1 A cm\textsuperscript{-2} current density, the syngas mixture containing 40% CO required 0.4 V, while the WGS reactor required just 0.15 V and pure H\textsubscript{2} required 0.55 V.

From Figure 6.2a-6.2d, it was observed that all anode gas mixtures showed performance improvement when the temperature was increased from 160 °C to 220 °C. The QPPSf-PBI HT-PEM enables the cell operation at 220 °C, allowing the cell to have better tolerance to CO. Additionally, the better reaction kinetics and mass transport of PTFSPA electrode binder enable better cell performance. The HT-PEM ECHP shows a very high tolerance to CO at 220 °C. From Figure 6.2a-6.2d, it is clearly evident that the concentration of CO takes a stall on HT-PEM ECHP performance at low temperatures (160 °C–180 °C), whereas at high temperatures (>200°C), HT-PEM ECHP sanctioned better tolerance to CO.
Figure 6.2. Single-cell ECHP polarization behavior, using PTFSPA as the electrode binder and 1 mgPt cm\(^{-2}\) for each electrode, for a.) syngas b.) reformate mixture c.) WGS mixture d.) H\(_2\)-CO blend at different temperatures. The MEA used the QPPSf-PBI H\(_3\)PO\(_4\) PEM.

Figure 6.3 compares the performance of HT-PEM ECHP with different anode gas mixtures at 220 °C. At 220 °C, the performance of HT-PEM ECHP was a stronger function of H\(_2\) in the anode feed rather than the effect of CO on the electrodes. For instance, at 0.25 A cm\(^{2}\) of current density, all the hydrogen-hydrocarbon-contaminant mixtures require 0.025 V - 0.045 V, showcasing that the cell performance was not affected by the presence of contaminants in the
anode feed at 220 °C, whereas, by the hydrogen dilution (the concentration of hydrogen present in the inlet anode gas feed).

![Figure 6.3. Single-cell ECHP polarization behavior, using PTFSPA as the electrode binder and 1 mg Pt cm⁻² for each electrode, for different anode gas mixtures blend at 220 °C. The MEA used the QPPSf-PBI H₃PO₄ PEM.](image)

6.3 Initial conclusions and future work

HT-PEM ECHP using PTFSPA electrode binder with 1 mg Pt cm⁻² for each electrode and 50:50 QPPSf-PBI membrane separator was used to demonstrate the ECHP performance with different anode feed mixtures that had various CO and hydrogen concentrations. It was observed that the higher temperature operation of ECHP enabled better tolerance to CO contaminant in the anode feed due to the less adsorption and interference of CO on Pt electrocatalyst. The lowest polarization for an HT-PEM ECHP was also demonstrated at 220 °C with pure hydrogen and with challenging hydrogen mixtures. However, the polarization was primarily governed by hydrogen concentration rather than the contaminants in the anode feed at 220 °C. The better
tolerance of HT-PEM ECHP to contaminants demonstrates the advantage of high-temperature operation for purifying challenging hydrogen operations.

The stability of HT-PEM ECHP at elevated temperatures with hydrogen gas mixtures will be assessed in the future. Additional future studies include examining performance under differential pressure conditions. The performance loss encountered with these contaminants can be further mitigated through a more judicious selection of catalyst materials such as platinum-ruthenium (Pt-Ru) alloys at the anode that mitigate CO adsorption instead of pure platinum.
Chapter 7
Other Applications Using HT-PEMs

7.1 A solid-state and flexible supercapacitor that operates across the temperature range of -70 to 220 °C

7.1.1 Introduction

Supercapacitors are energy storage devices that demonstrate high cycling stability in addition to providing high power density. These properties are responsible for the ever-increasing interest in supercapacitors for a wide-range of energy storage purposes (e.g., biomedical devices, starting electric vehicles, etc.). Supercapacitor electrolytes are usually categorized into liquid electrolytes (ionic, organic, and aqueous liquids) and solid-state electrolytes (mainly polymer or particle gels). Supercapacitors featuring water-based electrolytes are typically only evaluated at room temperature as water starts to freeze at 0 °C and boil near 100 °C. Organic liquid electrolytes, on the other hand, are the most prevalent and commercially available electrolytes used in supercapacitors due to their good thermal stability in the range of -40 °C to 70 °C.

Solid-state electrolytes potentially perform better at both extremely high temperatures (> 100 °C) and low temperatures (< 0 °C). Additionally, solid-state electrolytes offer the prospect to mitigate problems associated with liquid electrolytes, such as shunt currents and fire hazards. Plus, they enable a thinner and flexible design. However, the main limitation of using solid-state electrolytes relates to their lower conductivity (100 to 1000 times lower) compared to liquid electrolytes. Therefore, overcoming the ionic conductivity hurdles of solid-state electrolytes are needed to realize supercapacitors that operate effectively over a wide temperature range.

Most solid-state electrolytes for supercapacitors utilize a polymer or particle gel host. The dense nature of these materials hinders device flexibility and does not provide good ionic conductivity. A less explored option as a solid-state electrolyte for supercapacitor devices is ion-exchange membranes (e.g., proton exchange membranes (PEMs) and anion/hydroxide exchange membranes (AEMs)). PEMs and AEMs have been deployed in various electrochemical processes, such as fuel cells. These membrane variants for these applications do not traditionally contain any excess electrolyte that can flow in and out of the membrane, making them undesirable for supercapacitor applications. Furthermore, their ability to provide ionic conduction is strongly correlated to high levels of hydration for counterion ion dissociation from tethered ionic groups to the polymer backbones.

Enabling anhydrous proton conduction in PEMs for fuel cells that operate in the temperature range of 120 to 180 °C was achieved over 25 years using phosphoric acid (H₃PO₄) doped PBI. These PEMs, H₃PO₄-PBI, has been implemented in solid-state, high temperature (25 to 150 °C) supercapacitors. Still, they have not been evaluated at temperatures below 25 °C (even frigid temperatures of less than 0 °C), and their performance cannot be assessed above 180 °C as the H₃PO₄ starts to evaporate from PBI. The temperature range of anhydrous PEMs has been extended through the use of polycation-PBI polymer blend doped with H₃PO₄. The polycation in the blend was Udel® poly(arylene ether sulfone) featuring quaternary benzyl pyridinium cations (QPPSf). The H₃PO₄-QPPSf-PBI showed remarkably high in-plane proton conductivity (up to 290 mS cm⁻¹ at 220 °C) and excellent mechanical properties (11.9 MPa at break and 30% elongation), while also endowing long-term thermal stability at 220 °C and stability in the presence of water vapor.
In this work, it was not only shown that the solid-state electrolyte membrane (QPPSF-PBI 50:50) of H$_3$PO$_4$-QPPSf-PBI blend could extend the temperature range to 220 °C for an all solid-state, flexible supercapacitor with rGO electrodes, but this QPPSF-PBI 50:50 also fostered proton conduction as low as -70 °C. Therefore, the polycation-PBI QPPSF-PBI 50:50 incorporated with rGO electrodes has resulted in a supercapacitor technology for applications necessitating a wide temperature range.

7.1.2 Results and discussion

Figure 7.1 illustrates the sandwich type device made by flash reduced rGO electrodes and the 50:50 H$_3$PO$_4$-QPPSf-PBI. The inset of Figure 7.1 shows the chemical structure of the H$_3$PO$_4$-QPPSf-PBI. From chapter 5, among the prepared varying blends of H$_3$PO$_4$-QPPSf-PBI, the 50:50 blend yielded the highest conductivity and best mechanical and thermal stability. Hence, the 50:50 H$_3$PO$_4$-QPPSf-PBI blend was evaluated as an QPPSF-PBI 50:50 for supercapacitor device studies.

**Figure 7.1.** Sandwich type supercapacitor design featuring rGO electrodes and H$_3$PO$_4$-QPPSf-PBI QPPSF-PBI 50:50. The chemical structure of the H$_3$PO$_4$-QPPSf-PBI QPPSF-PBI 50:50 is given in the inset

Using the HT-PEM, QPPSf-PBI 50:50 fabricated in Chapter 4, an all-solid-state supercapacitor using rGO electrodes were engineered. The supercapacitor's electrochemical
properties were measured across a wide temperature range. Figure 7.2a shows the CV plot of supercapacitor at a scan rate of 50 mV s\(^{-1}\) in the temperature range of -70 °C to 25 °C. The inset for Figure 7.2a highlights that the device still operated at -70 °C. The device's current density continued to drop when cooling the capacitor from 25 °C to -70 °C. Figure 7.2b presents the supercapacitor device's CV curves in the high-temperature range of 25 to 220 °C. The CV traces in both Figures 7.2a and 7.2b were fairly symmetrical when operated across the voltage range of 0 to 1 V. The current response of the supercapacitor with the QPPSF-PBI 50:50 continued to increase, ramping the temperature from 25 °C to 160 °C. The CV curve at 100 °C and 160 °C were almost similar. Increasing the temperature beyond 160 °C resulted in smaller current responses at 180 °C and 220 °C.

Figure 7.2. Electrochemical properties of the solid-state supercapacitor at different temperature values. a.) CV of supercapacitor at a scan rate of 50 mV s\(^{-1}\) in the temperature range of -70 to 25 °C. b.) CV of supercapacitor in the range 25 to 220 °C

The resultant device capacitance values from the CV curves in Figures 7.2a and 7.2b were plotted as a function of temperature in Figure 7.3. There are two critical takeaways from Figure 7.4: i.) the maximum capacitance was observed at 100 °C, and the value at 160 °C was
pretty close to the value at 100 °C and ii.) the supercapacitor’s capacitance value was on the same order of magnitude across the temperature range of -20 °C to 220 °C. Cooling the capacitor below -20 °C still resulted in a device that always operated but with a capacitance value about two orders in magnitude smaller.

![Graph showing specific capacitance vs temperature]

**Figure 7.3.** Different values of areal capacitance determined from CV plots at a scan rate of 50 mV s⁻¹. The maximum capacitance of the device was 6.8 mF cm⁻² and it was obtained at 100 °C.

To better understand why the supercapacitor displayed the highest capacitance at 100 °C and 160 °C and a dramatic reduction in capacitance at temperatures below -20 °C, electrochemical impedance spectroscopy (EIS) was performed to delineate the ohmic and diffusion resistance of ions in the electrodes as a function of temperature. **Figure 7.4** shows the EIS of the supercapacitor with an QPPSF-PBI 50:50 at different temperatures. The Nyquist plots exhibited linear tails starting over the entire frequency range illustrating a diffusion-controlled mechanism for charge storage in the temperature range of -40 to 220 °C.
Figure 7.4. Nyquist plots from EIS at high (a) and low (b, c) temperature values. a.) The Nyquist plots at different elevated temperatures for the supercapacitor devices from 40 °C to 220 °C show that the device's equivalent series resistance decreases by increasing the temperature from room temperature up to 140 °C and then increases gradually up to 220 °C. b.) The equivalent series resistance increases by reducing the temperature from room temperature to -40 °C. c.) Displays a diffusion-controlled charge-storage mechanism in the electrodes. The formation of the semi-circles observed in (c) signifies that a charge-transfer resistance may be present when decreasing the temperature at or below -50 °C.

The high-frequency resistance (HFR) and the diffusion resistance were extracted from the Nyquist plots by fitting an electric circuit equivalent model to the data. The HFR occurred where the Nyquist trace crosses the x-axis. The diffusion resistance was determined from the slope of the real resistance ($Z'$) versus reciprocal of the square root of frequency ($\omega^{-0.5}$) in the linear regime of the Nyquist plot (see Figure 7.5).
Figure 7.5. $Z'$ vs. frequency from EIS experiments at a different temperature to attain the diffusion resistance. Slope values, diffusion resistances are given with each trace. a.) Plots for low temperatures and b.) plots for high temperatures

Figure 7.6 plots the HFR and diffusion resistances as a function of temperature. The higher capacitance values that were commensurate with increasing temperature from 25 °C to 100 °C originated from improved structural proton diffusion in the QPPSF-PBI 50:50 that ultimately enhanced the conductivity of the QPPSF-PBI 50:50, leading to a lower HFR value. Plus, the improved conductivity also reduced the diffusion resistance of H$_3$PO$_4$ in the rGO electrodes. Between the temperature of 100 °C to 160 °C, the diffusion resistance started to increase in Figure 7.6. At 180 °C, the HFR also started to increase when increasing the temperature to 220 °C. The larger individual resistance values accounted for the decrease in capacitance observed above temperatures of 160 °C. At elevated temperatures, the migrated excess H$_3$PO$_4$ to the rGO electrodes may start to evaporate as there are no cationic groups to anchor them to the electrode – unlike the QPPSF-PBI 50:50.

Furthermore, a fraction of the phosphoric acid undergoes dehydration at temperatures above 160 °C forming triphosphoric, pyrophosphoric, or polyphosphoric acid. These more
prominent acids may cause a slight drop in QPPSF-PBI 50:50 ionic conductivity and, as a result, a higher HFR value. Plus, these bigger acids cannot migrate as easily from the QPPSF-PBI 50:50 host into the rGO electrodes resulting in a larger diffusion resistance.

**Figure 7.6.** Diffusion resistance and high-frequency resistance (HFR) values versus temperature. These resistances were determined from EIS.

At temperatures below -40 °C, a drastic increase in the HFR and diffusion resistance is observed. Since the proton conductivity is inversely proportional to the HFR, fewer available ions for the double layer formation were expected. Therefore, the increase in resistance at low-temperature conditions leads to much lower capacitance values (i.e., below 1 mF cm$^{-2}$) compared to higher temperatures. Another reason for the rapid rise of diffusion resistance is attributed to the freezing of the H$_3$PO$_4$ in the polymer host, restricting structural H$_3$PO$_4$ diffusion. Interestingly, semi-circles appeared in the Nyquist plot at -50 °C, -60 °C, and -70 °C. These semi-circles indicated that a charge-transfer resistance might be occurring at these low
temperatures. The origin of the apparent charge-transfer elements, which can be represented by a capacitor and a constant phase element in parallel, is currently unknown and will focus on future investigations. Suppose the semi-circles are related to an electron-charge transfer process, such as corrosion of the electrodes or oxidation/reduction of oxygen, electrolyte, or water. In that case, it is unclear at the moment why this process would occur at -50 to -70 °C and not at greater temperatures. One possibility to explain the observation beyond a formal charge-transfer process may be related to the electrolyte's freezing causing a poor interface between the electrode-electrolyte. This poor interface may be abrupt and could potentially be explained by a resistor and constant phase element in parallel. Supercapacitors' molecular behavior as such low temperatures is relatively unexplored and will be investigated in greater detail in the future.

Overall, the supercapacitor device developed herein with H₃PO₄-QPPSf-PBI SEM and rGO electrodes displayed energy storage capacity across an extensive temperature range (-70 °C to 220 °C). Figure 7.7 compares the areal capacitance vs. operating temperature range of our device and other similar recently published works. Accordingly, the supercapacitor with the QPPSf-PBI 50:50 in this work shows competitive areal capacitance and the largest temperature operation range compared to ionic liquid (IL) electrolytes and polyampholyte hydrogels. Although the areal capacitance for polyvinyl alcohol (PVA) gel-based electrolytes is higher than what is reported in this work, the operating temperature of a supercapacitor with a polyvinyl alcohol (PVA) gel-based electrolytes is limited to the temperature range of -40 to 60 °C. Additionally, the H₃PO₄ doped PBI electrolyte only operates from room temperature to 160 °C. The wide operating temperature range of our device makes it possible to tolerate harsh environmental conditions in the range of -70 to 220 °C.
wide-temperature range is necessary for numerous applications that vary from wearable electronics to transportation and aerospace.

![Graph showing areal capacitance vs. operating temperature range]

**Figure 7.7** Comparison of areal capacitance vs. operating temperature range for this work and data available in the peer-reviewed literature

### 7.1.3 Conclusion

In this work, a solid-state and flexible supercapacitor was realized for extreme temperature applications using a novel polymer blend membrane and flash reduced graphene oxide electrodes. H₃PO₄ imbibed QPPSf-PBI blended membranes showed impressively high conductivity of 289 mS cm⁻¹ at 240 °C. The device's outstanding performance and thermal resistance were confirmed by several electrochemical tests over a wide temperature range of -70 to 220 °C. Our solid-state supercapacitor showed a maximum capacitance of 6.8 mF cm⁻² at 100 °C. Energy density and power density were measured to range from 0.83 to 2.79 mW h cm⁻² and 90 to 125 mW cm⁻², respectively. The formation of double-layer capacitance was observed at
extremely low (-70 °C) and high (220 °C) temperatures. As a result, the fully solid-state and flexible supercapacitor successfully operates in the temperature range of -70 to 220 °C as well as outperforming most of the current state of art solid-state supercapacitors at room temperature. Merging the properties mentioned above reveals new horizons for extreme temperature supercapacitors for challenging energy storage applications such as aerospace, transportation, and micro-electronics.
Chapter 8
HT-PEMFC Performance Using New Phosphonic Acid Electrode Binder

8.1 Introduction

A detailed study on HT-PEMFC performance in Chapter 5 revealed that further improvement HT-PEMFC cell performance warrants the kinetic and mass transport resistances addressed. Figure 8.1 clearly shows the various sources of resistances that contribute to loss in HT-PEMFC performance with H₂/O₂, with 50:50 QPPSf-PBI membrane with QPPSf GDEs (0.5 mgPt cm⁻²) at 220 °C/0% RH. The cell had very low ohmic overpotential. For example, 20 mV ohmic overpotential would occur if the cell were operated near 2 A cm⁻², near the peak power density for this H₂/O₂ demonstration. The large activation overpotential observed in the lower current density regime is the significant contributor of the charge-transfer resistance. The activation overpotential values are substantially higher than the ohmic resistances in the cell and highlight that the HT-PEMFC’s performance is primarily reaction kinetics limited, at a low current density regime, which is due to the presence of H₃PO₄ doped polymers. In H₃PO₄ doped polymers used as electrode binders, phosphate type anion adsorption to electrocatalyst surfaces block sites for reactant adsorption and hindering reaction kinetics.

Further, in the high current density regime, a large concentration overpotential is observed. The large concentration overpotential is due to liquid H₃PO₄ in the electrodes, preventing the reactant gas delivery to the electrocatalyst surfaces. To further improve the cell performance, the kinetic and mass transport resistances need to be addressed. The kinetic and mass transport resistances are due to the ionomer binders in the electrodes. Therefore, further improvement in HT-PEMFC performance necessitates the invention of new polymer electrolytes as ionomer binders with better reaction kinetics and lower mass transport resistance.
Figure 8.1. (a) Source of overpotential in fuel cell polarization curve with H₂/O₂, with 50:50 QPPSf-PBI membrane with QPPSf GDEs (0.5 mgPt cm⁻²) at 220 °C/0% RH with 60 kPa of back pressure on both the anode and cathode.

From Chapter 5, both IDE and MEA studies for hydrogen pumps demonstrated that PTFSPA was a more effective electrode binder as it promotes reaction kinetics and gas transport. Hence, using PTFSPA as electrode binder with 0.5 mgPt cm⁻² and 50:50 QPPSf-PBI HT-PEM, the polarization behavior of HT-PEMFC under H₂/O₂ at high temperatures was evaluated.

8.2 Results and discussions

Using PTFSPA as electrode binder with 0.5 mgPt cm⁻² and 50:50 QPPSf-PBI HT-PEM, the polarization behavior of HT-PEMFC under H₂/O₂ at high temperatures was evaluated.

Figure 8.2a shows the performance comparison of HT-PEMFC employed with PTFSPA and H₃PO₄-QPPSf as electrode binders at 220 °C. The PTFSPA electrode binder offers better cell
performance, and a peak power density of 900 mW cm⁻² was achieved using 175 kPa_abs backpressure at 220 °C. Figure 8.2b shows the EIS of HT-PEMFC polarization using PTFSPA and H₃PO₄-QPPSf as electrode binders in the MEAs. By switching the electrode binder, the HT-PEMFC performance was improved. The new PTFSPA binder enabled a reduction in charge-transfer resistance (R_{ct}), allowing better reaction kinetics at high temperatures. R_{ct} ≤ 0.03 Ω·cm⁻² at 0.7 V for HOR and ORR with PTFSPA and 50:50 QPPSf-PBI HT-PEM was observed. This showcases the effectiveness of the new electrode binder for HT-PEM architectures.

Figure 8.2. a.) Fuel cell polarization curve with H₂/O₂, with 50:50 QPPSf-PBI membrane with QPPSf and PTFSPA GDEs (0.5 mgPt cm⁻²) at 220 °C/0% RH with 175 kPa of absolute backpressure on both the anode and cathode. b.) Nyquist plots of 50:50 QPPSf-PBI membrane with QPPSf and PTFSPA electrodes at 220 °C/0% RH for H₂/O₂

8.3 Conclusions and future work

In summary, PTFSPA is a more effective electrode binder for HT-PEM architectures involving hydrogen, over QPPSf-H₃PO₄ binders because it does not contain liquid acid known to obfuscate hydrogen gas permeability and hinder reaction kinetics due to phosphate anion adsorption on the electrocatalyst surface. The 50:50 QPPSf-PBI membrane and PTFSPA
ionomer binder in GDEs gave a competitive power density of 900 mW cm\(^{-2}\) with H\(_2\)/O\(_2\) at 220 °C. This study highlights the importance of phosphonic acid functionalized polymer electrolytes as ionomer binder materials for HT-PEM architectures. The interesting observation in improvement in polarization behavior of HT-PEMFC motivates future studies to improve the fuel cell performance. By utilizing thinner and reinforced membranes and better optimizing the HT-PEMFC architecture, the polarization behavior of HT-PEMFC could be explored.

The new PTFSPA binder has shown promising results in reducing the kinetic resistance in both HT-PEM ECHP (see Figure 4.10a) and HT-PEMFC (see Figure 8.2a). It is vital to address the mass transport resistance, increasing hydrogen and oxygen permeability at higher current densities and enhancing device performance. Further reduction in mass transport resistance could be achieved by employing a thin reinforced membrane to handle more backpressure. From Figure 4.27, it could be visualized that the HT-PEMFC operation is hindered at 220 °C after 36 hours due to mechanical failure of the membrane. Instead, the membrane chemistry being very stable. Figure 8.3 shows the advantage of using reinforced membranes in HT-PEM architectures.

![Figure 8.3](image)

**Figure 8.3.** Schematic representation of employment of reinforced membranes in HT-PEM architecture for improving device performance
Chapter 5 showcases the significant improvement in HOR/HER kinetics and permeability using the new PTFSPA electrode binder in HT-PEM architectures. In the case of HT-PEMFCs, the ORR in the cathode has sluggish reaction kinetics compared to HOR. Therefore, for further improving the HT-PEMFC performance from 900 mW cm\(^{-2}\) of power density, understanding the interaction of the new PTFSPA electrode binder with ORR in the cathode becomes vital. Also, to reduce the PGM loading in the electrodes, studying oxygen with an electrode binder in the cathode is essential. **Figure 8.4** shows the microelectrode setup to compute O\(_2\) permeability at high temperatures. The anode compartment consists of GDE fabricated using PTFSPA. In contrast, the cathode compartment consists of an uncatalyzed GDL coated with an ionomer binder of interest, in our case PTFSPA, followed by a thin Pt wire which would act as a microelectrode. By stepping the working electrode (Pt wire) potential down from the OCV to 0.4 V vs. SHE, where the ORR is diffusion-limited, the oxygen reduction current profile could be monitored. The O\(_2\) transport through the polymer could be analyzed using unsteady state Fick’s law in a cylindrical geometry, given by the Cortell equation.

\[
I = nFACD \left( \frac{1}{\sqrt{\piDt}} + \frac{0.422}{r} \right)
\]

(6.1)

Where \(t\): time (s), \(C\): oxygen concentration (mol cm\(^{-3}\)), \(D\): diffusion coefficient (cm\(^2\) s\(^{-1}\)), \(r\): radius of Pt wire (cm)
Figure 8.4. Microelectrode study to compute O$_2$ permeability in the cathode
Chapter 9
Conclusions

This dissertation demonstrated the improvements in HT-PEMFC and ECHP performance by fabricating a new high temperature (HT-) polymer electrolyte that was deployed as a membrane separator (50:50 QPPSf-PBI) and as an ionomer binder (PTFSPA) in the electrodes that addressed the overpotential sources. In addition to the device level demonstrations, the material and structural properties of high-temperature polymer electrolytes, as membranes and electrode ionomer binders, were investigated. The dissertation unequivocally shows that the high-temperature operation of hydrogen fuel cells and ECHP facilitated by the high-temperature polymer electrolytes curtails CO adsorption's effect on the electrodes and necessitates better device performance.

The newly synthesized HT-PEM based on PC-PBI blend (50:50 QPPSf-PBI) displayed excellent ionic conductivity and water resiliency under a wide-temperature range of -70 °C to 240 °C. The superlative ionic conductivity of HT-PEM was attributed to the polycation (PC) promoting more significant hydrogen bonding frustration, and the PBI was facilitating higher H$_3$PO$_4$ uptake. The new class of HT-PEM enables the operation of hydrogen fuel cells and ECHPs under a wide temperature range, and concurrently promotes a better performance by reducing the ASR.

The high temperature (HT-) polymer electrolytes exploited as ionomer electrode binders served as a thin adhesive coating on the electrocatalyst/electrocatalyst support particles and profoundly impacted the HT-PEMFC and ECHP cell performance. The newly synthesized phosphonic acid-functionalized high-temperature polymer electrolyte, PTFSPA, is a more effective electrode binder for hydrogen fuel cells and ECHPs over PC-H$_3$PO$_4$ binders because it does not contain liquid acid known to obfuscate hydrogen gas permeability and hinder reaction.
kinetics due to phosphate anion adsorption on the electrocatalyst surface. Though phosphonic acid-functionalized polymer electrolytes conduct protons under hydrated and anhydrous conditions, they have poor mechanical integrity, restricting their employment as HT-PEM in hydrogen fuel cells and ECHPs. Owing to the thin coating of ionomer used in the electrocatalyst layer, high ionic conductivity and mechanical integrity are not essential for an ionomer binder. Rather the electrochemical properties such as the charge-transfer reaction kinetics and gas permeability have a more profound impact on the electrochemical device performance. Using the IDE platform decorated with nanowire platinum catalysts for HOR/HER studies, it was unequivocally demonstrated that the measured thin-film polymer electrolyte electrochemical properties of PTFSPA enable better HOR/HER kinetics and gas permeability at high temperatures.

Using 50:50 QPPSf-PBI HT-PEM and PTFSPA as ionomer binders, an excellent ECHP performance of 1 A cm\(^{-2}\) at 55 mV at 220 °C was achieved. By employing the new PTFSPA electrode binder, >0.9 W cm\(^{-2}\) of power density was performed in HT-PEMFCs with H\(_2\)/O\(_2\) at 220 °C. The augmented performance HT-PEMFC and HT-PEM ECHP were achieved due to the high-temperature operation enabled by the new HT-PEM and enhanced reaction kinetics and gas permeability PTFSPA electrode binder. The high-temperature operation of HT-PEM ECHP enabled better tolerance to CO and other contaminants in the anode feed. Moreover, the high-temperature operation enabled accelerated desorption of Pt conceding better device performance.

The maneuver of high-temperature polymer electrolytes synthesized and employed in this dissertation reveals new horizons for the wide-temperature operation of hydrogen fuel cells and ECHPs for challenging energy conversion and separation applications aerospace, transportation, electricity generation, and separations. Also, the high-temperature operation of hydrogen fuel cells
and ECHP improves clean energy production and separation technology's cost competitiveness. Improving the cost competitiveness will economically incentivize the market for an easier and faster transition to fuel cell and hydrogen pump technology.
Appendix
Permission to Use Copyrighted Materials

A.1 Permission to Use Chapter 4, Section 4.2.1, and 4.2.3 – 4.2.8, Text and Figures

A.2 Permission to Use Chapter 4, Section 4.2.2, and Chapter 7, Text and Figures
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Vita

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