Modifying Carbon Supports for Improved Ion-Exchange Capacity in Proton-Exchange Membrane Fuel Cells

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MODIFYING CARBON SUPPORTS FOR IMPROVED ION-EXCHANGE CAPACITY IN PROTON-EXCHANGE MEMBRANE FUEL CELLS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Chemistry

by
Bryan L. Bill
December 2019

Accepted by:
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Dr. Joseph S. Thrasher
Dr. Sourav Saha
ABSTRACT

Sulfonated perfluorocyclobutyl phosphonate (s-PFCB-PO₃) polymers are studied extensively in proton-exchange membrane (PEM) fuel-cell applications for their favorable ionic-conducting properties. Inspired by their high chemical, mechanical and thermal stability, PFCB polymers have been used by several groups as grafting compounds onto zirconia-decorated carbon black (ZrC) catalyst supports. The trifluorovinyl ether (TFVE) moiety of the aryl bis-TFVE monomer provides a template for polymerization by step-growth [2+2] cycloaddition to afford PFCB polymers which upon subsequent sulfonation can have high ion-exchange capacity and high proton conductivity. Aryl phosphonic acid substitution onto the terminal TFVE groups provides a route to anchoring the ionic polymers onto the surface of ZrC supports by binding of phosphonates onto zirconia particles. Electrodes prepared from such materials are expected to be mixed ionic and electronic conducting (MIEC) composites, which allows for their use in a PEM fuel cell without diminishing proton transport due to water exposure.

Herein, a sulfonated PFCB polymer is synthesized from a precursor PFCB polymer and characterized by ion-exchange capacity (IEC) and NMR spectroscopy measurements. The molecular weight and average number of repeat units per PFCB polymer chain are calculated from ¹⁹F-NMR spectroscopy data. An IEC of 2.35 meq/g is expected upon mono-sulfonation of each repeat unit in the polymer. Neutralization titration reveals a much higher 3.94 meq/g IEC, which may be due to a combination
of impurities from the sulfonation and/or hydrolysis reactions, and from some polymer repeat units having more than one sulfonation site.

Electronic resistance measurements were made using an electrochemical hydrogen-pumping device as a diagnostic tool to calculate the effective ionic conductivity of composite materials made from the s-PFCB-PO₃ polymer and the ZrC material. The ZrC and s-PFCB-PO₃-ZrC (the MIEC) catalyst inks are used to make s-PFCB-PO₃-ZrC layers that are placed in a sandwich configuration between Nafion membranes in an electrochemical hydrogen-pump cell to isolate the ionic resistance contributions from the immobilized PFCB polymer.

A composite consisting of 25 weight percent Nafion® (1,100 equivalent weight) and 75 weight percent s-PFCB-PO₃-ZrC has an ionic conductivity of 66.0 mS/cm, whereas a control composite containing 100 weight percent ZrC has an ionic conductivity of 57.9 mS/cm. These results provide new insight into the proton transport properties of composites made from ionomer polymers and carbon-based electrocatalyst supports.
ACKNOWLEDGEMENTS

I would like to personally thank my advisor Dr. Stephen Creager and Dr. William Pennington for their support in my first year at Clemson University. Even when I was met with adversity you both have been extremely helpful in providing counsel and guidance. A special thanks to committee members Dr. Joseph Thrasher and Dr. Sourav Saha for guiding through the sometimes-difficult writing process. Your help is greatly appreciated. I would also like to thank my excellent lab co-workers, Dr. Saheed Bukola and Kyle Beard, for their lending their extensive expertise in electrochemical fuel-cells and synthetic chemistry. My project would have not progressed without their tremendous efforts in teaching me to conduct resistance measurements. Moreover, Dr. Bukola and Kyle were more than colleagues; they were good friends and often made lab days quite enjoyable.

A special thanks to the entire Department of Chemistry faculty and staff whose efforts were dedicated to organizing and advising graduate students as we matriculate at Clemson University. I want you all to know how much I appreciate your hard work and dedication in providing me with academic support both financially and personally.

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3-PBSA................................................................. 3-phosphono benzenesulfonic acid
AFCs............................................................................ Alkaline fuel cells
Ar—H........................................................................... Aromatic hydrogen atoms
CB................................................................................ Carbon black
I/V................................................................................ Current/Voltage
CV.............................................................................. Cyclic voltammogram
DBFCs ....................................................................... Direct-borohydride fuel cells
DCFCs.......................................................................... Direct-carbon fuel cells
DEFCs.......................................................................... Direct-ethanol fuel cells
DFAFCs......................................................................... Direct-formic acid fuel cells
DMFCs.......................................................................... Direct-methanol fuel cells
DS.................................................................................. Degree of sulfonation
eBFCs .......................................................................... Enzymatic biological fuel cells
Equiv wt......................................................................... Equivalent weight
FC.................................................................................. Fuel cell
GDL................................................................................ Gas-diffusion layer
H₂/O₂.......................................................................... Hydrogen and oxygen chemical reaction
HT-PEMFCs.................................................. High-temperature proton exchange membrane fuel cells
IEC................................................................................. Ion-exchange capacity
LT-PEMFCs.................................................. Low-temperature proton exchange membrane fuel cells
List of Abbreviations (Continued)

MEA.......................................................................................... Membrane electrode assembly
mBFCs.......................................................................................... Microbial biological fuel cells
Mmol .......................................................................................... Millimole
m-SPPA.................................................................................. meta-sulfophenyl phosphonic acid
MW.......................................................................................... Molecular weight
Nafion®-212 ........................................................................... Nafion® membrane (thickness: 50 μm)
ns-PFCB.................................................................................. Non-sulfonated perfluorocyclobutyl
PEM.......................................................................................... Proton exchange membrane
PEMFC.................................................................................. Proton exchange membrane fuel cell
PFSA.......................................................................................... Perfluorinated sulfonic acid
PAFCs.................................................................................. Phosphoric acid fuel cells
PO_3 di-acid .................................................................................. Aryl phosphonic di-acid
PO_3 di-ester ............................................................................ Aryl phosphonate di-ester
PPA.......................................................................................... Phenyl phosphonic acid
PTFE.................................................................................... Polytetrafluoroethylene
Pt/C........................................................................................ Platinum-coated carbon
RPM...................................................................................... Revolutions per minute
s-PFCB.................................................................................. Sulfonated perfluorocyclobutyl
V-72........................................................................................ Vulcan-XC 72
Wt %........................................................................................ Weight percent
ZrC........................................................................................... Zirconia decorated Vulcan carbon black
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CHAPTER 1

INCREASING DEMANDS FOR ALTERNATIVE ENERGY SOURCES

1.1 Renewable and alternative energy

Renewable energy sources—such as wood—available during early civilizations were well diverse leading up to the Medieval period in the 1500s. As productivity demands grew exponentially during the Industrial Revolution fossil fuels became an important source of non-renewable energy for economic advancement.\(^1\) Energy is deemed renewable if it is derived or acquired from natural resources\(^2\) and requires no human input to restore or replace. In contrast, alternative energy sources are adopted as a means to transition from the currently dominant energy supply (fossil fuels since the mid-1800s). Society has made numerous shifts among major energy sources that demand a more modern and precise description of alternative energy. Resources that produce waste energy, but limit emission of greenhouse gases and/or carbon emissions are considered suitable alternative energies. Some examples involve natural gas from fracking, H\(_2\) energy in fuel-cell devices, and biofuels which do not expend natural resources.\(^3\)

Progress in developmental technology eventually led to the widespread adoption of the internal combustion engine (ICE) in the automotive industry. By the 1970s anxiety grew over the global environmental effects of the ICE’s sole reliance on

1
these fossil fuels in large-scale public transportation. World governments began to respond rapidly to a wave of published news and academic analyses in the late 1990s condemning fossil energy consumption due to its environmental impact.\textsuperscript{4,5} Several media outlets regularly cited global warming and ozone depletion as chief reasons to implement initiatives aimed at diversifying into alternative resources.\textsuperscript{6,7} By the end of the 20\textsuperscript{th} century, the United States Environmental Protection Agency (EPA) had successfully passed amendments to the Clean Air Act, Zero Emission Mandates and the National Environmental Education Act in a collective effort to accelerate education and exploration into clean and efficient fuels.\textsuperscript{8,9}

An interesting narrative articulated by astrophysicist Nikolai Kardashev describes the long-term trajectory of civilizations harvesting stored energy on Earth. Kardashev believed gains made in pursuit of alternative energy would propel humans to inhabit other worlds. Though Kardashev’s ideas were quite ambitious, his astronomy work is notable for evaluating and quantifying the world’s progress on efficient energy consumption in 1964.\textsuperscript{10} He compared the energy output of the Sun available on the Earth ($4 \times 10^{26}$ watts) to the total energy consumed by humans, $4 \times 10^{12}$ watts. Kardashev sought to identify society’s inefficiencies in energy conversion by devising a progressive scale divided into several categories. Calculations from Kardashev’s manuscript also highlighted a positive correlation between human’s progression in energy consumption and technological advancement. The work
produced a finding that suggests society stands to benefit immensely from embracing fossil fuel alternatives that better meet all the needs for global energy consumption.

1.2 Fuel-cell types and their applications

Christian Friedrich Schönbein is credited as the first scientist to describe the chemical conversion of energy from a chemical reaction between hydrogen and oxygen (H₂/O₂) into useful electrical energy in 1839. His findings marked among the earliest reports of a hydrogen fuel-cell in the early 19th century. A few years later in 1845, proof of concept for developing and testing a fully-functioning (but meager in power generation) fuel-cell device was first accomplished by Sir William Robert Grove. This principal achievement by Grove went on into the upcoming 20th century to serve as one of many clean-energy alternatives to fossil fuels for global energy consumption. Though limited in commercial development, fuel cells (FCs) grew considerably in popularity because their electrical energy harvested from stored chemical energy enabled them to power a wide range of portable and stationary devices.

The world would not see its first functioning fuel-cell put to practical use until 1959 when Francis T. Bacon introduced an alkaline fuel-cell (AFC) capable of delivering 5 kW of power. By the 1960s growing popularity in fuel-cell technology—with the advent of a polymer electrolyte membrane—eventually led to their use in the Apollo space program (1961) providing electricity for launching, landing, and
onboard power. Fuel cells have also made their way into consumer markets powering portable laptops, cordless phones, cameras, and wireless power tools. Surprisingly, fuel-cell development has flourished in the industrial sector because standard considerations like start-up times, long battery-life, and good physical durability are not always critical factors for their utility. Large fuel-cell stations typically are used in uninterrupted power supply (UPS) units such as office buildings, hospitals, warehouses, and universities. Unfortunately, most fuel-cell applications have been limited to back-up power supply systems. This narrow market position is partly due to their low power density, tendency to corrode in outdoor climates, and temperature-induced deformations from often expanding and contracting. These changes in components of the fuel cell (FC) can have an adverse effect on the lifetime of the device.

H₂/O₂ fuel cells require a perpetual supply of hydrogen gas as fuel, which is one considerable inconvenience for its usage in portable devices. Other frequently encountered problems are high cost of the electrocatalyst and membrane, limited membrane durability, and low energy-conversion efficiency. Some advantages include much lower carbon emission and pollution levels, and less waste energy accumulation compared to fossil-fuel devices such as combustion engines.

Incorporation of fuel cells into electric vehicles has also been slow to emerge. Though scientists continue the search for new alternatives, older battery technologies such as nickel-cadmium and zinc-air batteries generate electrical power ranging from
65–120 watt hours/kilogram\(^5\) whereas FC power is typically reported near the low end of this range. Currently, H\(_2\) utilization in FCs is afflicted with poor performance. Recurrent issues such as low H\(_2\) storage capacities (4.5–wt % capacity H\(_2\) storage), low FC power output, sub-optimal charging/discharging rates and short life spans can collectively result in limited applications for H\(_2\) fuel cells. Circumventing the storage density problem with hydrogen has proven difficult though solutions using compressed gas storage are emerging. Energy conversion is also compromised if the fuel cell becomes too dehydrated as this causes ion conductivity to decline, which diminishes power output. Conversely, too much water can lead to membrane swelling\(^{15}\) and electrode flooding which inhibit fuel and oxidant mass transport resulting in lower power. Thus, water management inside the fuel cell is complex and warrants continued research to identify optimal FC designs.

A typical proton-exchange membrane fuel cell (PEMFC) in **Figure 1.1** uses H\(_2\) as a fuel source and oxygen from air as an oxidant. Hydrogen PEMFCs transport compressed H\(_2\) and O\(_2\) gas inside and out of the cell. Bipolar field plates regulate the flow of H\(_2\) and O\(_2\) gas through a network of channels and separators constructed to evacuate inlet gases and prevent condensed-vapor accumulation inside the cell. The gas diffusion layer—often consisting of a porous array of carbon fibers—allows efficient mass transport of gases (fuel and oxidant) as well as ions in the catalyst layer and rapid removal of heat and excess moisture from the membrane electrode assembly (MEA). The electrocatalyst layer—often made up of a platinum-coated
carbon support on woven cloth—is located immediately adjacent to the proton-exchange membrane (PEM). The reduction of hydrogen to produce protons is catalyzed by the platinum electrocatalyst.

![Diagram of a hydrogen fuel-cell](image)

**Figure 1.1.** Key components of a hydrogen fuel-cell.

The protons produced from hydrogen oxidation cross the ion-permeable membrane from the anode to the cathode. The electrons, however, are re-routed to
an external circuit for energy production. Protons arriving on the cathode side combine with electrons to reduce oxygen with the aid of the platinum catalyst producing water.\[16\]

Among fuel cells, several types exist using a wide range of fuel sources for a diversity of applications. Those using a proton exchange membrane (PEM) as an electrolyte can vary between 30–100 °C, i.e., low-temperature PEM fuel cells (LT-PEMFCs) and > 110–180 °C, i.e., high-temperature PEM fuel cells (HT-PEMFCs) consisting of polymer electrolytes Nafion® or polybenzimidazoles (PBI).\[14\] Table 1.1 provides some of the many fuel sources and catalyst materials used in conventional fuel cells such as direct methanol (DMFCs), ethanol (DEFCs), formic acid (DFAFCs) and direct borohydride (DBFCs), just to name a few. Several fuel-cell operations extend beyond the scope of proton exchange and function as anion-exchange membranes instead. DBFCs, alkaline fuel-cells (AFCs), direct-carbon fuel cells (DCFCs) and DEFCs each use alkaline electrolytes as membranes to facilitate ion transport.
Table 1.1. Fuel-cell types and function.\textsuperscript{14}

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<th>Mobile ion</th>
<th>Electrolyte</th>
<th>Operating Temperature</th>
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<tr>
<td>LT-PEMFCs</td>
<td>proton (H\textsuperscript{+})</td>
<td>Solid Nafion\textsuperscript{®}</td>
<td>60 – 80 °C</td>
</tr>
<tr>
<td>HT-PEMFCs</td>
<td>proton (H\textsuperscript{+})</td>
<td>Nafion\textsuperscript{®}/PBI doped in phosphoric acid</td>
<td>110 – 180 °C</td>
</tr>
<tr>
<td>Direct-methanol (DMFCs)</td>
<td>proton (H\textsuperscript{+})</td>
<td>Solid Nafion\textsuperscript{®}</td>
<td>Ambient – 110 °C</td>
</tr>
<tr>
<td>Direct-ethanol (DEFCs)</td>
<td>Proton (H\textsuperscript{+})</td>
<td>Nafion\textsuperscript{®}/Alkaline media</td>
<td>Ambient – 120 °C</td>
</tr>
<tr>
<td>Direct-borohydride (DBFCs)</td>
<td>sodium ion (Na\textsuperscript{+})</td>
<td>Solid Nafion\textsuperscript{®}/Anion exchange membrane</td>
<td>20 – 85 °C</td>
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<td>Alkaline (AFCs)</td>
<td>Hydroxide ion (OH\textsuperscript{-})</td>
<td>KOH in water solution/Anion exchange membrane</td>
<td>0 – 230 °C</td>
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<tr>
<td>Phosphoric acid (PAFCs)</td>
<td>proton (H\textsuperscript{+})</td>
<td>H\textsubscript{3}PO\textsubscript{4} solution in silicon carbide</td>
<td>160 – 220 °C</td>
</tr>
<tr>
<td>Direct-formic acid (DFAFCs)</td>
<td>proton (H\textsuperscript{+})</td>
<td>Solid Nafion\textsuperscript{®}</td>
<td>30 – 60 °C</td>
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<td>Direct-carbon (DCFCs)</td>
<td>oxygen ion (O\textsubscript{2}\textsuperscript{-})</td>
<td>Solid yttria-stabilized Zr/Molten carbonate/hydroxide</td>
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<td>proton (H\textsuperscript{+})</td>
<td>Ion exchange membrane</td>
<td>20 – 40 °C</td>
</tr>
<tr>
<td>Microbial fuel-cells (BFCs)</td>
<td>--</td>
<td>Glucose, acetate, waste-water</td>
<td>20 – 60 °C</td>
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Careful selection of the PEM, to serve as an electrolyte, and the fuel source is critical to achieving optimal cell performance. A desirable proton exchange membrane must be an efficient mediator of proton transport between the anode and cathode. Protons passing through the membrane must not be impeded by gases or water build-up at the electrode-catalyst interfaces while electrons are diverted through the external circuit. An electrocatalyst, e.g., platinum, is integrated into the membrane electrode assembly (MEA)—by hot-pressing for example—and helps supply the electrons by initiating hydrogen oxidation into protons and electrons at the anode. The electrons captured in this electrochemical reaction delivers the electrical current needed for power generation. Meanwhile, the membrane-permeable protons recombine on the other side at the cathode with electrons making water with the aid of an oxidant such as oxygen. The MEA fabrication is applied to a modified hydrogen-pump cell and will be discussed in detail in CHAPTER 4.
1.3 Scope of Work

The work presented in succeeding chapters will address the potential of the sulfonated perfluorocyclobutyl phosphonate (s-PFCB-PO$_3$) ionomer (Scheme 1.1) to function as an ion-conducting electrolyte in an electrochemical hydrogen-pump cell.

Scheme 1.1. Chemical structure of the s-PFCB-PO$_3$ ionomer.

PFCB polymers show some structural similarities to the commonly known perfluoro sulfonic acid (PFSA) electrolyte membrane Nafion®, Scheme 1.2, sharing chemically stable C—F bond units in the repeat chain. Both ionomers contain sulfonic acid groups responsible for the proton-conducting properties inside the cell.
The PFCB polymer functionalized with sulfonic acid groups (s-PFCB) can be neutralized by titration to determine the number of moles of ion-exchange groups per gram of sample (i.e., ion-exchange capacity). Acknowledging that sulfonation is limited to more electron-rich positions in the bi-aryl moiety of the PFCB polymer, the percent or degree of sulfonation (% DS) can also be estimated. And, the extent of ion exchange can be represented by the moles of protons neutralized per gram (i.e., IEC), or the number of R—SO₃H groups per repeat unit (i.e., degree of sulfonation). IEC is an important measurement that correlates with ion conductivity since the flow of electrons is dependent upon the rate of ion migration across the ion-permeable membrane.

Polymer electrolytes containing many sulfonic acid groups in the repeat unit are likely to have high solubility in water. This solubility can cause the polymer electrolyte to wash away from the electrodes, thus reducing electrode ionic conductivity. One solution to this problem was published by Shetzline et al in 2017,¹⁷ whereby the polymer electrolyte is anchored to mesoporous carbon black. Zirconia

\[
\text{Scheme 1.2. A general chemical structure of Nafion®.}
\]

\[
\begin{array}{c}
-\text{(CF}_2-\text{CF}_2)_x-\text{(CF}_2-\text{CF)}_y- \\
\text{O-\text{CF}_2-\text{CF}_2)_m-}\text{O-}\text{(CF}_2)_n-\text{SO}_3^- \text{H}^+
\end{array}
\]

\[
\text{CF}_3
\]
nanoparticles are integrated within the pores of carbon black (ZrC) and serve as organophosphonate anchors through robust Zr—O—P linkages.

Motivations for this approach originated from a 2010 report by Wang et al. that describes the coupling of phosphonate end-terminated polymers (R—PO₃) with zirconia oxide (ZrO₂). This led to the electrolyte-carbon anchoring described earlier to form a mixed-conductor composite (s-PFCB-PO₃-ZrC) capable of electronic and ionic conductivity.

The work presented in the following three chapters will describe the synthesis, ion-exchange capacity measurement and ionic conductivity properties of the standalone s-PFCB-PO₃ ionomers and the s-PFCB-PO₃-ZrC composite materials. Chapter 2 will cover the synthesis, chemical modifications, and NMR characterization of the sulfonated PFCB polymer. The chemical modifications will give the PFCB polymer ionically-conductive properties through sulfonic acid attachments along the polymer backbone. In Chapter 3, the ZrC-anchored s-PFCB ionomer will be compared by ion-exchange capacity measurements to the free-standing s-PFCB-PO₃ ionomers and a smaller organic acid, 3-phosphono benzenesulfonic acid (also referred to as m-SPPA). The purpose of this comparison is to provide some insight on how ionomer anchoring to zirconia-decorated carbon (ZrC) affects its ion-exchange capacity and thereby its ionic conductivity. And last, Chapter 4 describes the resistance measurements of the s-PFCB-PO₃-ZrC composite material in a miniaturized electrochemical hydrogen-pump cell. The goal of this project is to demonstrate the
utility of a hydrogen-pump cell as an electrochemical device and a diagnostic tool for measuring the electronic and ionic resistance of carbon-based ionomer composites. Although the hydrogen-pump cell does not generate electrical power like a typical fuel-cell, it can indirectly determine the conductivity and thus avoid the pitfalls associated with the measurement of conductivity through other techniques such as electrochemical impedance spectroscopy, which rely heavily upon equivalent circuit models to convert measured impedances into electrode and material properties.\textsuperscript{19–21}
CHAPTER 2
SYNTHESIS AND CHARACTERIZATION OF SULFONATED
PERFLUOROCYCLOBUTYL ARYL PHOSPHONIC POLYMERS

2.1 Introduction

2.1.1 Synthesis and chemical functionalization of the PFCB polymer

In 2012, Jung-Min Oh and co-workers\textsuperscript{22} described a polymerization reaction that produces the PFCB polymer, end-group phosphonation of that polymer, and aryl sulfonation and hydrolysis of the phosphonate ester end-groups (Scheme 2.1) to create a PFCB polymer with sulfonated repeat units and phosphonate end groups to allow for polymer anchoring onto zirconia surfaces. The PFCB polymer used in the work described in this chapter was obtained commercially from Tetramer Technologies Inc. and was synthesized via a [2+2] cycloaddition of aryl bis- (trifluoro vinyl ether) monomers. This cycopolymerization gives the PFCB polymer containing bi-aryl repeat units. The average molecular weight reported by the supplier for the polymer used in this work is 8,000 g mole\textsuperscript{-1} MW—though the degree of polymerization can be modulated. Diethyl (4-hydroxyphenyl) phosphonate was added to the non-sulfonated, ns-PFCB, polymer by a current co-worker, Kyle Beard via nucleophilic 1,2– addition of the phenol to the TFVE end groups of the PFCB polymer. This chemical modification provides the anchoring sites to which zirconia-
decorated carbon supports are later attached. Further functionalization of this terminally-functionalized PFCB polymer was independently carried out after obtaining the ns-PFCB-PO$_3$ polymer from co-worker Kyle Beard. These reactions include aryl sulfonation and acid-catalyzed hydrolysis of the phosphonate di-ester end-groups to generate the phosphonic acids responsible for the anchoring to zirconia.

The first step (Scheme 2.1) in the synthesis of the PFCB polymer is the thermally-initiated, stepwise polymerization of the aryl bis (trifluoro-vinyl ether) monomers at 160 °C, carried out by Tetramer Technologies. A polymer with repeating perfluorocyclobutyl (PFCB) units can be obtained following chain extension of the [2+2] cycloaddition reaction. In Step 2, the PFCB polymer was refluxed at 80 °C for 5 hours under sodium hydride and $N,N$-dimethylformamide in the presence of diethyl (4-hydroxyphenyl) phosphonate by co-worker Kyle Beard to give the ns-PFCB-PO$_3$ di-ester polymer. The polymer is then refluxed in concentrated chlorosulfonic acid and dichloromethane for 1 hour at 36 °C to obtain the s-PFCB-PO$_3$ ionomer in Step 3. Finally, the phosphonate di-ester end-groups were hydrolyzed, in Step 4, by refluxing the s-PFCB-PO$_3$ di-ester polymer in 6 M HCl solution for six days to yield the s-PFCB-PO$_3$ di-acid polymer. Covalent attachment of the sulfonated PFCB polymer onto zirconia-decorate carbon is done by dispersing the zirconia carbon (ZrC) catalyst support in a solution of the s-PFCB-PO$_3$ di-acid polymer in water. The mixture is
heated at 100 °C for 5 hours to obtain a mixed ionic and electronic conducting (MIEC) composite (i.e., the s-PFCB-PO$_3$-ZrC electrode).
Scheme 2.1. Synthesis and chemical functionalization of the s-PFCB-PO₃ polymer.
2.1.2 Determining the degree of sulfonation of s-PFCB phosphonate di-ester

Degree of sulfonation (DS) is an important characterization tool for determining ion-exchange capacity of ionomers. \(^1\)H-NMR spectroscopy was used to estimate the DS of the s-PFCB-PO\(_3\) di-ester ionomer. Protons arising from the sulfonic acid (SO\(_3\)H) group are not typically visible in \(^1\)H-NMR spectra due to rapid dissociation and hydrogen-bonding interactions. Calculation of the degree of SO\(_3\)H group functionalization is accomplished indirectly through the resolution of aromatic hydrogen atoms (Ar—H) in the bi-aryl group influenced by neighboring SO\(_3\)H groups. Once sulfonation alters the electronics in the aryl ring further sulfonation is meta-directing of which only one site remains available for a second SO\(_3\)H substitution. Presence of an electron-withdrawing SO\(_3\)H group in the aryl ring induces a downfield shift on adjacent proton signals in the \(^1\)H-NMR spectra. This remote proton signal is distinguishable from other Ar—H in the aryl ring and provides an appropriate means for determining DS of the s-PFCB-PO\(_3\) di-ester or di-acid ionomers. The structure of the bi-aryl ether linkage in the repeat unit of the sulfonated PFCB polymer after single sulfonation is depicted below in **Scheme 2.2**: 
The peak area from NMR integration of the aromatic protons adjacent to a SO$_3$H group (H$_A$ in Scheme 2.2) produces a unique relative intensity value, defined as $iH_A$. The integrated peak areas from all remaining Ar—H produces six relative intensity values defined as $iH_1$, $iH_2$, $iH_3$, $iH_3'$, $iH_4$, and $iH_4'$, respectively. Since it is known that aryl rings become more de-activated by the addition of an electron-withdrawing group di-substitution, while possible, is not believed to readily occur under mild conditions. Thus, we can assume that if sulfonation occurs, the aromatic ring will often contain a maximum of one SO$_3$H group per repeat unit. Thus, the degree of sulfonation can be defined conventionally as the number of repeat units successfully sulfonated, relative to the number of repeat units that were available for sulfonation, in each case assuming mono-sulfonation per repeat unit. Once each repeat unit contains at least one SO$_3$H group, the polymer is considered to be 100% sulfonated.
Again, due to the proton’s rapid dissociation in solution, the proton signal from the SO$_3$H group is typically not visible in $^1$H-NMR spectra. However, the neighboring Ar—H signal is de-shielded in the presence of the SO$_3$H group. This allows for simple integration of the adjacent Ar—H signal. The relative intensity of the Ar—H adjacent to a sulfonate group, ($iH_A$), and all of the remaining Ar—H signals ($iH_1$, $iH_2$, $iH_3$, $iH_3'$, $iH_4$, and $iH_4'$) can be expressed in Equation 2.1 using the following relationship between the proton signal and the integrated peak area:

\[
\frac{n}{(8 - 2n)} = \frac{iH_A}{\Sigma(iH_1, iH_2, iH_3, iH_3', iH_4, iH_4')} , \quad 0 \leq n \leq 2 \quad \text{Equation 2.1.}
\]

where $n$, ranging from 0 to 2.0, is the number of sulfonated sites per bi-aryl repeat unit. This number can be expressed as equivalents of sulfonates per repeat unit or percent degree of sulfonation, expressed as: $n \times 100\% = \text{DS (\%) }$.

In the case of one sulfonation site per repeat unit, there are seven total aromatic hydrogens remaining in the repeat unit of the s-PFCB-PO$_3$ di-ester ionomer. Proton NMR signals produced from the aromatic hydrogen atoms total 7 signals. One signal corresponds to the aromatic hydrogen adjacent to a sulfonate group. The six remaining signals overlap each other and correspond to the aromatic hydrogen atoms non-adjacent to the sulfonate group.

Since the hydrogen atoms from the SO$_3$H and $H_A$ are both equivalent to the ratio of SO$_3$H protons per repeat unit, the values of their relative intensities are
considered identical (\# of SO\textsubscript{3}H = \# of \textit{H}\textsubscript{A}). Also, these two protons can be excluded from the total number of aromatic hydrogen atoms not found adjacent to a SO\textsubscript{3}H group (i.e., 8 – 2n). Another way to think about these two protons is they do not contribute to the overall intensity signal found in the conglomerate of peaks between 7.3 and 7.7 ppm shown in Figure 2.4. The \textit{H}\textsubscript{A} proton, however, can be expressed as the relative intensity signal (n) occurring at ~ 8.1 ppm.
2.2 Experimental

2.2.1 Sulfonation of the ns-PFCB phosphonate di-ester

A glass vial, pre-treated with three dichloromethane washes, was charged with 1 mL of dichloromethane and a stir bar. The non-sulfonated perfluorocyclobutyl phosphonate (ns-PFCB-PO₃) di-ester polymer (52 mg, 7.3 μmol based on a polymer MW of 7,124 g mole⁻¹) was dispersed in the liquid to achieve dissolution. Chlorosulfonic acid (0.14 mL, 2.1 mmol) was added in a single portion upon which the pale brown solution turned dark brown. The reaction proceeded with vigorous stirring at an internal temperature of 36 °C for 70 min. Excess acid was quenched with 6 mL of cold distilled water, which immediately turned the dark precipitates to a stone-white color shown in Figure 2.1. The product was recovered by filtration under vacuum and washed with dichloromethane several times. The stone-white solid was collected and dried for 48 hours in a vacuum oven at room temperature (69 mg, 93% yield assuming a molecular weight of 8,620 g mole⁻¹ for the product polymer).
Figure 2.1. Sulfonation product of the ns-PFCB-PO₃ di-ester polymer.

2.2.2 Hydrolysis of the s-PFCB phosphonate di-ester

The s-PFCB-PO₃ di-ester polymer (130 mg, 15 μmol based on a polymer MW of 8,620 g mole⁻¹) and 6M hydrochloric acid solution (3 mL, 89 mmol) were charged to a 20 mL thick-walled pressure tube with PTFE bushing and Viton® O-ring equipped with a stir bar.²² The mixture was stirred vigorously at 130 °C for six days. The reaction mixture was then concentrated by evaporating the solvent under a continuous stream of argon. The resulting red solid (Figure 2.2) was dried under vacuum at 60 °C for 24 h (103 mg, 81% yield assuming a product molar mass of 8,508 g mole⁻¹).
2.2.3 Preparation of the 3-phosphono benzenesulfonic acid-ZrC nanocomposite material

A quantity of 3-phosphono benzenesulfonic acid (440 mg, 1.8 mmol) was dissolved in 25 mL of distilled water by sonicating for 20 min to make a 70 mM stock solution. ZrC (75 mg) was dispersed in the orange 3-phosphono benzenesulfonic acid (3-PBSA) solution and stirred continuously at 100 °C for 5 h. The black suspension was filtered through a 0.2 μm pore membrane and rinsed with 0.01 N HCl solution to convert the s-PFCB-PO₃ polymer into its all-proton form. The black solid is then washed with distilled water to remove the excess acid. The IEC measurement by
titration (see **CHAPTER 3**) shows 13 mg of the 3-PBSA attaches to 75 mg of the ZrC nanocomposite. The resulting black solid was dried in a vacuum oven at 85 °C for 24 h (59 mg).

### 2.2.4 Preparation of the s-PFCB phosphonate-ZrC nanocomposite material

The sulfonated perfluorocyclobutyl phosphonate (s-PFCB-PO₃) di-acid was synthesized by aryl sulfonation of the non-sulfonated perfluorocyclobutyl (ns-PFCB)-PO₃ di-ester followed by acid-catalyzed hydrolysis of the di-ester end-groups as described previously. The s-PFCB-PO₃ di-acid is then covalently attached to zirconia-decorated carbon (ZrC) *via* a Zr—O—P network between the zirconia nanoparticles and the phenyl phosphonic acid (PPA) groups as shown in **Scheme 2.3**.

**Scheme 2.3.** Chemical attachment of the s-PFCB-PO₃ to zirconia-modified carbon.

The s-PFCB-PO₃ di-acid polymer (14 mg, 1.6 μmol based on a polymer MW of 8,508 g mole⁻¹) was dispersed in 14 mL of warm distilled water until dissolved. Zirconia-modified carbon (64 mg) was dispersed in the orange 0.07 mM ionomer
solution (aq.) and stirred vigorously at 100 °C for 5 h. The solution was cooled in the
glass vial to room temperature and filtered through a 0.2 μm pore membrane. The
solid was then washed with 10 mL of 0.01 N hydrochloric acid to ensure complete
protonation of the sulfonate groups. The IEC measurement by titration (see
CHAPTER 3) shows that 12 mg of the s-PFCB-PO₃ di-acid polymer attaches to 64 mg
of the ZrC nanocomposite. The resulting s-PFCB-PO₃-ZrC nanocomposite was washed
with warm distilled water to remove excess acid and dried in a vacuum oven at 80 °C
for 48 h (62 mg, 82% yield).

2.2.5 Characterization and analysis of ns-PFCB-PO₃ and s-PFCB-PO₃ di-ester
and s-PFCB-PO₃ di-acid ionomers by ¹H, ¹⁹F and ³¹P-NMR

¹H-NMR, ¹⁹F-NMR and ³¹P-NMR spectra were obtained on a Bruker Avance
300 MHz FT-NMR to ascertain the chemical structure of each aryl phosphonate
polymer. ¹⁹F-NMR analysis of the ns-PFCB-PO₃ di-ester was used to estimate the
average number of repeat units in the polymer. ³¹P-NMR spectroscopy was used to
characterize the of conversion of the s-PFCB-PO₃ di-ester to the di-acid ionomer. ¹H-
NMR spectral analysis of the s-PFCB-PO₃ di-ester was used to confirm sulfonation and
estimate degree of sulfonation (DS). In the ¹H-NMR spectra residual protons from
acetone-₆ are assigned a chemical shift value of 2.06 ppm.
2.3 Results and Discussion

The results of $^1$H-NMR spectroscopy, which was used to characterize the ns-PFCB-PO$_3$ di-ester and the sulfonated (s-PFCB) polymer before and after the sulfonation reaction, will be discussed. $^1$H-NMR analysis of the ns-PFCB-PO$_3$ di-ester ionomer in acetone-$d_6$ (Figure 2.3) reveals seven characteristic peaks, not counting the residual peaks due to water and acetone.

The Ar–H signals in the bi-aryl repeat unit (peaks c and d) are shown at 7.32 and 7.71 ppm, whereas the PO$_3$ Ar–H signals in the aryl-phosphonate end groups correspond to peaks a and b at 7.50 and 7.92 ppm, respectively. Typically, the integration ratio of Ar–H in the repeat unit to end-terminated PO$_3$ Ar–H gives the total number of repeat units. However, the integration ratio of these peaks ($((13.53+13.38)/(1.00+0.99))$ is 13.5, or ~ 5,300 g mole$^{-1}$ MW which is less than the ~ 8,000 g mole$^{-1}$ MW estimate from Tetramer Technologies, supplier of the PFCB polymer. Similarly, $^1$H-NMR integration of the Ar–H signals in Figure 2.4 is not a reliable means for estimating degree of sulfonation (DS). Therefore, DS is not reported for the s-PFCB-PO$_3$ di-ester polymer.
The vicinal fluoroether group contains fluorine atoms in the non-repeating backbone of the PFCB polymer. Conveniently, the PFCB unit repeats with six fluorine atoms forming the ether bridge between the bi-aryl groups. Employing $^{19}$F-NMR spectroscopy provides a convenient alternative to estimating the number of repeat units in the PFCB polymer. This method to estimate the number of repeat units and to determine the MW of the polymer will be discussed later in this section using $^{19}$F-NMR spectral analysis.

**Figure 2.3.** $^1$H-NMR (300 MHz, acetone-$d_6$*) of the ns-PFCB-PO$_3$ di-ester polymer.
Peaks e and f in the $^1$H-NMR spectrum correspond to the phosphonate di-ester end groups $-\text{CH}_2-$ and $-\text{CH}_3$ respectively. The integration ratio of $f/a$ and $f/b$ are (2.96/1.00) and (2.96/0.99) as expected from the number of hydrogen atoms in Table 2.1. Peak e, however, did not produce the 2/3 hydrogen ratio expected from the e/f integration ratio. Instead, the ratios were 1.66/2.96 or 0.56 vs the expected 0.67. The reason for this discrepancy is at this point unclear.
Table 2.1. Characteristic $^1$H-NMR signals of the ns-PFCB-PO$_3$ di-ester.

<table>
<thead>
<tr>
<th>NMR signal</th>
<th>Integration</th>
<th>Chemical shift, ppm</th>
<th>Expected # of H atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.00</td>
<td>7.92</td>
<td>4</td>
</tr>
<tr>
<td>b</td>
<td>0.99</td>
<td>7.50</td>
<td>4</td>
</tr>
<tr>
<td>c$^i$</td>
<td>13.53</td>
<td>7.71</td>
<td>--</td>
</tr>
<tr>
<td>d$^i$</td>
<td>13.38</td>
<td>7.32</td>
<td>--</td>
</tr>
<tr>
<td>e$^i$</td>
<td>1.66</td>
<td>4.11</td>
<td>8</td>
</tr>
<tr>
<td>f</td>
<td>2.96</td>
<td>1.30</td>
<td>12</td>
</tr>
<tr>
<td>g$^i$</td>
<td>0.43</td>
<td>6.45–6.65</td>
<td>2</td>
</tr>
</tbody>
</table>

$^i$Superscript denotes NMR signals with inconsistent NMR integrations.

Peak g shown at 6.45–6.65 ppm arises from the 1,2– addition of the PO$_3$ end-groups in step 2 as depicted in Scheme 2.1. Peak integration ratio of 1.00/0.43 from a:g suggests approximately a 2/1 hydrogen ratio, which is consistent with the expected hydrogen ratio of a/g. The PFCB polymer contains two trifluoro vinyl ether terminal end-units prior to nucleophilic addition. Investigating the mechanism of the nucleophilic 1,2– addition reveals two possible reaction pathways; one leading to a difluoro vinyl ether (R–O–CF=CF–Nu) and a NaF salt, and another in which the trifluoro ethylene ether (R–O–CHF–CF$_2$–Nu) is obtained after quenching the excess sodium hydride. Assuming the nucleophilic addition proceeds through a common transition state, then both products would be present in relatively equal amounts. This would give an a:g peak integration ratio of 1/0.25 as opposed to the observed 1/0.43 a:g integration ratio. Thus, it is assumed that the 1,2–addition leading to a
doublet as a result of coupling between the hydrogen and fluorine atoms (H–C–F) is the predominant pathway of the nucleophilic substitution of the aryl phenol.

When acetone-\textit{d6} is used as a solvent, the residual peak for H$_2$O typically appears at 2.84 ppm as shown in \textbf{Figure 2.4}.\textsuperscript{25} Peaks due to internal standard (tetramethyl silane) and grease are present with chemical shift values 0.15 and 0.89 ppm.

The $^1$H-NMR spectrum obtained on the s-PFCB-PO$_3$ di-ester (\textbf{Figure 2.4}) and ethyl alcohol (\textbf{Figure 2.5}) also contain a number of residual peaks which supports possible solvent contamination from the acetone-\textit{d6} used. Impurity peaks in the $^1$H-NMR analysis of the s-PFCB-PO$_3$ di-ester polymer (\textbf{Table 2.2}) occur at 0.04–0.16, 0.88, 1.16, 2.27, 2.57–2.59, 3.53, and 6.14–7.07 ppm.
Figure 2.4. $^1$H-NMR (300 MHz, acetone-$d_6$) of the s-PFCB-PO$_3$ di-ester polymer.
Table 2.2. $^1$H-NMR chemical shifts of residual peaks in ethanol and s-PFCB-PO$_3$ di-ester.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Ethyl alcohol (ppm)</th>
<th>s-PFCB PO$_3$ di-ester (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i, –CH$_2$</td>
<td>3.56–3.58</td>
<td>3.53</td>
</tr>
<tr>
<td>j, –CH$_3$</td>
<td>1.13–1.29</td>
<td>1.16</td>
</tr>
<tr>
<td>k, –OH</td>
<td>2.96</td>
<td>not present</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>--</td>
<td>2.87</td>
</tr>
<tr>
<td>silicone oil</td>
<td>not present</td>
<td>0.04–0.10</td>
</tr>
<tr>
<td>TMS</td>
<td>0.14</td>
<td>0.15–0.16</td>
</tr>
<tr>
<td>grease</td>
<td>0.88</td>
<td>0.88</td>
</tr>
<tr>
<td>--</td>
<td>2.31</td>
<td>2.27</td>
</tr>
<tr>
<td>--</td>
<td>2.62</td>
<td>2.57–2.59</td>
</tr>
<tr>
<td>--</td>
<td>not present</td>
<td>5.21</td>
</tr>
<tr>
<td>--</td>
<td>6.7–7.10</td>
<td>6.14–7.07</td>
</tr>
</tbody>
</table>

Nearly all of these peaks are present in the $^1$H-NMR of ethyl alcohol, which was taken to observe any possible CH$_3$CH$_2$OH peak residues during PO$_3$ di-ester hydrolysis of the s-PFCB-PO$_3$ di-ester polymer. The peak at 5.21 ppm in the $^1$H-NMR spectrum of the s-PFCB-PO$_3$ di-ester (Figure 2.4) is unknown. However, peaks j and i at 1.16 and 3.53 ppm are identified in the spectrum as the —CH$_3$ and —CH$_2$ proton signals, though the relative integrations are not 3:2 as expected likely due to overlapping impurity signals. This conclusion is based on the similar chemical shift values found in the $^1$H-NMR spectrum of ethyl alcohol (1.13–1.29 and 3.56–3.58
ppm). The proton coming from the —OH signal (k at 2.96 ppm) in ethyl alcohol is labile which may explain its absence in the $^1$H-NMR of the s-PFCB-PO$_3$ di-ester.

![NMR spectrum of ethyl alcohol](image)

**Figure 2.5.** $^1$H-NMR (300 MHz, acetone-$d_6$*) of ethyl alcohol.

Peak h in the $^1$H-NMR spectrum of the s-PFCB-PO$_3$ di-acid (Figure 2.6) is visible downfield at 8.19 ppm and corresponds to the Ar—H adjacent to a SO$_3$H group. The large and broad peak at 6.7 ppm is unknown and appears often after several hydrolysis reactions. The broad peaks c and d, a result of sulfonation, lie directly on top the aryl phosphonate peaks a and b. Peak overlap and peak broadening makes it difficult to identify and integrate c and d precisely.
Figure 2.6. $^1$H-NMR (300 MHz, acetone-\textit{d6}*) of the s-PFCB-PO$_3$ di-acid polymer.

Therefore, the peak integration sum of c+d cannot be measured properly to calculate the integration ratio of (c+d)/h in the $^1$H-NMR spectrum.

$^{19}$F-NMR spectral analysis of the non-sulfonated perfluorocyclobutyl (ns-PFCB)-PO$_3$ di-ester polymer in acetone-\textit{d6} (Figure 2.7) reveals four characteristic signals—peaks l, m, n and o. Peak o, containing an agglomerate of six signals, at –129 – (–132) ppm corresponds to the six fluorine atoms in the PFCB repeat unit.
Peaks l and m from $-85.9$ – $(-87.3)$ ppm corresponds to the geminal fluorine atoms (R–CF₂) near the PO₃ di-ester end-groups. Peaks l and m are diastereotopic as a result of the adjacent chiral carbon present in the trifluoro ethylene ether. The j coupling constant is 145 Hz corresponding to an AB coupling system. This AB quartet spin system is in agreement with Dr. Park's J coupling constant of 148 Hz. Peak n, near the PFCB unit, is the chiral fluoroethylene (CHF–R) that appears more upfield at $-141.32$ – $(-141.52)$ ppm. Coupling between $^1$H and $^{19}$F nuclei supports the presence of CHF–CF₂–Nu, and not CF=CF–Nu. Peak n resembles a doublet of triplets, which
suggests the 0.22 (vs 0.50 expected) integration of peak g in $^1$H-NMR spectrum (Figure 2.3) is not attributed to the formation of the fluoroethylene during nucleophilic 1,2–addition. Reasons for this unexpectedly lower peak integration of g is unclear. The peak integration ratio 63.03/ (2.37+1.00) of o/ (l+m+n) in the $^{19}$F-NMR spectrum is ~ 18.7, which represents the average number of repeat units in the ns-PFCB-PO$_3$ di-ester polymer. Thus, the estimated MW of the polymer is ~ 7,124 g mole$^{-1}$ by $^{19}$F-NMR integration, while the estimated MW provided by Tetramer Technologies is close to ~ 8,000 g mole$^{-1}$.

$^{31}$P-NMR spectral analysis of the s-PFCB-PO$_3$ di-ester and di-acid was used to illustrate hydrolysis of the PO$_3$ di-ester (O=P–(OCH$_2$CH$_3$)$_2$) to the PO$_3$ di-acid (O=P–(OH)$_2$). The $^{31}$P-NMR spectrum of the s-PFCB-PO$_3$ di-ester polymer (Figure 2.8) was analyzed in acetone-$d_6$, while the s-PFCB-PO$_3$ di-acid polymer (Figure 2.9) was prepared in DMSO-$d_6$. This protocol was adopted from Park et al. so that the phosphorus signals can be similarly identified based on their chemical shift values. Peak p from the s-PFCB-PO$_3$ di-ester appears at ~ 17.1 ppm, which is consistent with the presence of the di-ester (O=P–(OCH$_2$CH$_3$)$_2$). Peak q from the s-PFCB-PO$_3$ di-acid appears upfield at 12.1 ppm and corresponds to the di-acid (O=P–(OH)$_2$) observed by Park et al. No signal for the phosphorus peak at 17.1 ppm (peak p) is present in the $^{31}$P-NMR spectrum of the PO$_3$ di-acid product which indicates complete conversion by NMR spectroscopy. These phosphorus signals are consistent with the NMR data reported by Park and co-workers.
Figure 2.8. $^{31}$P-NMR (121 MHz, acetone-$d_6$) of the s-PFCB-PO$_3$ di-ester polymer.
Figure 2.9. $^{31}$P-NMR (121 MHz, DMSO-$d_6$) of the s-PFCB-PO$_3$ di-acid polymer.
CHAPTER 3
ION-EXCHANGE CAPACITY OF IONOMER-MODIFIED CARBON SUPPORTS VIA TITRATION

3.1 Introduction

3.1.1 Titration of ionomer-modified zirconia-decorated carbon supports

The perfluorinated sulfonic acid ion-exchange polymer Nafion® has been the industry standard for proton-exchange membranes since the 1960s. Nafion® membrane's unique structure allows for protons to travel across a network of hydrated sulfonate clusters while remaining relatively resistant to thermal and mechanical degradation. In this chapter, we describe the ion-exchange capacity (IEC) measurement through a series of titration experiments on zirconia-decorated carbon (ZrC) and ionomer-modified ZrC supports that are composed of sulfonic acid groups similar to those in Nafion®. The 3-phosphono benzenesulfonic acid (3-PBSA) and sulfonated perfluorocyclobutyl (s-PFCB)-PO₃-modified ZrC supports will be compared to the standalone 3-PBSA and s-PFCB-PO₃ di-acid/di-ester materials, with the goal of revealing the relative amounts of protons that are attached to the carbon support. Going forward, the 3-phosphono benzenesulfonic acid will be referred to as meta-sulfophenyl phosphonic acid and abbreviated as m-SPPA.

Titration studies of the ion-exchange ratio between the ionomer and ionomer-modified ZrC composites will be used to assess the availability of sulfonate sites in
the s-PFCB-PO₃ ionomer as well as their ability to dissociate readily in solution. Results from this IEC study may provide some insight into what fraction of sulfonates in the ZrC-bound ionomer contributes to ion exchange and what role MW plays in increasing and/or decreasing the IEC. The 3-phosphono benzenesulfonic acid (m-SPPA) is a relatively small organic acid that is easy to synthesize and makes a simple model for determining efficiency of ion transport in larger aryl sulfonic acids. The m-SPPA can be synthesized from phenyl phosphonic acid (PPA) by sulfonation with chlorosulfonic acid and subsequent recrystallization. Neutralization of the m-SPPA and m-SPPA-ZrC with a base, such as a NaOH solution, will demonstrate the modification of ZrC supports through the covalent attachment of the organic acid.

The acid groups of the sulfonated perfluorocyclobutyl (s-PFCB) ionomers, Nafion®–212 film, and m-SPPA are immersed into 2 M NaCl solution to promote ion-exchange and convert the sulfonic acids to aqueous HCl. The resulting aqueous HCl solutions from the ionomers and the m-SPPA are then neutralized with a 0.01 N NaOH solution as a titrant to obtain titration curves. The equivalence point from the titration curves are used to estimate the millimole equivalents of acid from the organic acids. Titration curves of the acids were plotted in the 1st-order derivative, 2nd-order derivative, and Gran plots to obtain a precise estimate of the equivalence point for each curve. For reliable titration data, the compounds must be totally free of impurities, since the calculations rely heavily on the mass and its acid content. IEC values for the s-PFCB-PO₃ di-ester and s-PFCB-PO₃ di-acid ionomers will be
discussed. The ion-exchange capacity (IEC) is defined as the number of millimoles of acid (i.e., milliequivalents of SO₃H) per one gram of substance from the estimated equivalence point.

The organic acid/ionomer-modified ZrC supports were prepared by dispersion of the ZrC (obtained from co-worker Shetzline)¹⁷,²³ in an aqueous solution containing the organic acid or ionomer, as described in CHAPTER 2. The modified nanocomposites were compared to the standalone organic acid/ionomer via ion-exchange capacity. Nafion®–212 film was also studied as a benchmark since its IEC is known (0.92–0.95 meq/g).

### 3.1.2 Estimation of the equivalence point by the central difference method

Microscale titration is a useful experimental technique in determining ion-exchange capacity (IEC) of the carbon black (CB) nanocomposite and ion-conductive fluoropolymers in which the materials are in the all-proton form prior to titration. The volume of titrant required to reach the inflection point of a titration curve is used to determine the amount of titrant (often NaOH) delivered. Assuming the inflection point is the equivalence point of neutralized acid, the millimoles of acid is divided by the mass of titrated sample in grams to obtain the IEC in units of milliequivalents per 1 gram of substance Equation 3.1.
\[
\frac{\text{mmol of acid}}{\text{mass of substance}} = \text{IEC} \left( \frac{\text{milliequivalents}}{\text{gram}} \right)
\]

Equation 3.1.

The inflection point is estimated between the two points with the highest value in the first derivative plot known as the difference method. The central difference method specifically approximates the midpoint between two points in the second derivative plot that lies closest to zero. This method is often compared with the highest inflection point in the first derivative plot as well to evaluate whether these points determined to be the equivalence point in the 1st and 2nd derivative plots are in good agreement.
3.2 Experimental

3.2.1 Microscale titration of the organic acids and carbon composite materials

The organic acids and organic acid/ZrC composites were titrated using a microscale titration method that was developed specifically for this project. The apparatus consists of a narrow-bore glass-membrane pH probe purchased from HANNA Instruments, a 2,000 μL Gilmont Instruments burette, and a pH meter. The sample solution volumes range from 50 to 500 μL since the amount of composite and organic acid materials used in the hydrogen-pump cell for obtaining a resistance measurement is small, often less than 10 mg of sample. The probe used to measure the pH of the solution is positioned at the bottom surface of a glass vial along with the micropipette as shown in Figure 3.1. The pH probe contains a sturdy glass tip to prevent damaging or cracking the probe.
3.2.2 Carbon-zirconia nanocomposite (ZrC) titration with HCl solution

The ZrC composite was titrated as a control to ensure that the ZrC by itself contained little or no titratable acid. A ZrC sample (5 mg) was dispersed in 1.5 mL of 2 M NaCl solution. The suspension was stirred for 24 h and the liquid was separated after 10 min of centrifugation at 14K RPM. The aqueous liquid was collected and transferred in 500-μL portions for microtitration. The aqueous liquid was spiked with 50 μL of 9.2 mM standardized HCl solution and titrated using the microscale titration apparatus as shown in Figure 3.1 to determine an ion-exchange capacity baseline for ZrC.
3.2.3 Ion-exchange capacity of the phenyl phosphonic acid via titration

Phenyl phosphonic acid (5 mg, 31 μmol) was dissolved in 1.5 mL of 2 M NaCl solution and stirred for 24 h. The phenyl phosphonic acid solution was transferred in 500 μL portions for microtitration and spiked with 50 μL of hydrochloric acid solution. The resulting acid solution was neutralized by titration using a solution of 8.9 mM NaOH. The moles of acid titrated from the HCl spike was equivalent to the moles of acid expected from 50 μL of HCl, which suggests no acid was present in the phenyl phosphonic acid compound.

3.2.4 Ion-exchange capacity of the 3-phosphono benzenesulfonic acid-ZrC composite via titration

The 3-phosphono benzenesulfonic acid-ZrC (m-SPPA-ZrC) composite (420 mg, 70 mmol), prepared as described in CHAPTER 2, was dispersed in 1.5 mL of 2 M NaCl solution and stirred for 24 h. The suspension was centrifuged at 14K RPM to sufficiently separate the aqueous solution from the ZrC, upon which eight 500-μL portions of the aqueous solution were transferred and titrated with 8.9 mM NaOH.

3.2.5 Comparison study of Nafion®–212 membrane via ion-exchange capacity

Nafion®–212 films cut into 2 cm x 2 cm squares (5 mg each) were dispersed in 1.5 mL of 2 M NaCl solution. The mixture was stirred for 24 h, and the liquid
transferred in 500 μL portions for microtitration. The ion-exchange capacity as determined by neutralization titration was 0.86 meq/g, which compares well with the literature-reported value of 0.92–0.95 meq/g.28

3.2.6 Ion-exchange capacity of the s-PFCB phosphonate ZrC via titration

The s-PFCB-PO₃-ZrC composite (22 mg) was dissolved in 1.5 mL of 2 M NaCl solution and stirred for 24 h. The suspension was centrifuged at 14K RPM to sufficiently separate the aqueous solution from the modified ZrC material, upon which three 400-μL portions of the aqueous solution were transferred and titrated with 8.9 mM NaOH.

3.2.7 Ion-exchange capacity of the s-PFCB phosphonate di-acid via titration

The s-PFCB-PO₃ di-acid ionomer (5.0 mg, 0.59 μmol based on a polymer MW of 8,508 g mole⁻¹) was dissolved in 1.5 mL of distilled water and stirred for 24 h. Neutralization titration analysis was carried out on a Gilmont Instruments microtitration apparatus to determine the ion-exchange capacity. The apparatus includes a 2,000 μL micro burette with a 2 μL minimum delivery capacity. The ionomer stock solution was transferred in three 100-μL portions and titrated with 8.9 mM NaOH leaving behind the remaining aliquot. The ion-exchange capacity determined by this neutralization titration was 3.60 meq/g in distilled water and 1.25 meq/g in 2 M NaCl solution.
3.2.8  **Ion-exchange capacity of the s-PFCB phosphonate di-ester via titration**

The s-PFCB-PO$_3$ di-ester ionomer (5.0 mg, 0.58 $\mu$mol based on a polymer MW of 8,620 g mole$^{-1}$) was dissolved in 1.5 mL of distilled water instead of NaCl solution and stirred for 24 h to effect dissolution. The *aqueous* liquid was transferred in 500 $\mu$L portions for microtitration. The ion-exchange capacity (IEC) determined by this titration was 3.94 meq/g in 2 M NaCl solution compared to the experimental s-PFCB-PO$_3$ di-acid ionomer value of 3.60 meq/g.
3.3 Results and Discussion

Ion-exchange capacity (IEC) measurement by titration with 0.01 N NaOH solution as a titrant was used to characterize the s-PFCB-PO$_3$ di-ester and s-PFCB-PO$_3$ di-acid ionomers. Titration of the standalone s-PFCB ionomers and the organic acids attached to the ZrC nanocomposites can provide the degree of sulfonation (DS) as well. The DS of each ionomer can be compared to the results from $^1$H-NMR spectroscopy and IEC measurements. Titration and quantification of the acid present in the s-PFCB ionomers and the organic acid-ZrC composites requires an estimation of the equivalence point.

An approximation of the 1$^{st}$-order derivative ($\Delta \text{pH}/\Delta V$) of the titration curves (see Appendix A) is carried out using the central difference method. Contrary to the forward and backward difference, the central difference method approximates the distance midway between two points approaching a maximum in the 1$^{st}$-order derivative plots. This method can be applied to the 2$^{nd}$-order derivative ($\Delta (\Delta \text{pH}/\Delta V)/ \Delta V$) when the difference between two points approaches zero. However, approximation of the equivalence point from the 1$^{st}$-order derivative plots of the ionomers and ionomer-ZrC composites is adequate. Titration curves presented hereafter show the volume of titrant vs pH while the IEC values reported are calculated from their 1$^{st}$-order derivative plots.
Neutralization titration is used to estimate the ion-exchange capacity (IEC) of sulfonated organophosphonates in solution. The titration curves typically have an initial pH of 3 indicating a strongly acidic material and a final pH of 10 once the acid has been neutralized and an excess of base exists. A titration curve for ZrC spiked with HCl solution is shown in the top-left corner of Figure 3.2, to show that there is no additional acid present in the ZrC nanocomposite material besides that which was added in the 50 μL addition of HCl solution. The pH levels out at 10 on the titration curve after passing the endpoint.

Phenyl phosphonic acid (PPA) is a small organic acid with a PO$_3$ acid group similar to the PO$_3$ di-acids of the PFCB polymer, which can be chemically attached to ZrC. Covalent attachment of the PO$_3$ acid group to zirconia should render the compound non-acidic. Titration of this PPA-modified ZrC, spiked with HCl solution is shown in the top-right corner of Figure 3.2, and demonstrates that no additional acid beyond that of the HCl spike is present in the PPA-ZrC composite. The initial and final pH values from the PPA-ZrC curve are 3 and 10 respectively, which is similar to the shape and pH range of the ZrC sample that was spiked with HCl solution. The moles of base added are equivalent to the number of moles of acid coming from the HCl spike solution. So, ZrC and PPA-ZrC do not contain any titratable acid.

The acid content available from sulfonated organophosphonates for deionization is quantifiable, but lower than the free acid in solution. The 3-phosphono benzenesulfonic acid (m-SPPA) is a suitable choice for demonstrating that acid is
present in sulfonated organophosphonic acids when chemically bound to the ZrC nanocomposite.

**Figure 3.2.** Titration of ZrC and ZrC-attached organic acids PPA, m-SPPA, and s-PFCB-PO$_3$ di-acid.

In the bottom-left corner of Figure 3.2, the initial pH of 4 for the titration of m-SPPA-modified ZrC shows less acid is present than in the HCl-spiked composite.
materials, ZrC and PPA-ZrC, that were titrated with HCl solution. But, the titration curve of the m-SPPA has a final pH of 10 showing similar stabilization of the pH in excess NaOH titrant solution.

The titration curve of the s-PFCB-PO₃ di-acid-ZrC composite, shown in the bottom-right corner of Figure 3.2, has a pH ranging from 3.5 to 10. This pH range shows that the solution contains titratable acid. The shape of the curve deviates from the HCl-spiked ZrC composites by rising rapidly during addition of the first 50 µL of NaOH solution.

The titration curves of polymer electrolytes s-PFCB-PO₃ di-ester and s-PFCB-PO₃ di-acid, Figure 3.3, are compared. The s-PFCB di-acid titration curve has a pH ranging from 3 to 7, considerably acidic relative to the 3–10 pH range of the s-PFCB di-ester. Though, the di-ester ionomer’s pH range is similar to the m-SPPA-ZrC composite, its exposure to chlorosulfonic acid and HCl, discussed in the results and discussion of section 2.3, may explain the high IEC measurements of 3.94 and 3.60 meq/g for the di-ester and di-acid ionomers, respectively. Assuming DS of the s-PFCB-PO₃ polymer is 1 equivalent of SO₃H per gram, the expected IEC is 2.35 meq/g. When DS is 2 SO₃H per gram, the IEC expected of the s-PFCB-PO₃ polymer is 3.95 meq/g. From this observation, the IEC measured by titration is unusually high and may suggest acid impurities are present in the s-PFCB-PO₃ polymers.

The protocol for preparing the ionomer in 2 M NaCl solution resulted in a hazy mixture of the s-PFCB-PO₃ di-ester and an IEC of 1.25 meq/g, which is considerably
lower than expected. This finding prompted development of an alternative to this strategy whereby the s-PFCB-PO₃ di-ester was dissolved in distilled H₂O yielding the IEC of 3.94 meq/g. We ruled out ionomer preparation as a cause of error and speculate that excess acid originated from the sulfonation reaction. Thus, H₂SO₄ (originating from the quenching of chlorosulfonic acid) and HCl may be present in the s-PFCB-PO₃ di-ester and s-PFCB-PO₃ di-acid ionomers, which are not observed in the ¹H-NMR spectra.
Figure 3.3. Titration of free organic acids s-PFCB-PO₃ di-acid, s-PFCB-PO₃ di-ester and Nafion®-212.

Nafion®-212 was titrated as a standard to compare it’s IEC with the s-PFCB ionomers at the bottom of Figure 3.3. The pH range of 2.5 to 11 shows that this sample is strongly acidic, and the curve is consistent with the HCl solution spikes in ZrC and PPA-ZrC composites. The experimental IEC of Nafion®-212 obtained in this way is
0.86 meq/g. This is in good agreement with the Nafion®-212's known IEC of 0.92–0.95 meq/g obtained from the supplier, Fuel Cell Store.

Elemental analysis of the s-PFCB-PO₃ di-acid (Figure 3.4) was used to determine the amount of sulfur and hydrogen present in the sample, and is reported as a % mass. A percent hydrogen of 3.29% from elemental analysis is 50.2% higher than the 2.19% hydrogen calculated from the MW and the chemical structure of the di-acid polymer. The IEC of the s-PFCB-PO₃ di-acid (3.60 meq/g) is also 53.2% higher than the expected IEC of 2.35 meq/g. Thus, the excess hydrogen found in the elemental analysis of the two ionomers can be largely attributed to the acid impurities (such as HCl and/or H₂SO₄) from the sulfonation and/or hydrolysis reactions.

Elemental analysis of the s-PFCB-PO₃ di-acid polymer shows 10.00% sulfur by mass, which corresponds to a carbon-to-sulfur ratio of 1:3. If degree of sulfonation (DS) of the s-PFCB-PO₃ di-acid polymer is one molar equivalent of sulfonate per gram of polymer, then the mass % sulfur would be 17% based on a MW of 8,508 g mole⁻¹. This result suggests that the s-PFCB-PO₃ di-acid polymer contains less than one sulfonate group per repeat unit. Therefore, DS can be estimated from the ratio of % mass of sulfur of the di-acid polymer (obtained from elemental analysis) to the % mass of sulfur of the di-acid polymer containing one SO₃H per repeat unit. The DS of the s-PFCB-PO₃ di-acid polymer estimated from elemental analysis is 0.59 equivalent of SO₃H per gram of repeat unit. This notation eliminates the ambiguity in reporting
% DS, where 100 % DS is either not clearly defined or inconsistent when comparing % DS with polymer materials from other authors.

Assuming each polymer repeat unit of mass 346 grams contains two sulfonate groups, the estimated ion-exchange capacity is 3.95 meq/g.
Figure 3.4. Elemental analysis of the s-PFCB-PO₃ di-acid.

Table 3.1 summarizes the results of IEC determinations from composite materials and compounds discussed in this chapter. The findings reported in the table show that the ion-exchange capacity of the s-PFCB-PO₃ di-ester was higher than the s-PFCB-PO₃ di-acid (3.94 vs 3.60 meq/g) which may be a result of the s-PFCB-PO₃ di-acid’s limited solubility in aqueous solutions. The low solubility of the polymer in salt solutions is apparent by the much lower calculated IEC of 1.25 meq/g. The s-PFCB-PO₃ di-acid was slightly soluble in salt solutions characterized by a white hazy
mixture in 2 M NaCl solution (1.25 meq/g). This observation is consistent with the polymers' tendency to de-solvate under high salt concentrations (> 1 mol/L).22,29

Table 3.1. Ion-exchange capacity determined by titration of Nafion®–212, s-PFCB-PO₃ di-ester, s-PFCB-PO₃ di-acid, s-PFCB-PO₃-ZrC, and m-SPPA-ZrC.

<table>
<thead>
<tr>
<th>Polymer composite</th>
<th>aIEC by titration (meq/g)</th>
<th>bIEC by titration (meq/g)</th>
<th>95% Confidence Interval (meq/g)</th>
<th>Trials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®–212</td>
<td>0.86 ± 0.12</td>
<td>0.92–0.95</td>
<td>0.77–0.95</td>
<td>9</td>
</tr>
<tr>
<td>s-PFCB di-ester</td>
<td>3.94 ± 0.23,</td>
<td>--</td>
<td>3.81–4.07</td>
<td>15</td>
</tr>
<tr>
<td>s-PFCB di-acid</td>
<td>3.60 ± 0.09,</td>
<td>3.30²²</td>
<td>3.39–3.82</td>
<td>3</td>
</tr>
<tr>
<td>s-PFCB-PO₃-ZrC</td>
<td>0.48 ± 0.04</td>
<td>0.45²²</td>
<td>0.29–0.67</td>
<td>2</td>
</tr>
<tr>
<td>m-SPPA-ZrC</td>
<td>0.10 ± 0.02</td>
<td>0.19²³</td>
<td>0.08–0.12</td>
<td>8</td>
</tr>
<tr>
<td>PPA-ZrC</td>
<td>32.6 ± 2.80</td>
<td>--</td>
<td>29.6–33.7</td>
<td>10</td>
</tr>
</tbody>
</table>

aIEC by titration  bIEC by NMR spectroscopy  cIEC by titration from previous authors.

Moreover, Park et al. observed that ionomer-ZrC composites' IEC depends on salt concentration. This observation prompted us to repeat the titration in distilled H₂O to enhance solubility, and consequently enhance effective concentration of the s-PFCB-PO₃ di-acid. It is thought that the s-PFCB PO₃ di-acid's dissociation activity is perturbed in the absence of an ion-exchange salt such as Na₂SO₄ or NaCl. Thus, the s-PFCB-PO₃ di-ester's greater ion-exchange capacity reported from dispersion in 2 M NaCl solution is likely a result of greater effective concentration.
Equation 3.2 demonstrates an ideal situation where the concentration of the non-ionized polymer (H–A) is equivalent to the ionized polymer (A–) concentration indicating complete acid dissociation in solution. The quantity of protons dissociated into solution is analogous to the ion-exchange capacity of the polymer in an aqueous or salt medium.

\[
\frac{A^-}{H - A} = 1
\]

Equation 3.2.
CHAPTER 4
RESISTANCE MEASUREMENTS OF NAFION® AND IONOMER-MODIFIED CARBON SUPPORTS

4.1 Introduction

4.1.1 Electrical resistance measurements of hydrogen-pump cells

Electrochemical hydrogen-pump cells are a convenient platform for testing the cell voltage loss due to the ohmic resistance of electrolyte membranes. Since they require only hydrogen gas as a fuel and an oxidant, resistance measurements in proton-pumping cells benefit from simpler construction compared to fuel cells. The electrochemical hydrogen-pump cell used in this study is a miniaturized diagnostic device extending approximately 4–in. in length and 1.5–in. in width that has been previously described by previous colleagues for fuel-cell research.\textsuperscript{17,23,30} The apparatus is designed as a convenient diagnostic tool to test small amounts of numerous internal components quickly by allowing easy re-assembly of the cell. However, ohmic losses often arise from the internal components that interfere with performance in H\textsubscript{2} pump cells and fuel cells alike such as the gas-diffusion layers (GDLs), the electrolyte, and mass transport limitations. Of these, the internal resistance due to polymer electrolytes such as Nafion® and the s-PFCB-PO\textsubscript{3}-ZrC electrode will be the main focus of Chapter 4.
The miniaturized hydrogen-pump cell assembly used to perform electrical measurements on polymer electrolytes is composed of several basic components. As shown in Figure 4.1, these include a pair of current collectors fitted with Teflon screw caps to prevent gas leakage. Details of the pump cell components will be discussed later in this Chapter.
Figure 4.1. Schematic of the hydrogen pump-cell and its components.\textsuperscript{23}

Graphics in Figure 4.1 are used with permission from Dr. Shetzline’s PhD. dissertation.
4.1.2 An Introduction to Ohm’s Law in hydrogen fuel and pump cells

A potentiostat is connected to the electrochemical hydrogen-pump apparatus which is used to generate current/voltage plots and measure cell resistance. The flow of electrical charge between two electrodes (typically platinum-coated carbon) is the result of moving charge carriers. In electrolytes such as Nafion® and the s-PFCB-PO₃ polymer, the charge carriers are ions—more specifically protons. In the zirconia-modified carbon support (ZrC) electrons are the charge carriers, although the mechanism of electron mobility through the carbon layers is not well understood.

As humidified hydrogen gas is passed through the gas flow channels in the current collectors in the hydrogen-pump cell, mobile charge carriers are routed to the potentiostat. The electrical current is measured by applying a voltage across the pump cell and the resulting signal is received at the working electrode. Using this cell configuration, electrical resistance is acquired from the relationship between current (I), voltage (V) and resistance (R) of the current/voltage (I/V) curve. The equation, \( V = IR \), relating these three terms succinctly defines Ohm’s Law. Resistance (measured in \( \Omega \)) is acquired from the slope \( (I/V) \) of the line equation on the current (measured in mA) vs voltage (measured in mV) plot. The mathematical relationship between electrical conductivity (\( \sigma \)) and electrical resistance (\( R \)) can be used to calculate the conductivity of the electrolyte materials in the pump cell when the electrolyte’s thickness (\( t \)) and surface area (\( A \)) are known. Since electrical conductivity (measured in \( \Omega^{-1}/\text{cm} = \text{S/cm} \)) is reciprocal to electrical resistivity (\( \rho \)),
this calculation can be a convenient way to quantify the ionic conductivity of electrolytes (i.e., Nafion® and the s-PFCB-PO₃-ZrC).

\[ R = \rho \left( \frac{t}{A} \right) \]  

Equation 4.1.

\[ \rho = R \left( \frac{A}{t} \right) \]  

Equation 4.2.

\[ \sigma = \frac{1}{\rho} = \frac{1}{R} \left( \frac{t}{A} \right) \]  

Equation 4.3.
4.1.3 Hydrogen oxidation and reduction reactions in fuel cells

Proton-exchange membrane fuel cells (PEMFCs) utilize redox reactions of hydrogen to generate electrical power. In a conventional fuel cell, hydrogen gas is oxidized at the anode, while oxygen gas is reduced by migrant protons and electrons at the cathode producing water. Electrical energy is procured through an external circuit from the potential difference between these two half-reactions (Scheme 4.1).

\[
\begin{align*}
\text{Anode:} & \quad 2 \text{H}_2 & \rightarrow & \quad 4\text{H}^++4\text{e}^- \\
\text{Cathode:} & \quad \text{O}_2 + 4\text{H}^++4\text{e}^- & \rightarrow & \quad 2\text{H}_2\text{O} \\
\text{Overall Reaction:} & \quad \text{O}_2 + 2\text{H}_2 & \rightarrow & \quad 2\text{H}_2\text{O}
\end{align*}
\]

**Scheme 4.1.** Hydrogen oxidation and oxygen reduction reactions

The anode and cathode are distinguished in the cell and illustrate an asymmetric net flow of electrons from the anode to the cathode. The net result is a potential difference between the anode and cathode, which drives the electromotive force that provides power to an external circuit. In a hydrogen-pump cell, inlet hydrogen gas is supplied at both electrodes and simultaneously undergoes oxidation and reduction reactions that generate no net potential difference. The electrodes are therefore indistinguishable as they function mutually as both the anode and cathode. At the electrolytic interface ions migrate to each electrode by passing through a
hydrated network of sulfonate sites\textsuperscript{32} to counter electron flow between the two electrodes. PFSAs such as Nafion\textsuperscript{®}—developed by DuPont in the 1970s—commonly are manufactured to operate in the membrane electrode assembly (MEA) as proton-conducting membranes for electrochemical devices. The MEAs used in the hydrogen-pump cell were fabricated into two half-cell MEAs with the layer composition composed of: Pt/C electrode | Nafion\textsuperscript{®}–212 | Nafion\textsuperscript{®}–212 | Pt/C electrode.\textsuperscript{17,23,24} The Nafion\textsuperscript{®} membranes act as mechanical supports to situate a mixed ionic/electronic conducting (MIEC) composite, s-PFCB-PO\textsubscript{3}-ZrC, between the two Nafion\textsuperscript{®}–212 membranes inside the hydrogen-pump cell apparatus below in Scheme 4.2.\textsuperscript{19,20,33}

Overall, the polymer electrolytes must serve two basic functions inside the hydrogen-pump cell: one, the polymer must be able to form chemically, thermally and mechanically resistant films, two, the polymer should permit efficient ion transport between the electrodes with little to no resistive losses.
Scheme 4.2. Half-cell MEA fabrication and mixed ionomer inclusion.\textsuperscript{17,24}

The miniaturized hydrogen-pump cell apparatus used to perform electrical-resistance measurements (Figure 4.2), consists of a pair of current collectors (e.g., titanium or graphite), gas diffusion layers (GDLs), and a MEA consisting of an ionomer membrane and two platinum-coated carbon (Pt/C) electrodes. Standard \( \frac{3}{4} \)-in. diameter polytetrafluoroethylene (PTFE) sleeves were fitted onto the titanium-rod current collectors to make firm contact with the MEA. The hydrogen pump-cell is also equipped with a pair of rubber O-rings and compression fittings to form a gas-tight seal on each side of the MEA. Each titanium rod current collector was drilled with two \( \frac{1}{16} \)-in. diameter holes to allow for transport of humidified hydrogen gas to-and-from each side of the MEA. Symmetric hydrogen-pumping experiments are performed by connecting two PTFE tubes supplied with humidified hydrogen gas to both electrodes in the cell.\textsuperscript{17,23,30}
Current collectors must make intimate electrical contact with the electrodes in the MEA as well as possess high electrical conductivity. Good electrical contact is required at the interfaces between the Pt/C electrodes, the proton-conducting membrane and the s-PFCB-PO₃-ZrC mixed ionic/electronic conducting (MIEC) electrode. The Pt/C electrodes were received from the manufacturer (Fuel Cell Store) and were pre-treated with a Nafion® coating as a binder to provide improved ionic contact between the Pt/C electrodes and Nafion® membranes.

Half-cell MEAs were fabricated from a pair of 3/4-in. Nafion®–212 membranes and platinum-coated carbon (Pt/C) electrodes. The Pt/C electrodes were cut to disproportionate sizes of 1/4-in. and 5/32-in. diameter disks to minimize edge effects.
and to establish a consistent current area between the two electrodes. MEA fabrication was accomplished by the hot-press method at 600 lb. force for 7 min.\textsuperscript{34} Prior to use, the half-cell MEAs were hydrated by submerging them in distilled water for approximately 10 min to ensure sufficient proton-exchange within the sulfonate network during operation of the hydrogen pump cell.

Vulcanized carbon black (V-72) was decorated with zirconia nanoparticles by Shetzline \textit{et al.}\textsuperscript{23} to mechanically anchor ion-conducting electrolytes such as the s-PFCB aryl phosphonic di-acid (s-PFCB-PO$_3$ di-acid) to the carbon support (ZrC), which is water insoluble. The chemical attachment of the ionomer to ZrC by way of the end-terminating phosphonic di-acid groups prevents the s-PFCB-PO$_3$ polymer from being washed away by water during operation in the hydrogen-pump cell. The phosphonate-anchored polymer bound to the electronically conducting ZrC support forms a mixed ionic and electronic conducting (MIEC) composite. In this form, the mixed composite can be integrated into the hydrogen-pump cell to measure the ionomer’s contribution to cell voltage loss. However, before the s-PFCB-PO$_3$-ZrC can be successfully integrated within the hydrogen-pump cell, the mixed composite is dispersed in a liquid Nafion\textsuperscript{®} binder for greater adhesion to the MEA surface. Current/voltage ($I/V$) data is then collected for the ionomer-ZrC/Nafion\textsuperscript{®} MIEC composite and compared to a baseline containing ZrC/Nafion\textsuperscript{®} MIEC composite material.
4.2 Experimental

4.2.1 Catalyst ink preparation and integration into half-cell MEAs

The ZrC and s-PFCB-PO$_3$-ZrC composites described in Chapter 2 and 3 were used to make an electrocatalyst ink to measure electrical resistance in the hydrogen-pump cell. The ZrC and s-PFCB-PO$_3$-ZrC composites were dispersed into a 15% Nafion®/alcohol solution. The suspension was sonicated for 45 minutes to evenly disperse the composites and Nafion® solution. The resulting mixed ionomer-ZrC/Nafion® and ZrC/Nafion® suspensions were added dropwise with a micropipette to the Nafion® surface of a hydrated half-cell MEA containing the smaller 5/32-in. diameter Pt/C electrode. The suspensions were allowed to air dry for 5 min to bind the s-PFCB-PO$_3$-ZrC composite or ZrC onto the Nafion membrane surface in the half-cell MEA. The practice of using Nafion® as a binder allows for the ionomer-ZrC/Nafion composite to adhere to the Nafion® membrane layer in a sandwich construction while minimizing gaps for higher proton conductivity.

The composite (now containing the mixed ionic and electronic conductor—s-PFCB-PO$_3$-ZrC) was prepared in three different concentrations of ZrC/Nafion® binder: 10%, 20%, and 30% wt ZrC. Electrical measurements of 25% wt s-PFCB-PO$_3$-ZrC/Nafion® binder were also compared to ZrC without a binder as a baseline for evaluating only the ionic properties of the s-PFCB-PO$_3$ polymer.
4.2.2 Nafion®–212 resistance measurements

Current/voltage (I/V) plots were collected using the described half-cell fabrication method. Cyclic voltammetry (CV) data were collected in duplicate scans of negative (−20 to 0 mV), positive (0 to +20 mV), and full potentials (−20 to +20 mV) at a 1 mV/s scan rate in 0.5 mV sample intervals. The six I/V plots were used to calculate the average ohmic resistance of a single 50-μm thick Nafion®–212 membrane layer. A third Nafion®–212 membrane was sandwiched between the two half-cells which allowed another I/V plot. Additional single Nafion®–212 membranes of up to four layers were added to the sandwiched MEA to obtain a linear plot of the average ohmic resistance per membrane layer. This average resistance (0.73 Ω per membrane layer) was used as a basis to determine the series resistance contribution from the hydrogen-pump cell without the MEA (~0.31 Ω as shown in Figure 4.5). The initial cell resistance determined in this manner was compared to a measurement of the initial cell resistance without an MEA installed using a digital multimeter (~0.42 Ω).

I/V data were also collected on hydrated and non-hydrated Nafion® membrane films and the ZrC/Nafion® composite electrodes using the same parameters described. In this manner, the resistances from the Nafion® membrane films, ZrC, and the Nafion® binder can be used to calculate the effective ionic resistance of the s-PFCB-PO₃ polymer.
4.3 Results and Discussion

$I/V$ curves of the Nafion®-212 membrane films were obtained prior to $H_2O$ treatment (green line in Figure 4.3) by performing cyclic voltammetry (CV) experiments. The CV scans, which reflect passage of electrical current through the plane of the Nafion® membranes, were conducted by potential sweeps starting at 0 mV to –20 mV to +20 mV. The hydrogen-pump cell was taken apart following the CV experiments to retrieve the two Nafion® half-cell MEAs, which were soaked in distilled water to fully hydrate the MEAs. CV experiments of the hydrated half-cell MEAs were then performed after reassembly of the hydrogen-pump cell. The $I/V$ curves of the Nafion® membrane films that were hydrated (blue line in Figure 4.3) were performed using the same method described for the non-hydrated Nafion® membranes. The resistances from the $I/V$ plots representing the Nafion® membranes prior to and after $H_2O$ treatment can be compared based on the slopes of each curve. The hydrated Nafion® MEAs show a lower relative resistance given by a higher slope of the equation line.
Figure 4.3. Current/Voltage CV of hydration effects on Nafion®–212 membrane.

Electrical resistance (R) is determined by the reciprocal of the slope of the I/V curve. The average resistances of the two Nafion® membranes before and following H₂O treatment were 2.06 and 1.62 Ω, respectively. The resistances reported hereafter account for the 0.42 Ω pump cell resistance determined by using a 11060S Autoranging digital multimeter supplied by Southwire™ Tools. The resistance of the non-hydrated and hydrated Nafion®–212 membranes highlight the importance of
water content on the proton conductivity of Nafion®–212 (39.9 vs 57.9 mS/cm) as shown in Table 4.1.

**Table 4.1.** s-PFCB-PO₃-ZrC resistance, resistivity, and conductivity.

<table>
<thead>
<tr>
<th>Membrane composition</th>
<th>Cell resistance (Ω)</th>
<th>Calculated resistivity (Ω cm)</th>
<th>Calculated conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total cell resistance</td>
<td>2.48 ± 0.06</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Nafion®–212 MEAs before H₂O treatment</td>
<td>2.06 ± 0.06</td>
<td>25.1</td>
<td>39.9</td>
</tr>
<tr>
<td>Nafion®–212 MEAs after H₂O treatment</td>
<td>1.62 ± 0.02</td>
<td>17.3</td>
<td>57.9</td>
</tr>
</tbody>
</table>

Note: The non-hydrated MEA thickness measures \( t = 102 \, \mu \text{m} \), and the hydrated MEA measures \( t = 116 \, \mu \text{m} \).

Membrane swelling as a result of hydration was measured in microns (\( \mu \text{m} \)) using a digital micrometer. The two Nafion® membranes together measure 102 \( \mu \text{m} \) thick (50.8 \( \mu \text{m} \times 2 \)) prior to H₂O treatment. The two hydrated Nafion® membranes swelled 14 \( \mu \text{m} \) to a total of 116 \( \mu \text{m} \) thick. The resistivity of the Nafion® membranes is used to compare the different resistances of materials by accounting for their thickness and the Pt/C electrode area of 0.12 cm² (area of the \( \frac{5}{32} \)-in. diameter electrode) which is 17.3 Ω cm. And, the conductivity of the Nafion®–212 membranes is then the inverse of resistivity, which is 57.9 mS/cm. This conductivity of Nafion®–
212 membranes is in good agreement with values reported for Nafion® in the literature from groups including Slade et al.,
Lefebvre et al., and Affoune et al.

The temporal stability of the electrical current is an important factor for establishing steady-state conditions whereby cell voltage loss remains constant for extended periods in an electrochemical cell. The current stability was studied in this work using continuous scanning cyclic voltammetry (CV) to observe changes in the slope of the I/V curve with time. Since no net potential difference arises when the electrochemical half-reactions at each electrode are identical, multiple cycles of CV experiments that show overlapping curves should suffice to assess the stability of the electrical current. The I/V plots in Figure 4.4 show the three CV potential sweeps performed approximately 1 minute after the preceding CV cycle has been completed. The plots sweep at negative potentials between –20 and 0 mV, positive potentials between 0 and +20 mV, and full potentials from 0 to –20 mV to +20 mV. The three CV scans lay over one another and demonstrate consistent ionic conductivity of Nafion® over periods of up to 20 min.
Figure 4.4. Current/Voltage CV of Nafion®–212 comparing negative, positive, and full potential sweeps overtime.

The change in cell resistance with the sequential addition of Nafion® membranes to the cell is used to measure the average conductivity per Nafion® membrane. The cell configuration starts with two Nafion® membranes from the two half-cell MEAs. Successive membranes are hydrated and inserted between the two MEAs in a sandwich construction to measure the resistance change. This process was repeated for up to six total membranes to acquire a curve with the average resistance.
of one Nafion® layer. The equation of the fitted line in Figure 4.5 shows an average incremental resistance increase of 0.73 Ω for each single layer of hydrated Nafion®–212 membrane. Linear regression of the data for the resistance and number of hydrated Nafion® layers has a R² of 0.95. Although the resistances measured for the third and fourth Nafion® layers (2.70 vs 2.76 Ω) are nearly the same. The y-intercept of 0.31 defines the electrical resistance of the hydrogen-pump cell without the MEA, which is slightly low compared to the 0.4 Ω estimate obtained using a digital multimeter.

If the sum of two Nafion® membranes within the half-cell MEAs is 1.46 Ω (0.73 Ω x 2), then the contributions from the hydrogen-pump cell to the total resistance (i.e., 0.31 Ω) would give a 1.77 Ω (1.46 Ω + 0.31 Ω) result. However, the average resistance measured over many MEAs—consisting of two Nafion®–212 membranes—in the hydrogen-pump cell is 1.94 ± 0.06 Ω, and the lowest resistance measured is 1.84 ± 0.04 Ω. The 0.4 Ω measurement from the digital multimeter better fits these resistances of Nafion®–212. The resistivity of Nafion® from the two hydrated half-cell MEA construction is 23.6 Ω cm, whereas the six half-cell MEA resistivity per Nafion® membrane is 19.0 Ω cm. This observation suggests the differences in resistivity between the two measurements originate largely from the non-linear distribution of the 2nd and 3rd points (i.e., Nafion®–212 layers # 3 and # 4) in the resistance curve of Figure 4.5.
Figure 4.5. Resistivity trend of Nafion®–212 membrane.

The I/V data were collected on a series of carbon-based composites positioned between two Nafion®–212 membranes in a hydrogen pump-cell to identify effective ionic conductivity from the s-PFCB-PO₃ ionomer in the composites. Table 4.2, below, shows the total cell resistance (R), the MIEC resistance (R), and the MIEC conductivity (σ) of the mixtures of ZrC/Nafion® binder composites: 10%, 20%, and 30% wt ZrC, and the 100% wt ZrC and 25% wt ZrC/Nafion® binder composites. MIEC resistance

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decreases from 10 to 20 wt % ZrC compositions from (0.90–1.32 Ω) to (0.60–0.76 Ω), which is consistent with the observed trend made by Shetzline et al, albeit with mesoporous carbon-based composites.\textsuperscript{24} The ZrC/Nafion® composites showed a sharp increase in the cell resistance (1.23–1.27 Ω) once the ZrC composite reached 30 wt %. Similar behavior of conductivities peaking in semi-conductive composites of increasing carbon content have been studied in detail by other groups.\textsuperscript{24,38,39} The Nafion® binder, though increases electrical contact for electron/ion mobility, was left out of a 100 wt % ZrC electrocatalyst to measure the electronic conductivity of the Vulcan-72 carbon black without ionomer. The 100 wt % ZrC prepared by dispersion in water was found to have the highest ionic conductivity (113 mS/cm) of all the composite materials studied. This result is unexpected because the ZrC by itself is not expected to be a good proton conductor. This finding is not yet understood, and more studies are needed to establish whether ZrC is in fact a good ionic conductor.

The 25 wt % s-PFCB-PO\textsubscript{3}-ZrC dispersed in Nafion® binder has an ionic conductivity of 106 mS/cm. This lower conductivity is believed to be caused by the ionic resistance contributions from the Nafion® binder and s-PFCB-PO\textsubscript{3} polymer (0.57 Ω cm). The ionic resistivity of the Nafion® binder (5.55 Ω cm) is determined by the difference in resistivity of the 20 wt % ZrC/Nafion® binder (14.4 Ω cm) and the 20 wt % ZrC (8.85 Ω cm). A crucial measurement involves quantifying the electronic conductivity of the s-PFCB-PO\textsubscript{3} polymer. This result represents the effective resistivity of the s-PFCB-PO\textsubscript{3} polymer. Effective conductivity, calculated from the
conductivity difference between the 25 wt % s-PFCB-PO₃-ZrC and the 30 wt % ZrC, is 66.0 mS/cm whereas Nafion®-212 is 57.9 mS/cm.

**Table 4.2.** Electrical measurements of carbon-based composites.

<table>
<thead>
<tr>
<th>MIEC Composite electrodes</th>
<th>Cell Resistance (Ω)</th>
<th>MIEC Resistance (Ω)</th>
<th>MIEC Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt % ZrC/Nafion®</td>
<td>2.83 – 3.21</td>
<td>0.90 – 1.32</td>
<td>0 – 363</td>
</tr>
<tr>
<td>20 wt % ZrC/Nafion®</td>
<td>2.54 – 2.70</td>
<td>0.60 – 0.76</td>
<td>0 – 679</td>
</tr>
<tr>
<td>30 wt % ZrC/Nafion®</td>
<td>3.18 – 3.20</td>
<td>1.23 – 1.27</td>
<td>0 – 1553</td>
</tr>
<tr>
<td>100 wt % ZrC only</td>
<td>2.14 – 2.50</td>
<td>0.25 – 0.59</td>
<td>0 – 519</td>
</tr>
<tr>
<td>25 wt % s-PFCB-PO₃-ZrC/Nafion®</td>
<td>2.41 – 2.55</td>
<td>0.37 – 0.51</td>
<td>0 – 869</td>
</tr>
</tbody>
</table>

Note: All data is normalized for cell and Nafion® membrane resistances. The s-PFCB-PO₃-ZrC/Nafion® composite 75 μm in thickness and 0.16 cm² area.

The cell resistance from hydrogen-pumping is the result of the MIEC composite materials sandwiched between two half-cell MEAs containing the Pt/C electrodes as described in Scheme 4.2. Calculation of the MIEC resistance is accomplished by subtraction of the cell resistance containing the two Nafion®-212 membrane MEAs without the MIEC. The standard cell resistance (without any MEA
or MIEC composite) measured using a digital multimeter (0.42 Ω) is also subtracted from the cell resistance to obtain just the MIEC resistance as shown in Table 4.2.

The MIEC resistance of the composite materials are reported with high uncertainties because these calculated resistances are much lower than the measured total cell resistance in column 1 of Table 4.2. As a result, the ionic conductivity of the MIEC consisting of the s-PFCB-PO₃-ZrC composite is 0–869 mS/cm, and accounting for the resistances of the ZrC and Nafion binder the ionic conductivity of the polymer alone is estimated as ~ 66.0 mS/cm. This ionic conductivity of the s-PFCB-PO₃ polymer is slightly greater than the 57.9 mS/cm estimate of the Nafion®–212 membranes.
CHAPTER 5
CONCLUSIONS AND FUTURE DIRECTIONS

The s-PFCB-PO₃ di-acid polymer was successfully functionalized in three synthetic steps as previously reported. ¹H-NMR spectral analysis of the s-PFCB-PO₃ di-acid did not provide DS. However, the result from ¹⁹F-NMR spectroscopy estimates approximately 18.7 average repeat units for a MW of 7,124 g mole⁻¹. From this data, the expected IEC is 2.35 meq/g if all the repeat units of the s-PFCB polymer are mono-sulfonated. The experimental IEC of 3.60 meq/g for the s-PFCB-PO₃ di-acid is 53.2% higher due to H₂SO₄ and/or HCl from the polymer’s reaction with chlorosulfonic acid and HCl solution. Elemental analysis corroborates this conclusion by revealing 50.2% excess hydrogen content than expected from the polymer’s molecular formula. Nafion®–212 was titrated to rule out inconsistencies in the titration method. The experimental IEC of Nafion®–212 is 0.86 meq/g, which reasonably agrees with its literature value of 0.92–0.95 meq/g.

The m-SPPA containing one sulfonate group was compared to the PFCB ionomer when both are anchored to the carbon support. The ionomer showed a 4.8-fold increase in proton exchange compared to the m-SPPA analog containing a mono-sulfonated aromatic ring. Similar IEC studies conducted by Shetzline show a 2.5-fold improvement in IEC, of which both demonstrate greater ionomer functionality of the polymer’s hydrophobic backbone even when attached to a carbon support. The ionic conductivity is 66.0 mS/cm
for the s-PFCB-PO₃ polymer, which is higher than the 57.9 mS/cm result obtained from the Nafion®–212 electrolyte.

In future work, exploring 95-97% H₂SO₄ as a sulfonating reagent in place of chlorosulfonic acid could address the issue of residual acid in the polymer after the reaction work-up. A sulfonation reaction performed in conditions such as two hours refluxing at 40 °C can produce a sulfonated PFCB polymer with an off-white color. This finding is a result of performing a series of reactions in dilute chlorosulfonic acid with refluxing times varying from one to five hours at temperatures of up to 45 °C. Titration studies may also yield a more reliable calculation of the s-PFCB polymer’s ion-exchange capacity if the polymer is free of acid contaminants from the sulfonation and hydrolysis reagents. Spiking all of the carbon composites and organic acids with HCl solution prior to titration may improve the shape of the curves. The titration curves from the organic acids free of an HCl spike tend to have a higher pH before titrant is added and at the equivalence point.

High uncertainty in the electronic resistance measurement of the carbon electrocatalyst made it difficult to calculate ionic conductivity. Performing resistance measurements at higher wt % carbon gives lower uncertainty due to the percolation phenomenon. Thus, it is possibly advantageous to perform resistance measurements above 30% wt zirconia-carbon (i.e., percolation threshold) where the observed standard deviation is much lower, and ionic conductivity can be estimated with greater precision.
APPENDICES
Appendix A

Derivative (1st and 2nd) and Gran Plots of organic acids and nanocomposite materials

Figure A-1. Equivalence point estimation of the vulcanized carbon decorated with zirconia nanoparticles (ZrC) following a 50 μL spike of 0.01 N HCl solution.
Figure A-2. Microscale titration of the PPA-ZrC following a 50 μL spike of 0.01 N HCl solution for back titration.
Figure A-3. Microscale titration of the $m$-SPPA-ZrC.
Figure A-4. Microscale titration of the s-PFCB PO₃ di-acid-ZrC.
Figure A-5. Microscale titration of the s-PFCB PO₃ di-acid.
Figure A-6. Microscale titration of the s-PFCB PO₃ di-ester.
Figure A-7. Microscale titration of the Nafion®-212.
Appendix B

Attempts to make free-standing films with Zirconia decorated carbon/Nafion® binder drying in a PTFE well

Figure B-1. 50% wt ZrC/Nafion® binder pipetted (left) and air-dried (right) for 90 minutes.
Figure B-2. 67% wt ZrC/Nafion® binder pipetted (left) and air-dried (right) for 90 minutes.
Figure B-3. 17% wt ZrC/Nafion® binder pipetted (left) and air-dried (right) for 90 minutes.
REFERENCES


(8) US EPA. Overview of the Clean Air Act and Air Pollution.


(33) Iacono, S. T.; Budy, S. M.; Ewald, D.; Smith, D. W. Facile Preparation of Fluorovinylene Aryl Ether Telechelic Polymers with Dual Functionality for


