ELECTROLYTE INCORPORATION INTO COMPOSITE ELECTRODES FOR PROTON-EXCHANGE MEMBRANE FUEL CELLS AND LITHIUM-ION BATTERIES

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ELECTROLYTE INCORPORATION INTO COMPOSITE ELECTRODES FOR PROTON-EXCHANGE MEMBRANE FUEL CELLS AND LITHIUM-ION BATTERIES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Jung Min Oh
December 2011

Accepted by:
Dr. Stephen Creager, Committee Chair
Dr. Darryl DesMarteau
Dr. George Chumanov
Dr. Joseph Thrasher
ABSTRACT

This dissertation describes research on the preparation and characterization of composite electrodes for use in proton-exchange membrane (PEM) fuel cells and lithium ion batteries. The general focus of the research was on high-surface-area carbon supports for platinum catalysts in fuel cells, and integration of electrolytes, particularly fluoropolymer electrolytes, into composite electrodes both batteries and fuel cells. Results are described for work in the following three specific topical areas.

1. Carbon nanofibers for use as platinum (Pt) catalyst supports in fuel cells were prepared by carbonization of electrospun acrylic fibers. The resulting carbon nanofibers were found to contain mainly micropores. Following grinding to a powder form, the carbon nanofibers were used as supports for Pt nanoparticles. The pulverized carbon nanofibers were found to be not suitable as supports for Pt catalysts because the microporosity of the individual carbon nanofibers cannot provide continuous porous channels in the electrode. As a result, the Pt utilization was found to be low.

2. Mesoporous carbon composites containing nanoscale embedded zirconia particles (ZCS) were prepared and found to be highly porous and electrically conductive. Surface modification of the composites with organic compounds having phenylphosphonic acid groups (e.g., phenylphosphonic acid, \( m \)-sulfophenylphosphonic acid, or sulfonated fluoropolymer ionomer having terminal phosphonic acid groups) was accomplished by simple exposure of the carbon composite to organophosphonate solutions. Nanoscale ZrO\(_2\) surfaces present in the composite skeleton acted as reactive sites for anchoring of phosphonates through formation of robust Zr–O–P bonding. Proton-exchange sites were
introduced onto the nanocomposite surface by grafting $m$-sulfophenylphosphonic acid or a sulfonated fluoropolymer ionomer. Modification with the ionomer provided an increase in proton-exchange capacity relative to that found following modification with $m$-sulfophenylphosphonic acid because of the higher SO$_3$H content of the ionomer. Even higher proton-exchange capacity was achieved using ionomer solution to which inert salt (Na$_2$SO$_4$) had been added to cause ionomer chains to become less extended in solution, thereby allowing more ionomer to fit into mesopores in the carbon composite support. Platinum nanoparticles were deposited onto the carbon composite supports with the platinum crystalline structure and size retained. Ionomer attachment to the Pt/ZCS composites was accomplished and the resulting materials were found to be effective catalysts for the oxygen reduction reaction.

3. Carbon-coated LiFePO$_4$ and acetylene carbon black were blended with a short-side-chain perfluorosulfonate ionomer in lithium form to prepare composite cathodes. The cathodes were tested in a full-cell configuration against Li$_4$Ti$_5$O$_{12}$ anodes using LiPF$_6$-EC/DEC electrolytes. Comparison was made with cathodes prepared using polyvinylidene difluoride (PVDF) as a nonionic fluoropolymer binder. At a discharge rate of C/5, both cathode types exhibited similar voltage profiles and charge-discharge capacities. However, under higher rate discharge conditions (e.g., > 1C, up to 5C) cathodes prepared using ionomer binder showed better discharge rate capability than cathodes having the nonionic binder. This phenomenon was more pronounced when the salt concentration in the electrolyte was low. These findings suggest that the use of ionic binders can help compensate for electrolyte depletion from the electrode porous space, as
lithium ions are intercalated into lithium-deficient LiFePO$_4$ particles during rapid discharging.
DEDICATION

This dissertation is dedicated to my parents (Moonhwan Oh and Donggee Shin), aunts (Kyungsook Shin, Donghee Shin, and Donrim Shin), brother (Seunghun Oh), cousin (Snaghee Won), and last but not least, wife (Jiyoung Park), who have made my life meaningful and have provided endless love, support, encouragement, and concerns during my academic years here in the United States.
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I would like to thank my adviser Dr. Creager for his guidance and support while working on this dissertation. His dedication, knowledge, and patience are highly appreciated. The research experience that I have had with him will be valuable to my future career.

I am also grateful to Dr. DesMarteau for his guidance and support while working on the lithium-ion battery research. Many valuable discussions with him encouraged me to keep working while I was struggling with the battery assembly.

Many thanks go to Dr. Geiculescu for his help with fundamental scientific problems. His scientific knowledge and optimistic nature have encouraged me since I joined the group. In addition, all of Dr. Creager’s group members, including the past and present are appreciated for their help and the memories that we have shared together.

I also have to express special thanks to all those who helped me with instrumental analysis including Dr. Joan Hudson, Dr. Taghi Darroudi, Dr. Haijun Qian, Donald Mulwee, Dayton Cash, and Kim Ivey.
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CHAPTER 1
INTRODUCTION

1.1 Proton-exchange membrane (PEM) fuel cells

Fuel cell systems are potentially more efficient and environmentally friendly than currently used power supplies that burn fossil fuels. Therefore, much effort has been made in development of fuel cell systems for commercial use over a wide range of applications. Many recent reviews and books have appeared that summarize the state of the art in fuel cell science and technology. Among the various fuel cells under development, a PEM fuel cell offers unique advantages of high power density, low operating temperature (e.g., 60-90 °C), and fast start-up times. The main components of a PEM fuel cell include an anode, a polymer membrane electrolyte, and a cathode (Figure 1.1). The electrodes must be porous enough to allow the reactants and products, which are often gaseous or ions to diffuse to and from catalytic sites. The polymer membrane electrolyte is a proton conductor. During operation for a PEM fuel cell using H₂ as fuel, H₂ (g) is fed into the anode where H₂ is oxidized into protons (H⁺) while losing electrons. The protons pass through the membrane electrolyte to the cathode while the electrons move through an external circuit in order to produce electricity. O₂ (g) is supplied to the cathode and combines with the protons and the electrons to produce H₂O (l). More precisely, the electrochemical reactions take place on the surface of electrocatalysts. Gases, electrons, and protons all contribute to the electrochemical reactions. Therefore, the reactions occur at a region of the catalyst surface where all of the three species meet (e.g., three-phase reaction zones). In most cases, both the anode and cathode are
comprised of platinum (Pt)-based electrocatalysts, which are often supported on carbon particles. For facile chemisorption of gases on electrocatalyst surfaces, the metals should have empty d-orbitals which can accept electrons from the reactant gases. When the large number of such empty d-orbitals is available in the catalyst, the reactants are be strongly chemisorbed, and their desorptions are difficult. The most efficient chemisorptions and desorption is expected for a transition metal having the smallest possible number of empty or singly occupied d-orbitals. Platinum best fulfills this requirement among the transition metals (e.g., Pt electron configuration: [Xe] 6s\(^1\) 4f\(^{14}\) 5d\(^{9}\)).\(^{10}\)

**Figure 1.1** Schematic representation of a proton-exchange membrane fuel cell showing H\(^+\) ions transfer through proton exchange membrane (PEM) and electrons flow through the external circuit from anode to cathode. (GDL, diffusion layer; and CL, catalyst layer)
One of the important issues in the development of highly efficient PEM fuel cells is the development of more efficient Pt electrocatalysts having a high surface area for electrodes. A common practice to obtain the high-surface-area electrocatalysts is to support them on high-surface-area carbon particles. The most commonly used carbon support is furnace carbon black (for example, XC-72R, produced by Cabot Corp.) due to its low cost and high availability. Carbon black is usually thought to consist of many primary particles of carbon black with an average diameter of approximately 20 nm, which are fused together to form an aggregate structure. The aggregates associate together by van der Waals forces to form large agglomerates.\textsuperscript{11} The carbon blacks have high specific surface area, which in many cases consists mostly of micropores. The presence of many micropores would be disadvantageous when the catalytic layer is composed of the carbon black-supported Pt catalysts because mass transports of reactants and products will be limited for Pt particles that reside inside of micropores.\textsuperscript{11} For this reason, new classes of carbon materials, which have large specific surface areas and also a mesoporous texture, have been proposed as supports for electrocatalysts. The commonly studied carbon materials include mesoporous carbons (MC), carbon aerogels, carbon nanotubes (CNTs), carbon nanohorns (CNHs), carbon nanocoils (CNCs), and carbon nanofibers (CNFs).\textsuperscript{11-21}

Among these new classes of carbon, mesoporous carbons have received much attention because of their ease of preparation and relatively low cost.\textsuperscript{22} Hard templating methods are usually employed to prepare mesoporous carbons with a controlled pore architecture and relatively narrow pore size distribution.\textsuperscript{23} The general procedure
followed in hard templating methods includes the following steps: 1) formation of a composite by adding hard templates (e.g., silica or zeolite templates) into appropriate carbon precursors (e.g., resorcinol and formaldehyde); 2) carbonization of the composite at ~1000 °C under inert condition; and 3) removal of templates with aqueous NaOH or HF.22,24-27 The resulting mesoporous carbons possess high surface area, high pore volume, and large pore diameter of which structural properties are suitable for Pt impregnation and mass transport of gaseous reactant and products. Although intensive research efforts are still being conducted,11,28,29 those attractive features suggest their promise as efficient supporting materials for Pt electrocatalyst.

1.2 Lithium-ion batteries

In the last several decades, commercial rechargeable lithium-ion batteries (Li-ion batteries) have emerged as the power source of choice for portable electronic devices as they offer a high energy density.30 They have a higher energy density than most other types of rechargeable battery because lithium is one of the most electropositive elements (-3.04 V vs. standard hydrogen electrode) as well as the lightest electrochemically active metal.31 In its most common configuration, a lithium ion battery consists of a lithium-ion interaction anode (e.g., graphite and silicon), a lithium-ion intercalation cathode (e.g., LiCoO₂ and LiFePO₄), and a non-aqueous liquid electrolyte. The electrolyte is typically a mixed organic carbonates (e.g., ethylene carbonate, diethylene carbonate, or propylene carbonate) containing a lithium salt (e.g., LiPF₆).32 The electrodes are typically prepared as inks and are coated onto current collectors, which are thin foils having a high electrical conductivity, often copper (Cu) for the anode and aluminum (Al) for the cathode, and
separated by a lithium-ion conducting electrolyte imbedded in an ion-permeable membrane (separator). Figure 1.2 shows a schematic diagram of a typical lithium-ion battery configuration. Upon charging, lithium ions in the cathode are extracted into the electrolyte. Lithium ions move through the ion-permeable separator and intercalate into the anode. At the same time, electrons are released from the cathode and travel to the anode through an external circuit. Discharge of the battery reverses this process.

![Diagram of a lithium-ion battery](image)

**Figure 1.2** Schematic representation of the charge and discharge cycle for a lithium-ion battery. The circles indicate lithium ions.

Now, the lithium-ion batteries are considered as promising candidates for use in hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) applications. However, the commonly used cathode materials for portable electronic applications (e.g., LiCoO$_2$) cannot meet the requirements for automotive applications in terms of cost,
safety, environmental concerns, and energy and power densities. Therefore, alternative cathode materials and suitable cell designs have been under intense research and development.\textsuperscript{33,34} Since its discovery in 1997, olivine structure lithium iron phosphate (LiFePO\textsubscript{4}) has been attracting much attention as a new cathode material for lithium-ion batteries because of its low cost, low toxicity, high structural / thermal stability (due to Fe–P–O bond), and high theoretical specific capacity (~170 mAh g\textsuperscript{-1}).\textsuperscript{35-37} In addition to these appealing features, LiFePO\textsubscript{4} can reversibly intercalate Li at a voltage of ~3.4 V (vs. Li/Li\textsuperscript{+}), which is compatible with most existing electrolyte systems.\textsuperscript{38-40} However, LiFePO\textsubscript{4} exhibits a poor electrical conductivity of around 10\textsuperscript{-11} S cm\textsuperscript{-1}, compared with that of LiCoO\textsubscript{2} (10\textsuperscript{-3} S cm\textsuperscript{-1}), which leads to poor rate capability.\textsuperscript{35,41} Also lithium-ion diffusion is slow within the micrometer-sized LiFePO\textsubscript{4} particle. This results in a limited rate capability as well.\textsuperscript{36,42} To enhance electrical conductivity, coating the surface of LiFePO\textsubscript{4} with a conductive material such as carbon is a widely used approach. Commercial carbon-coated LiFePO\textsubscript{4} contains about 1-5 wt.% carbon.\textsuperscript{43} To improve lithium-ion diffusion, reduction of the particle size to a nanometer range has been proposed as an effective approach to improve lithium ion diffusion.\textsuperscript{44-49} Using these approaches, an increased rate capability of LiFePO\textsubscript{4}-based batteries has been reported. However, intensive research is still in progress to meet the required rate capability for HEV and PHEV applications.

The conventional anodes used in commercial lithium-ion batteries are based on carbonaceous materials.\textsuperscript{50} One of the major safety concerns in lithium-ion batteries for hybrid electric vehicle applications is the growth of metallic lithium dendrites on the
carbon anode during a fast charge of the battery because the potential of the carbon-based materials approach almost 0 V (vs. Li/Li⁺) at the end of lithium insertion. A solid electrolyte interface (SEI) formed on the anode surface may prevent the formation of the metallic lithium plating to some degree. However, such a SEI layer is known to cause an irreversible capacity loss, impeding the movement of lithium ions. Furthermore, continuous growth of metallic lithium can eventually destroy the SEI layer on the surface of the carbon, resulting in an internal short circuit. In this regard, spinel lithium titanate (Li₄Ti₅O₁₂) has attracted great interest as an alternative anode material for lithium-ion batteries because its electro-activity (e.g., Li insertion) occurs at a voltage of ~1.55 V (vs. Li/Li⁺), which avoids the growth of lithium dendrites and the electrolyte decomposition, and the formation of SEI layer hardly occurs at such a voltage. However, a drawback exists in use of Li₄Ti₅O₁₂ as an anode material. The rate capability of Li₄Ti₅O₁₂ is low because of its poor electrical conductivity (<10⁻¹³ S·cm⁻¹) and sluggish lithium ion diffusion. It has been reported that a higher rate capability can be achieved via reducing the particle size of Li₄Ti₅O₁₂ since the diffusion length in the small particle (e.g., nanostructured Li₄Ti₅O₁₂) is minimized. Also the electrical conductivity can be improved by doping with metal ions or surface coating with conductive species such as silver or carbon. Again, intense research on this anode material is in progress in order to improve its electrochemical performance.

Lithium-ion batteries require electrolytes that contain lithium ions. The electrolytes used in lithium-ion batteries should have desired properties such as high ion conductivity (e.g., >10⁻³ S·cm⁻¹), wide voltage window (e.g., 0 to 5 V), and high thermal stability (e.g.,
Most commercial lithium-ion batteries employ non-aqueous electrolyte solutions where lithium salts are dissolved in aprotic organic solvents. The gel polymer electrolytes used in lithium-ion polymer batteries are also considered as a liquid electrolyte, which are immobilized into a high molecular polymer such as polyethylene oxide (PEO), polyacrylonitrile (PAN), or polyvinylidene difluoride/hexafluoropropylene copolymer (PVDF-HFP). Most of the liquid electrolytes used in the commercial lithium-ion batteries are derived from lithium hexafluorophosphate (LiPF₆) salt. Other lithium salts (e.g., LiClO₄, LiBF₆, and LiAsF₆) are limited in the commercial applications because of safety, poor ionic conductivity, or toxicity. Usually, 1 M LiPF₆ is prepared in the mixture of carbonate solvents selected from cyclic carbonates such as ethylene carbonate (EC) and propylene carbonate (PC) and linear carbonates such as dimethyl carbonate (DMC) and diethyl carbonate (DEC). Because of low volatility and high flashpoint, the organic carbonates are the preferred solvent class in commercial lithium-ion batteries.

1.3 Composite electrode systems for PEM fuel cell and Li-ion battery electrodes

As mentioned above, both lithium-ion batteries and PEM fuel cells are the electrochemical cells that convert chemical energy into electrical energy (i.e., electricity) via electrochemical redox reactions. In common, both of them commonly consist of an anode where oxidation occurs, a cathode where reduction occurs, and an electrolyte through which ions can travel between the anode and the cathode. Electrons are transported through an external electrical lead between the electrodes. To complete the electrochemical redox reactions, ionic conduction through the electrodes as well as the
electrolyte is assured. Therefore, the electrode layers for both PEM fuel cells and lithium-ion batteries must be not only electrochemically active and electrically conductive, but also ionically conductive. A single component usually cannot satisfy all of these functions. As a result, PEM fuel cell and lithium-ion battery electrodes usually employ composite electrode systems composed of electrochemically active, electrically conductive, and ionically conductive components.

1.4 Ionomer incorporation onto carbon supports in fuel-cell electrodes

A typical PEM fuel cell electrode is prepared by spraying or painting catalyst inks that are obtained by mixing carbon-supported catalysts with a proton-conducting polymer solution (e.g., Nafion® solution). The proton-conducting polymer (i.e., ionomer) acts as both a binder and a proton conductor in the electrode. Upon drying, the ink solution becomes a thin composite film with randomly oriented three-phase reaction sites during fabrication. In such morphology, the three-phase reaction zone may not be maximized resulting in the low utilization of Pt because 1) Pt particles are randomly dispersed on a carbon support; 2) carbon supports tend to agglomerate while blinding Pt particles; and 3) an ionomer may not reach Pt particles deep inside the pores in the agglomerate. Improvements are needed to provide for greater contact of electrolyte with Pt electrocatalysts.

One possible way to resolve this problem would be to modify carbon supports with proton-conducting agents by covalent bonding. One simple approach is to chemically modify carbon supports with molecular organic acid groups (e.g., 2-aminoethanesulfonic acid, 2-aminoethylphosphonic acid, and sulfonated silane), as reported by Qi and co-
workers. Modest improvements in fuel cell performance were observed by these workers due to improved electrolytic contact with catalysts. Mizuhata and co-workers reported on the use of the monomer solution (acrylamide tertiary butyl sulfonic acid) for graft polymerizing the electrolyte polymer onto carbon support. Using this method, Kuroki and co-workers reported that the electrochemically active surface area in the catalyst was increased sevenfold, compared with the case when the conventional method was used. Although this method ensures the covalent attachment of polymer electrolyte onto carbon support, it requires phenol groups on the carbon surface and multistep reactions to obtain the electrolyte-grafted carbon supports. In addition, PEM fuel cells typically use fluorinated proton conducting electrolytes (e.g., Nafion®) due to the very high oxidative stability of fluorinated ionomers compared with hydrocarbon ionomers. Therefore, it would be desired to attach fluorinated electrolytes onto carbon supports. Grafting of monomeric fluorinated electrolytes onto carbon has been reported. In this approach, an aromatic fluorosulfonimide electrolyte was bound onto a glassy carbon disk by electroreduction of fluorosulfonimide aryl diazonium zwitterions. Robust bonding of the electrolyte on the carbon surface was achieved.

We desired to have a simpler chemistry for grafting large amounts of fluorinated polymeric electrolyte onto carbon supports. To accomplish this, mesoporous carbon supports were prepared using the resorcinol-formaldehyde method with both silica and zirconia sols added, followed by wet chemical etching to remove silica but not zirconia. The resulting supports were mesoporous carbon nanocomposites containing nanoscale zirconia. Subsequent modification of these supports with a molecular phosphonic acid
(e.g., phenylphosphonic acid or meta-sulfophenylphosphonic acid) was accomplished. Elemental analysis and titration confirmed incorporation of sulfonic acid groups when meta-sulfophenylphosphonic acid was used as an anchoring molecule. The amount of incorporated sulfonic acid groups onto the composite support was able to be further increased by utilizing a telechelic sulfonated perfluorocyclobutyl (PFCB) ionomer having phenylphosphonic end groups.

1.5 Ionomer incorporation into a lithium-ion battery cathode layer

Lithium-ion battery electrodes are typically composed of the active materials, conductive additives (e.g., carbon black), and non-ionic polymer binders (e.g., poly(vinylidene difluoride), PVDF) to hold the powder structure together. The conductive additives give electronic conductivity to the whole electrode structure so that electrons can be transported to and from the active material. These components are integrated so as to leave sufficient porosity to allow the liquid electrolyte to penetrate the electrode structure which is necessary to allow ions to reach the reacting sites. Therefore, lithium ions are transported through the liquid electrolyte inside the composite electrodes. Rapid and full penetration of liquid electrolyte into the accessible pores of the composite electrodes, and rapid transport of lithium ions into and out of the pores via the liquid electrolyte, are necessary in such electrodes to access the available capacity at reasonable rates.

Modeling studies predict that salt concentration polarization and/or electrolyte depletion from the porous space in the electrodes are significant factors limiting the performance of lithium-ion batteries during high-rate charging / discharging. Salt
concentration polarization and/or depletion from the electrode pore space may take place because the salt concentration in the liquid electrolyte is low and also because anions in the electrolyte are mobile as lithium cations are consumed in electrode reactions. Lithium availability inside electrodes can become limited, and the electrode can become a poor lithium ion conductor. Some prior work has suggested the use of ionic polymers as electrode binders. For example, lithium-exchanged Nafion® has been employed as a component of the binder for battery electrodes. All of the authors suggested that the use of lithiated binder components offers advantages by providing both physical binding and also ionic conduction functions within the electrodes. In the prior work, reversible charge and discharge was demonstrated. However, systematic clarification on the effect of lithiated ionomer binders was not made, particularly regarding the possible effects that ionomer binders might have on the maximum possible power density. Also, explicit comparisons of cathodes with and without ionic binder, with a conventional liquid electrolyte, were not made. Improvements over standard cells were not noted either. Therefore, it will be interesting to investigate the composite electrode prepared with ionic binder (e.g., lithiated ionomer) on the battery performance in comparison with that with non-ionic binder (e.g., PVDF).

1.6 The scope of work for this dissertation

There are two thrust areas of this work. One area involves preparation of a nanoporous carbon-based material for use as a support for platinum catalysts and integration of a proton-conducting polymer electrolyte into this material to provide proton-conducting functionality. All preparative activities are to be accompanied by
characterization activities focusing on structural and proton-conducting properties. Another area involves the incorporation of a lithiated polymer into a lithium-ion battery cathode and investigating the advantage of using the ionic binder in the cathode over a conventional, non-ionic binder by battery testing in a full-cell configuration. Besides those two research areas, the use of pulverized electrospun carbon nanofibers as supports for platinum catalysts is also investigated.

Chapter 2 deals with preparation of carbon nanofiber from electrospun PAN-based fiber mat, which was provided by Dr. Brown’s group (Department of Materials Science and Engineering), and evaluates the carbon nanofiber as a supporting material for platinum catalysts.

Chapter 3 presents the preparation of nanocomposites of carbon containing nanoscale zirconia and the characterization of the resulting composites in terms of their textural structures. Surface modification of the composites with a commercial organophosphonic acid, phenylphosphonic acid, is also addressed. The surface properties after the modification are investigated using X-ray photoelectron spectroscopy (XPS).

Chapter 4 describes chemical grafting of proton conducting agents (e.g., meta-sulfophenylphosphonic acid and a telechelic sulfonated PFCB ionomer) onto the composite. The proton-exchange capacity of the resulting material is evaluated using elemental analysis and titration. The grafting of a telechelic sulfonated PFCB ionomer onto the composite-supported platinum catalyst is also attempted to achieve ionically conductive Pt catalysts.
Chapter 5 focuses on studies in which a lithium-ion form of a short-side-chain perfluorosulfonate (PFSA) ionomer is used as a binder in LiFePO₄-based lithium-ion battery cathodes. The cathodes are tested in a full-cell configuration against Li₄Ti₅O₁₂ anodes using 1.0 M LiPF₆-EC/DEC and 0.1 M LiPF₆-EC/DEC electrolytes in comparison with cathodes prepared using a non-ionic fluoropolymer (PVDF) as a binder.

1.7 References


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CHAPTER 2
ELECTROSPUN CARBON FIBERS FOR USE AS A PLATINUM CATALYST SUPPORT IN PEM FUEL CELLS

2.1 Introduction

Proton exchange membrane fuel cells (PEM FCs) require a noble metal catalyst. Platinum (Pt) is the most commonly used noble metal as a catalyst. One of the major barriers to using PEM fuel cells in practice is the high cost of Pt.\textsuperscript{1} In order to reduce the cost, it is necessary to improve the catalyst activity and utilization.\textsuperscript{2} Pt nanoparticles are usually supported on porous carbon materials for that purpose.\textsuperscript{3} The catalytic activity of Pt relies not only on its size and dispersion on the carbon supports but also on morphologies and physiochemical properties of the carbon materials.\textsuperscript{4-8} Therefore, many types of porous carbon materials (e.g., carbon black, mesoporous carbon, and carbon nanotubes) have been tested as Pt catalyst supports, and still many researchers are making efforts to develop more effective carbon supports.\textsuperscript{9-13} One of the efforts is focused on finding supporting materials having optimum microstructures (e.g., porous structures).\textsuperscript{11,14} In this regard, carbon fibers have been considered as a candidate for support materials because they are expected to provide both large pore structures and surface area to volume ratios.\textsuperscript{15}

Electrospinning techniques have been extensively used for producing polymer fibers having microscale or nanoscale diameters from polyacrylonitrile (PAN)-, pitch-, or rayon-based polymer solutions.\textsuperscript{16} The resulting electrospun polymer fibers are easily
converted into carbon fibers through thermal processes while retaining their microstructures.\textsuperscript{17-19} PAN is the most commonly used polymeric precursor for the fabrication of carbon fibers by electrospinning due to its high carbon yield and to its thermal processability.\textsuperscript{17,20,21} However, a homopolymer PAN is seldom used in electrospinning processes because of its limited drawability.\textsuperscript{22} This limitation can be controlled by using a comonomer such as itaconic acid (ITA), methyl acrylate (MA), methyl methacrylate (MAA), and vinyl acetate (VAC). Incorporation of such a comonomer into PAN during polymerization produces acrylic fibers with enhanced properties in terms of stabilization, mechanical strength, and processability.\textsuperscript{22,23} The comonomers act as internal plasticizers and improve the drawability while diminishing the crystallinity of the PAN structure. Therefore, commercial carbon fibers are mainly derived from PAN copolymers.\textsuperscript{17,24}

A typical electrospinning setup consists of three major components: a high voltage power supplier, a syringe with a metal needle, and a grounded conductive collector. A schematic illustration of the basic setup for electrospinning is shown in SCHEME 2.1. A syringe pump is also employed to slowly pump a polymer solution through a needle. A high voltage supply is connected between a nozzle and a grounded collector plate. An electrical potential of 5-20 kilovolts is typically applied to a polymer fluid protruding from the needle. This induces a charge on the surface of the polymer solution. As static charge builds, the solution droplet held by its surface tension at the needle tip is deformed into a conical shape referred to as a Taylor cone.\textsuperscript{25,26} When the charge at the surface of the polymer solution overcomes the surface tension, a charged jet of the fluid is ejected.
from the tip of the Taylor cone and travels toward a grounded target. The polymer solution jet undergoes solvent evaporation in the air, and solid fibers are consequently collected randomly on the target.\textsuperscript{25,27}

The morphology and diameter of electrospun fibers are affected by various parameters. These parameters are classified mainly into three categories, which are solution properties (e.g., viscosity, concentration, polymer molecular weight, and surface tension); processing conditions (e.g., applied voltage, solution feed rate, spinning distance, and needle size); and ambient conditions (e.g., temperature, humidity, and air flowing rate).\textsuperscript{28} Although all of the parameters should be optimally controlled to produce desired electrospun fibers, polymer concentration has been found to be the main factor controlling the electrospun fiber morphology and diameter.\textsuperscript{29-31} For examples, the fiber diameter increases with increasing polymer concentration because of the high viscosity that resists the electrostatic stretching force of the jet. As the concentration decreases (low viscosity), the emerging jet may also break up into small droplets or balls because a droplet at the need tip decreases in size as solvent evaporates; which leads to the increased charge density of its surface; this increase in charge density overcomes the surface tension of the droplet and easily causes the droplet to split into smaller droplets.\textsuperscript{29}

To convert the polymer fibers into carbon fibers, two thermal steps are necessary; they are stabilization and carbonization. The first thermal step, stabilization, is carried out in air at 200-300 °C.\textsuperscript{32} In this step, PAN undergoes cyclization and partly dehydrogenation where C≡N bonds are converted into C=N bonds, which leads to the formation of ladder-structured polymers. This ladder structure is stable against melting
during a subsequent carbonization process. The second step involves a carbonization process of the stabilized fibers at a temperature higher than 800 °C in an inert atmosphere where the carbon content increases while the non-carbon elements are removed as H₂O, NH₃, CO, HCN, CO₂, and N₂.³²-³⁴

**SCHEME 2.1** A home-made experimental setup for production of electrospun acrylic nanofiber mats.

In this Chapter, the use of electrospun carbon fibers as Pt supports is considered. The carbon fibers are prepared from acrylic fibers that are obtained by electrospinning an
acrylic solution in \(N,N\)-dimethyl formamide (DMF). The acrylic solution is prepared using commercial acrylic fabrics. Use of commercially available acrylic yarn or fabrics as precursor is inexpensive and convenient in processing. The electrospun acrylic fibers are characterized by thermogravimetry (TG) and differential scanning calorimetry (DSC). The structural and textural morphologies of the carbonized fibers are investigated using scanning electron microscopy (SEM) and nitrogen (N\(_2\)) sorption porosimetry. Carbon fiber-supported Pt electrocatalysts are prepared by immersing ground carbon fibers in a hexachloroplatinic acid (H\(_2\)PtCl\(_6\)) solution and reducing the Pt precursor with a mixture of sodium borohydride (NaBH\(_4\)) and ethylene glycol (EG). The Pt nanoparticle distribution and mean size are investigated by using transmission electron microscopy (TEM) and X-ray diffraction (XRD), respectively. Hydrogen (H) adsorption/desorption and carbon monoxide (CO) stripping voltammetry are employed for an estimation of electrochemical active surface area (ECSA) of Pt surfaces on the carbon fibers.

2.2 Experimental

2.2.1 Electrospinning of acrylic fiber mats

All of the electrospun polymer fiber mats used in this study were produced and provided by Dr. Philip Brown and his students at the Department of Materials Science and Engineering at Clemson University. Commercial acrylic fabrics composed of acrylonitrile (~94%), methyl acrylate (~5%), and itaconic acid (~1%) were used as a raw material for preparing the spinning solution. Research grade (99.98%) \(N,N\)-dimethyl formamide (DMF, Sigma Aldrich) was used as solvent. A spinning solution of acrylic (10 wt.%) in DMF was prepared with mechanical stirring for 24 h at 80 °C. The
Electrospinning was conducted using a home-made setup described in SCHEME 2.1. Under a fixed-applied potential of 15 kV, the polymer stream was ejected through a syringe needle (21 gauge needle) and collected on a grounded stationary collector plate. Aluminum foil was placed over the collector plate to receive the resulting acrylic fiber mat. A syringe pump was used to control the feed at a constant rate (0.5 mL·h⁻¹). A copper wire was wrapped around the needle and connected to the voltage source. The collection time was fixed at 1 h. The distance between the needle tip and the collector plate was fixed at 174 mm.

### 2.2.2 Stabilization and carbonization of electrospun acrylic fiber mats

The electrospun acrylic fiber mat was peeled from the aluminum foil after immersion in distilled water and dried at 80 °C overnight. The thermal stabilization was performed at 280 °C in a tube furnace (F79300 tube furnace, Barnstead-Thermolyne Corporation) under a flow of air while heating at a rate of 1 °C·min⁻¹ from ambient temperature to 280 °C. That temperature was held for 1 h to ensure complete stabilization. A constant flow of air was maintained during the stabilization process. The stabilized acrylic fiber mat was then carbonized in the same furnace at 800 °C for 1 h in nitrogen atmosphere at a heating rate of 5 °C·min⁻¹.

### 2.2.3 Preparation of electrospun carbon fiber-supported platinum catalysts

The resulting carbon fiber mat was pulverized to powder (≤ 10 µm) and used as a Pt catalyst support. Hydrogen hexachloroplatinate (IV) hexahydrate (99.9% H₂PtCl₆·6H₂O, Acros) was used as a Pt precursor. A suspension of sodium borohydride (NaBH₄) in
ethylene glycol (EG) was used as a reducing agent. The procedure of Pt deposition onto carbon-based supports using a combination of EG and NaBH₄ is described elsewhere. Briefly, the pulverized carbon nanofiber mat (0.1 g) was stirred in 10 mL EG (≥ 99%, Acros) for 24 h. To the dispersion, a known amount of Pt precursor prepared in 10 mL EG was added dropwise under vigorous stirring. After stirring for 24 h at room temperature, a reducing agent solution prepared by reacting EG (10 mL) with 0.27 g NaBH₄ (≥ 98%, Acros) was slowly added to the mixture. After stirring 20 h at room temperature, a 5-mL quantity of HCl solution (1.4 M) was added to assure the Pt deposition onto the carbon fiber support. The carbon precipitate was collected on a nylon membrane filter (pore diameter, 0.1 µm), washed with deionized (DI) water, and then vacuum-dried at 120 °C overnight. The resulting electrocatalyst was designated as Pt/ECF (i.e., Pt deposited on electrospun carbon fiber).

2.2.4 Thermal characterization of electrospun fiber mats

The electrospun acrylic fiber mat was subjected to thermogravimetry (TG, PerkinElmer TGA7 analyzer) and differential scanning calorimetry (DSC, PerkinElmer DSC7 analyzer), which provided the potential temperatures for thermal stabilization and carbonization of the electrospun polymer fiber mat. For TG, a sample (7 mg) was heated from 50 to 800 °C, at a rate of 20 °C·min⁻¹. For DSC, a sample (7 mg) was heated from 50 to 500 °C at 10 °C·min⁻¹. The analyses were conducted in a N₂ atmosphere. From the thermal results, the temperatures for oxidative stabilization and carbonization processes were determined.
2.2.5 Structural, textural, and morphological characterizations

The morphological appearance and size of the as-electrospun, stabilized, and carbonized fiber mats were investigated using a scanning electron microscope (SEM, Hitachi SEM 3400 and Hitachi FESEM 4800). Prior to SEM studies, the as-electrospun and stabilized fibers mats were sputter-coated with Pt to avoid charge accumulations. Nitrogen adsorption-desorption measurements were performed at 77 K on the pulverized carbon fibers with a Micromeritics ASAP 2010 analyzer. Prior to the measurements, the carbon fiber mat sample was degassed at 200 °C under vacuum for 24 h. The specific surface area of the carbon fiber was obtained using the Brunauer-Emmett-Teller (BET) method. The total pore volume was recorded at a relative pressure \( (P/P_o) \) of near saturation. The mesopore size distribution was obtained using the Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherms. Micropore volume and surface area were obtained using the t-plot method. Transmission electron microscopy images of the Pt/ECF catalysts were obtained using a STEM-Hitachi HD2000 electron microscope. TEM samples were prepared by dispersing the Pt/ECF onto a carbon film supported on a 200-mesh copper grid, followed by drying in air overnight. X-ray diffractograms were obtained using a Rigaku powder X-ray diffractometer (XRD), operating at 40 kV and 40 mA to produce Cu Kα radiation \( (\lambda = 1.541 \text{ Å}) \) to study the size and crystallinity of Pt nanoparticles deposited on the carbon fiber support.
2.2.6 Electrochemical characterization of Pt/ECF catalysts

The electrochemical characterization of the Pt/ECF catalysts was carried out on a CHI 660A electrochemistry workstation, using a Pt wire counter electrode and a mercury-mercurous sulfate (Hg / Hg₂SO₄ / 0.5 M H₂SO₄) reference electrode at room temperature. A supporting electrolyte solution was 0.1 M H₂SO₄ (aq). To prepare a working electrode, a glassy carbon (CH Instruments, 3 mm diameter) electrode was polished with 0.05 µm alumina media and coated with a thin layer of the catalyst ink. The catalyst ink was prepared by dispersing a 6 mg quantity of the Pt/ECF catalysts in a solution consisting of 1.2 mL DI water and 0.3 mL 5% Nafion® solution (EW 1100, Solution Technology). The ink suspension was stirred overnight to form a uniform catalyst ink. A quantity 2 µL of the resulting ink was drop cast onto the glassy carbon electrode and subsequently dried in air (Pt loading, ~0.07 mg·cm⁻²).

The electrochemical active surface area (ECSA) of the Pt/ECF was estimated using hydrogen (H) adsorption/desorption and carbon monoxide (CO)-stripping voltammetric methods. The H-adsorption/desorption voltammetry was carried out in 0.1 M H₂SO₄ solution. The voltammograms were obtained by cycling the potentials in the range from 0.7 V to -0.7 V at a sweep rate of 0.02 V·s⁻¹. The adsorption and stripping of CO was carried out in 0.1 M H₂SO₄. The CO adsorption was performed by bubbling CO gas (technical purity 99%, Matheson) into the electrolyte solution for 15 min while the potential was held at -0.25 V. Then, the electrolyte solution was purged with nitrogen for 15 min to remove dissolved CO from the solution. Finally, the stripping voltammograms were collected between -0.7 V and 0.7 V at a scan rate of 0.02 V·s⁻¹. All measurements
were conducted at ambient temperature. Prior to each measurement, nitrogen was purged to deaerate the electrolyte solution (H₂SO₄) for 15 min, and the potential was cycled between -0.6 and 0.6 V at 0.1 V·s⁻¹ until a stable voltammogram was obtained. The electrochemical potential is reported with respect to a Hg / Hg₂SO₄ / 0.5 M H₂SO₄ reference electrode in this work.

2.3 Results and discussion

2.3.1 Conversion of electrospun acrylic fiber mat into carbon fiber mat

The morphological appearance of the electrospun acrylic fiber mat was investigated using a scanning electron microscope. Figure 2.1 shows SEM images of the polymer fiber mat prior to heat treatment (e.g., thermal stabilization or carbonization). The entire fiber mat consisted of a non-woven, porous structure mainly governed by macropores. At low magnification, the as-spun fibers exhibited fine web uniformity although several spindles appeared probably due to capillary instability in the course of electrospinning. At higher magnification, many of the fiber diameters appeared consistent at 1 µm. In our electrospinning conditions, it was confirmed that a 10 wt.% polymer solution was substantially viscous to allow for the formation of smooth and uniform organic fibers without forming micro-droplets or -balls.
Figure 2.1 SEM micrographs of electrospun acrylic fibers at (a) lower magnification and (b) higher magnification. In electrospinning, the flow rate was 0.5 mL·h⁻¹, and the applied voltage was 15 kV.

The optimum temperature for stabilization was determined by DSC along with TG. For DSC measurement, the polymer fiber mat was chopped into short lengths and encapsulated in a crimped aluminum pan to obtain maximum thermal contact. The DSC curves are shown in Figure 2.2a where the sample was heated at 20 °C·min⁻¹ to 500 °C in a nitrogen atmosphere. The degradation of PAN-based materials during stabilization is associated with a large exotherm. As shown in Figure 2.2a, an exothermic reaction
began at 270 °C. This reaction rate rose rapidly until it peaked at 313 °C. A TG thermogram (Figure 2.2b) also shows a result in agreement with observation on DSC showing that the rapid weight loss began at around 313 °C. Usually, the temperatures between the onset temperature of the exothermic reaction and the peak temperature are considered as appropriate temperatures for a stabilization process in order to avoid overheat treatment of the fibers.\textsuperscript{36}

**Figure 2.2** (a) DSC (a) and (b) TG thermograms of the as-electrospun polymer fiber mat in nitrogen atmosphere.
Figure 2.3 SEM images of the stabilized polymer fiber mat in air, at (a) lower magnification and (b) higher magnification.

A high-temperature stabilization process may lead to the breakdown of ladder polymers which can cause a poor mechanical properties and micro-structural defects in the carbon fibers.\textsuperscript{36,37} In our case, the furnace temperature was set at 280 °C, which was slightly above the onset temperature. The stabilization process was performed for 1 h at that temperature. During stabilization, the electrospun polymer fibers absorb oxygen from the air and undergo cyclization, resulting in a ladder-like structure. This structure is
desired for the subsequent carbonization. SEM images of the air-stabilized polymer fiber mat at 280 °C are shown in Figure 2.3. The fibers retained their fibrous morphology, but the fiber diameter shrank to a submicron size (e.g., ~700 nm). The shrinkage in diameter is apparently due to the cyclization and mass loss during stabilization.

**Figure 2.4** SEM micrographs of the carbon fibers, which were obtained from the stabilized fibers, at (a) lower magnification and (b) higher magnification.
To obtain a carbon fiber mat, the stabilized fiber mat was subjected to heat at 800 °C in a nitrogen environment. Figure 2.4 presents SEM micrographs of the carbonized fiber mat. Compared with the stabilized fibers, the fibrous diameters of the carbon fibers shrank further to approximately 400 nm. Energy dispersive X-ray spectroscopy revealed that the carbonized nanofiber mat contained 97 wt.% carbon and 3 wt.% oxygen. No nitrogen was detected, which proved that carbonization had been complete. The presence of oxygen was probably due to the surface oxygen adsorbed on the carbon fiber mat.

2.3.2 Textural properties of carbon fibers

To characterize porous properties of the carbon fibers, nitrogen (N\(_2\)) adsorption / desorption isotherms were measured at 77 K. The adsorption/desorption isotherms and the corresponding pore size distribution are shown in Figure 2.5. Comparing the isotherms with standard IUPAC classification, the adsorption/desorption isotherm (Figure 2.5a) exhibited a combination of type I and type IV isotherms.\(^{38}\) This type of isotherms implies the co-existence of microporosity and mesoporosity. The initial part of the isotherm at low relative pressure (e.g., \(P/P_o \leq 0.05\)) shows a sharp increase, which represents micropore filling. Such a behavior is a typical feature of a type I isotherm, meanwhile the slope of the plateau at higher relative pressure (e.g., \(P/P_o \geq 0.05\)) corresponds to multilayer adsorption on the non-microporous surfaces (e.g., mesoporous, macroporous, and external surfaces).\(^{38,39}\) The hysteresis loop shown in the multilayer region shows that the adsorption and desorption branches were separated with a narrow interval of adsorbed amounts. Such a shape belongs to type H3 of the IUPAC classification\(^{38}\) and indicates a mixed type of microporous and mesoporous
The BET surface area of the carbon fibers was 338 m$^2$·g$^{-1}$. The major constituent of the total BET surface area was made up of the microporous surface area (e.g., micropore area, 293 m$^2$·g$^{-1}$).

**Figure 2.5** (a) N$_2$ sorption isotherms and (b) pore size distribution of carbon fibers.

The pore size distribution calculated by the BJH method shown in Figure 2.5b revealed that the carbon fibers contained pores with diameters of 1.7 to 40 nm. However, most of the pores were smaller than 3 nm with a maximum pore volume at 1.9 nm.
Therefore, the carbon fibers have more microporous characteristics (e.g., pore diameters less than 2 nm) than mesoporous (e.g., pore diameters between 2 and 50 nm).

In Table 2.1, the textural properties of the electrospun carbon fibers (ECF) are compared with those of a commercial carbon black (Vulcan XC-72R, Cabot). The mesoporosity of Vulcan XC-72R was close to 90%, which was higher than that of the carbon fibers (mesoporosity, 25%). The lower mesoporosity of the carbon fibers can be attributed to the higher microporous volume contribution of the carbon fibers. From this result, it can be anticipated that Pt nanoparticles may sink into the micropores which will reduce the number of three-phase boundary reactive sites, thus reducing the Pt utilization. This expectation will be proved by electrochemical measurements later in this Chapter.

Table 2.1 Textural properties of carbon fibers and carbon black (Vulcan XC-72R)

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$S_{BET}$ ($m^2 g^{-1}$)</th>
<th>$S_{micro}$ ($m^2 g^{-1}$)</th>
<th>$V_{total}$ ($cm^3 g^{-1}$)</th>
<th>$V_{micro}$ ($cm^3 g^{-1}$)</th>
<th>$V_{meso}$ ($cm^3 g^{-1}$)</th>
<th>$V_{meso}/V_{total}$</th>
<th>$d_{BET}$ (nm)</th>
<th>$d_{BJH}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECF</td>
<td>338</td>
<td>293</td>
<td>0.20</td>
<td>0.14</td>
<td>0.05</td>
<td>0.25</td>
<td>2.4</td>
<td>9.7</td>
</tr>
<tr>
<td>XC-72R</td>
<td>237</td>
<td>83</td>
<td>0.62</td>
<td>0.04</td>
<td>0.55</td>
<td>0.89</td>
<td>10.4</td>
<td>17.6</td>
</tr>
</tbody>
</table>

$S_{BET}$: BET surface area, $S_{micro}$: micropore surface area by t-plot, $V_{total}$: total pore volume at near saturation pressure, $V_{micro}$: total micropore volume, $V_{meso}$: cumulative volume of pores between 1.7 and 300 nm by BJH adsorption branch, $V_{meso}/V_{total}$: a ratio of $V_{meso}$ to $V_{total}$, $d_{BET}$, $d_{BJH}$: average pore width by 4V/A. The textural properties of XC-72R were adapted from the work done by Bing Liu in our research group.41

2.3.3 Characterization of carbon fiber-supported Pt catalysts

A carbon fiber-supported Pt catalyst (Pt/ECF) was prepared as described previously. The Pt mass fraction in the Pt/ECF was estimated by TGA and was 18 wt.%. Figure 2.6 presents direct evidence of the deposition of Pt nanoparticles onto the carbon fiber
surface. The Pt nanoparticles were well distributed on the carbon fiber surface. This result indicates that a reducing agent mixture of ethylene glycol (EG) and NaBH$_4$ effectively prevents the agglomeration of Pt nanoparticles as reported in the literature.$^{35}$ It has been reported that ethylene glycol first reacts with NaBH$_4$ to form a cyclic chelate structure of B\((\text{OCH}_2\text{CH}_2\text{O})_2\)$,$^{35,42}$ which serves as a reducing agent for the Pt precursor and as a stabilizer for the formation of non-agglomerated Pt nanoparticles.

![Figure 2.6 TEM images of Pt/ECF electrocatalyst at (a) low magnification and (b) higher magnification.](image)

**Figure 2.6** TEM images of Pt/ECF electrocatalyst at (a) low magnification and (b) higher magnification.
However, a small number of agglomerated Pt particles was still seen on the Pt/ECF sample, and this feature was also observed with the similar degree on a commercial Pt/Vulcan XC-72R sample (Figure 2.7). On the TEM images, the average size of Pt particles was estimated by measuring the sizes of 50 individual Pt particles. The average particle size was 3.4 (± 0.7) nm for Pt particles on the carbon fiber and 3.0 (± 0.5) nm for the commercial Pt/Vulcan XC-72R, respectively.

![Figure 2.7 TEM micrograph of a commercial Pt/Vulcan XC-72R (scale bar, 20 nm).](image)

The nature and crystallinity of the catalyst were investigated using X-ray diffraction (XRD). The XRD pattern of the Pt/ECF is presented in comparison with the pattern of Pt/XC-72R in Figure 2.8. The broad peak at around 23° is associated with the (002) plane of the graphite-like structure. This peak is observed on both the Pt/ECF and the
Pt/XC-72R. The diffraction peaks at 39.8°, 46.1°, 67.7°, and 81.4° can be attributed to Pt(111), Pt(200), Pt(220), and Pt(311) face-centered cubic planes, respectively.\textsuperscript{44}

![XRD diffractograms of (a) Pt/ECF and (b) Pt/Vulcan XC-72R.](image)

**Figure 2.8** XRD diffractograms of (a) Pt/ECF and (b) Pt/Vulcan XC-72R.

The average crystallite size of the Pt particles deposited on the different carbon supports was calculated using the Scherer equation, based on the diffraction peak of Pt (220) in order to avoid the disturbance caused by the diffraction of graphite crystallite.\textsuperscript{15,45} The Scherer equation\textsuperscript{46} is as follows:

\[
d(nm) = \frac{0.9\lambda}{\beta \cdot \cos \theta}
\]  

(2.1)
where \( d \) is the mean particle size (nm), \( \lambda \) is the wavelength of X-ray (e.g., 0.154 nm), \( \theta \) is the angle at the peak maximum, and \( \beta \) is the full width (in radians) of the diffraction peak at half height. The calculated mean particle size for Pt/EFC was 3.5 nm, which was larger than that (2.7 nm) for Pt/Vulcan XC-72R. The calculated Pt particle sizes for Pt/ECF and Pt/Vulcan XC-72R are listed in Table 2.2 and compared with the sizes measured on the TEM micrographs. The mean particle sizes obtained from the XRD data was used to estimate Pt specific surface areas. The specific surface areas (SSA)\(^{47}\) for Pt/ECF and Pt/Vulcan XC-72R were calculated using equation 2.2 with the assumption that Pt particles were spherical.

\[
\text{SSA (m}^2 \cdot \text{g}^{-1} \text{Pt}) = \frac{6000}{\rho \cdot d}
\]

where \( \rho \) is the density of Pt (21.4 g·cm\(^{-3}\)), and \( d \) (nm) is the average diameter of a Pt particle. The specific surface areas of Pt nanoparticles for Pt/ECF and Pt/Vulcan XC-72R are listed in Table 2.2. These values will be used to estimate the efficiency of Pt utilization for each catalyst later in this Chapter.

An electrochemically active surface area (ECSA) is a comparative parameter to determine a catalytic activity of Pt catalysts on different carbon supports. For the determination of ECSA, both H\(_2\) and CO adsorption methods were employed. Those methods are based on adsorption of H\(_2\) or CO molecules. The adsorbed molecules are then electro-oxidatively removed. The associated charges involved during these oxidation processes are used for ECSA calculation.\(^{48}\) In cyclic voltammograms (CVs), hydrogen adsorption and desorption processes are characterized by “current peaks” at
corresponding potentials. Figure 2.9a shows the cyclic voltammograms of the Pt/ECF
and Pt/XC-72R catalysts, which were normalized to the Pt loading mass. The CVs of all
of the catalysts exhibited typical features for a Pt electrode in the potential range between
-0.7 and -0.4 V, corresponding to hydrogen adsorption and desorption processes on a Pt
surface. The formation of surface Pt oxide was observed at potentials between 0.1 and
0.7 V in a forward scan (e.g., a positive direction). The removal of the surface oxide was
also observed at potentials between 0.1 and -0.3 V in a backward scan (e.g., a negative
direction). The ECSA was calculated from the total charge from the electro-desorption of
hydrogen using the following equation:\textsuperscript{48}

\[
\text{ECSA}_H (\text{m}^2 \cdot \text{g}^{-1} \text{Pt}) = \frac{Q_H}{0.21 \times [\text{Pt}]} \tag{2.3}
\]

where \(Q_H\) is the charge exchanged during desorption of hydrogen atoms on Pt (mC·cm\(^{-2}\));
[Pt] represents the Pt loading (mg·cm\(^{-2}\)) in the electrode; and a correlation value of 0.21
(mC·cm\(^{-2}\)) is the charge density required to oxidize a monolayer of hydrogen molecules
on Pt. To calculate the charge related to the desorption of hydrogen atoms, the peaks
between -0.7 V and -0.4 V were integrated. Then the charge associated with the double
layer charging was subtracted from the total charge. The ECSA calculated for the
Pt/ECF was 34 m\(^2\)·g\(^{-1}\). The ECSA for the commercial Pt/Vulcan XC-72R catalyst under
identical Pt loading indicated a higher value of 66 m\(^2\)·g\(^{-1}\). This result suggests that the
electrode layer made up of the carbon fibers having smaller pores did not allow facile
transport of electrolyte molecules. That is, the Pt nanoparticles were not well exposed to
the electrolyte because the carbon fibers had less porosity than that of the XC-72R, which
could in turn lead to smaller pore structures in the overall electrode layer. In addition, the slightly larger Pt size on the carbon fibers may have resulted in the smaller active surface area as well.

The CO stripping voltammogram of the Pt/ECF is compared with that of the Pt/XC-72R in Figure 2.9b. The hydrogen desorption peaks observed in Figure 2.9a did not appear in the first positive scan starting at -0.7 V. This behavior proves the saturation of the Pt surface with CO species. The single peak at around 0.1 V in the first forward scan represents the electrochemical oxidation of the adsorbed CO species. No CO oxidation was observed in the second forward scan, confirming the complete CO oxidation in the
first forward scan. The CO stripping charge \( Q_{CO} \) was used to calculate the ECSA, as described in the following equation:\(^49\)

\[
\text{ECSA}_{CO} \left( \text{m}^2 \cdot \text{g}^{-1} \cdot \text{Pt} \right) = \frac{Q_{CO}}{0.42 \cdot [\text{Pt}]} \quad (2.4)
\]

where \( Q_{CO} \) is the CO stripping charge (mC \cdot cm\(^{-2}\)); a correlation value of 0.42 (mC \cdot cm\(^{-2}\)) corresponds to the charge density (mC \cdot cm\(^{-2}\)) required to oxidize a monolayer of adsorbed CO on Pt; and [Pt] represents the Pt loading (mg \cdot cm\(^{-2}\)). To calculate the CO stripping charge, the area under the CO oxidation peak was integrated and corrected by subtracting the charge attributed to the double layer charging and surface oxide formation. Again, the Pt/XC-72R exhibited a higher electrochemical surface area (e.g., higher peak intensity and area) than the Pt/ECF. The calculated specific surface areas for the Pt/ECF and the Pt/XC-72R were 37 m\(^2\) \cdot g\(^{-1}\) and 68 m\(^2\) \cdot g\(^{-1}\), respectively. This result provides complementary data to that in Figure 2.9a.

**Table 2.2** Pt nanoparticle size, ECSA, SSA, and Pt utilization for carbon fiber and carbon black supported Pt catalysts

<table>
<thead>
<tr>
<th>Support</th>
<th>(d) (nm)(^{a})</th>
<th>(d) (nm)(^{b})</th>
<th>SSA (m(^2) \cdot g(^{-1}))(^{c})</th>
<th>(\text{ECSA}_H) (m(^2) \cdot g(^{-1}))(^d)</th>
<th>(\text{ECSA}_CO) (m(^2) \cdot g(^{-1}))(^e)</th>
<th>Utilization (%)(^f)</th>
<th>Utilization (%)(^g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECF</td>
<td>3.5</td>
<td>3.4</td>
<td>80</td>
<td>34</td>
<td>37</td>
<td>43</td>
<td>46</td>
</tr>
<tr>
<td>XC-72R</td>
<td>2.7</td>
<td>3.0</td>
<td>104</td>
<td>66</td>
<td>68</td>
<td>63</td>
<td>65</td>
</tr>
</tbody>
</table>

\(d\) (nm)\(^{a}\) is a mean diameter of Pt estimated by XRD; \(d\) (nm)\(^{b}\) is a diameter Pt estimated on TEM; SSA (m\(^2\) \cdot g\(^{-1}\))\(^{c}\) is a specific surface area calculated using the \(d\) (nm)\(^{a}\) and the equation (2.1); \(\text{ECSA}_H\) (m\(^2\) \cdot g\(^{-1}\))\(^d\) is the electrochemical active surface area obtained from the H\(_2\) adsorption method; \(\text{ECSA}_CO\) (m\(^2\) \cdot g\(^{-1}\))\(^e\) is the electrochemical active surface area obtained from the CO stripping method; utilization (\%)\(^f\) = (\(\text{ECSA}_H\)/SSA)\times100; and utilization (\%)\(^g\) = (\(\text{ECSA}_CO\)/SSA)\times100.
The electrochemical active surface area (ECSA) of Pt is often compared with its specific surface area (SSA) in order to estimate percent (%) efficiency of Pt utilization. The utilization efficiency was calculated using the following equation:\(^{50}\)

\[
\text{Utilization} \, (%) = \frac{\text{ECSA}}{\text{SSA}} \times 100
\]  

(2.5)

The calculated utilization (%) values for Pt nanoparticles on the carbon fibers and those on the XC-72R are listed in Table 2.2. Apparently, the Pt/XC-72R catalysts with smaller Pt particle size provided a higher specific surface area, exhibiting a 24 m\(^2\) more specific surface area than the Pt/ECF. In an electrochemical active surface area, the difference in the surface area between the Pt/ECF and the Pt/XC-72R was even larger. From these results, it can be speculated that not only the Pt particle size but also the accessibility of the electrolyte affected the efficiency of Pt utilization.

2.4 Conclusions

A carbon fiber mat was prepared for use as a Pt catalyst support through stabilization and carbonization of an electrospun acrylic fiber mat. Nanoscale Pt particles were successfully supported on the carbon fibers using a combination of EG and NaBH\(_4\) as a reducing agent for the Pt precursor. To obtain a high Pt activity, Pt nanoparticles should be uniformly dispersed on the surface of carbon supports, and also the entire electrode layer formed using Pt/carbon supports should possess a mesopore structure through which electrolyte molecules can easily transport. However, it was found that the prepared carbon fibers possessed mainly microporous characteristics. Mesoporosity for the electrospun carbon fibers was found to be 25\%, which was low compared with that of
Vulcan XC-72R (e.g., mesoporosity, 89%). Small porosity of individual supports cannot provide continuous porous channels in the electrode layer. In addition, Pt particles may be possibly enclosed and sheltered by partially aligned carbon fiber packs in the electrode layer. Such structural disadvantage may also result in a high resistance to flow of electrolyte molecules through the electrode layer while decreasing Pt utilization. The H-adsorption/desorption and CO stripping voltammetric results supported this speculation. The ECSA for Pt catalysts on the carbon fibers was lower, compared with that of Pt catalysts on the Vulcan XC-72R. Furthermore, the lack of surface functional groups on this particular carbon fiber may have increased a flow resistance of electrolyte. To resolve these, carbon fibers should be fabricated in a way that they can have more mesoporous characteristics and hydrophilic surface properties.

2.5 Note

When this work was completed in 2006, it was at the early stage for researchers to apply carbon nanofibers as supports for Pt catalysts in PEM fuel cells. Not many research papers regarding Pt/carbon nanofiber catalysts were available at that time. Compared to the research of Pt/carbon nanotube catalysts, Pt/carbon nanofibers seemed to be less attractive at that time. In dealing with the synthesis of the carbon nanofibers, most carbon nanofibers were prepared by vapor growth methods.\textsuperscript{2,51,52} And it was suggested that carbon fibers were so inert that oxidative surface treatment was required prior to Pt deposition.\textsuperscript{2,53} In this consideration, carbon fibers were chemically oxidized prior to Pt deposition inducing a more reactive surface. Chemical oxidation was usually carried out using oxidizing acids such as HNO\textsubscript{3} or HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4}.  

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Our goal was to use carbon fibers as a support for Pt nanoparticles without further chemical surface pretreatment. We employed an electrospinning technique to prepare carbon nanofibers because they were easily and inexpensively produced in a short period of time, compared with vapor grown carbon fibers.\textsuperscript{54} To prepare Pt/electrospun carbon fiber catalysts, a combination of NaBH$_4$ and ethylene glycol was employed as a reducing agent while expecting a stabilizing effect from the resulting complex structure obtained from the reaction between NaBH$_4$ and ethylene glycol.\textsuperscript{35} Without the chemical treatment of the carbon nanofibers, we were able to prepare well dispersed Pt nanoparticles. It seemed that the surface treatment of carbon fibers had minor impact on the Pt nanoparticle size and distribution in our carbon fiber support.

Recently, the effect of the oxidative treatment of carbon fiber supports on the Pt size and distribution has been reported in the literatures.\textsuperscript{43,55,56} In these reports, neither smaller Pt nanoparticles nor better Pt dispersion was observed. Instead, a wide size distribution and aggregated features of Pt nanoparticles prepared on the oxidatively treated carbon supports were observed. Consequently, the oxidizing treatment induced aggregation of the Pt particles. However, when the colloidal or polyol methods\textsuperscript{57} are used, no significant dependence on surface groups has been observed. These results from the literature agree with our results about the well-distributed Pt nanoparticles on the untreated carbon fibers, which were deposited using a mixture of NaBH$_4$ and ethyl glycol.

When it comes to the Pt utilization, many works show that Pt/carbon nanofibers are superior to a commercial Pt/ Vulcan XC-72R.\textsuperscript{15,44,58-60} The higher Pt utilization has been
attributed to the tubular morphology of carbon nanofibers. They speculated that the long
tubular morphology could help carbon fibers form continuous conductive network in the
electrode. However, they did not provide a definite type of porosity possibly present in
the electrode layer. The use of carbon nanofiber supports possessing large mesoporosity
should give better catalytic activities than microporous carbon nanofibers for which mass
transport is limited.61 Even though the metal catalysts are well dispersed, mass transfer
limitations decrease the apparent activity of the catalyst.62 Ismagilov et al presented that
Pt catalysts on carbon nanofibers exhibited inferior performance in comparison with
Pt/Vulcan XC-72R.63 When Pt/carbon nanofibers (ground, microporous sample) pack in
the electrode layer, the randomly packed Pt/carbon nanofibers would form pores only by
interconnection of the individual Pt/carbon fibers. In this randomly formed packing
configuration, it would be very difficult to control porosity in the resulting electrode
layer. In this regard, several studies report the use of electrospun carbon fiber mats to
retain the mesoporosity in the electrode layer.64-66 In this approach, Pt particles were
electrodeposited onto the electrospun carbon fiber mat. These studies imply that the
electrode should possess mesoporosity to effectively utilize Pt nanoparticles, which
indirectly supports our speculation on the Pt utilization.

2.6 References


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CHAPTER 3
PREPARATION OF NANOSCALE ZIRCONIA-EMBEDDED MESOPOROUS CARBON COMPOSITES

3.1 Introduction

Mesoporous and high-surface-area carbons\textsuperscript{1,2} are of great interest in many applications, including sorbents,\textsuperscript{3} filters,\textsuperscript{4} sensors,\textsuperscript{5} supercapacitors, catalysts, catalyst supports,\textsuperscript{6-9} templates in the preparation of inorganic nanostructures,\textsuperscript{10-15} and chromatographic packings.\textsuperscript{16,17} This interest derives from their excellent combination of high surface area, large pore volume, chemical inertness, and good mechanical stability.\textsuperscript{5,18} Typical ways to synthesize mesoporous carbons include catalytic activation of carbon,\textsuperscript{19,20} carbonization of polymer aerogels,\textsuperscript{21} carbonization of polymer blends,\textsuperscript{22,23} and templating with hard or soft materials to polymeric carbon precursors.\textsuperscript{2,24-30} Among those methods, the templating approach is an effective way to prepare porous carbon materials because it is one of the most promising and the simplest methods to prepare two- or three-dimensional porous carbon materials with well-defined structural, textural, and morphological properties.\textsuperscript{31-35} In this approach, the porous carbons are fabricated through the pyrolysis of a carbonizable polymer gel containing suitable templates, followed by subsequent removal of the templates by dissolution. The templates are occluded in the growing solid and leave a pore system after their removal.

In order to have the full advantages of porous carbon materials in many applications, chemical modification of the material surfaces is often necessary to provide a certain
specific functionality, surface reactivity, or to create active sites for the grafting of desirable compounds. Traditional modification methods mainly include surface oxidation and/or activation, halogenation, sulfonation, and grafting through diazonium chemistry. However, the modification of porous carbons by the aforementioned methods still encounters problems of poor controllability due to the chemically inert and hydrophobic nature of carbons. As a result, the functionalities are inhomogeneously created on the carbon surface, so the post-attachment of desired chemical moieties on the modified carbon surface is even more difficult to control. In this regard, the combination of active nanoscale materials and carbon to create functional systems is expected to be a valid approach to achieve functionalized carbon-based materials because this approach can provide not only a new functionality with highly dispersed nanoscale materials (e.g., nanoparticles) but also reliable controllability with various nanoparticle precursors in the designed surface property.

In prior work using sol-gel techniques, metal or metal oxide precursors have been introduced with carbon precursors at the nanocasting stage to produce carbon nanocomposites containing metal or metal oxide particles. Examples of metal and metal oxide particles, which have been incorporated into carbon composites in this way, include nickel, cobalt, iron, copper, silica, titania, and alumina. In this approach, the appropriate metal or metal oxide precursors are typically added directly into the carbonizable polymer precursor solutions. Upon the appropriate thermal treatment, the inorganic precursors are transformed into the corresponding inorganic nanoparticles entrapped in the carbon frameworks that are obtained from the carbonizable polymer.
The direct addition of the inorganic precursor into the polymer mixture allows for the formation of well-dispersed nanoparticles throughout the carbon nanocomposites.\textsuperscript{36} However, it has been reported that it is difficult to control the formation of mesoporous structures upon a direct addition of inorganic precursors into a synthetic mixture. In many cases, the textural structures become microporous.\textsuperscript{64-67} Therefore, it would be interesting to explore feasible synthetic routes for preparing mesoporous carbon nanocomposites with hard or soft templates because the templating approach is expected to provide the simple and reliable way for designing mesostructures in carbon nanocomposites with various physical and chemical properties while manipulating the type of inorganic precursors and the size of template materials.

Zirconia has received considerable attention because of its chemical and physical properties applicable to gas sensor, solid-oxide fuel cell, and acid-base bifunctional catalyst technologies. Preparation of zirconia / porous carbon composites has been lately reported by Li \textit{et al.}\textsuperscript{68} An inorganic zirconium salt (ZrOCl\textsubscript{2}·8H\textsubscript{2}O) and a phenolic resol precursor were used as zirconia and carbon precursors, respectively, and the triblock copolymer Pluronic F127 (EO\textsubscript{106}PO\textsubscript{76}EO\textsubscript{106}, EO = ethylene oxide and PO = propylene oxide) as a soft template. Li \textit{et al} showed that the resulting mesoporous carbon composite having nanocrystalline zirconia particles was efficiently used as a catalyst for oxidative dehydrogenation of ethyl benzene to styrene. Their composites possess an average pore diameter of 3.8 nm.

For post-modification of composite materials, a composite with mesopores of 10 nm or even larger should be desired. Herein, we report the silica-templating synthesis of
mesoporous carbon nanocomposites containing nanoscale zirconia. In our typical synthesis, a zirconia sol is included in a preformed resorcinol-formaldehyde solution (RF solution) containing Ludox HS-40 silica colloids as a template agent. The resulting mixture is aged at 85 °C to convert the RF sol to the corresponding gel (i.e., the cross-linked polymer of RF). Upon carbonization at 1000 °C in an inert atmosphere, the cross-linked polymer is transformed into a carbon structure, while nanometric crystalline zirconia is concurrently formed from zirconia sol and embedded within the carbon framework. Etching with sodium hydroxide (e.g., 5 M NaOH) solution removes only silica templates but not zirconia because zirconia is very stable against NaOH etching. The resulting materials are mesoporous carbon nanocomposites containing nanoscale zirconia. These zirconia / carbon nanocomposites possess large pores (average pore size, ~10 nm) enabling rapid mass transfer of reagents into and out of the pores, while the zirconia surfaces are acting as solid active sites for future chemical modification of the pore interiors. Subsequent modification of these composite materials with organic compounds having a phosphonic acid group was performed through the attachment of phosphonates (R–PO$_3^{2-}$) onto zirconia via formation of chemical covalent bonds (i.e., Zr–O–P bonds). Our goal was to develop a functionalized mesoporous carbonaceous composite material that would allow us to control both the amount and the distribution of robust active sites for grafting desirable organic functions. The preparation of these materials, the characterization of their microstructure, and the surface modification with phenylphosphonic acid are discussed in this Chapter.
3.2 Experimental

3.2.1 Preparation of nanoscale zirconia-mesoporous carbon composites

The overall synthetic route is shown in SCHEME 3.1. Zirconium \(n\)-propoxide [\(\text{Zr}(\text{O}^n\text{Pr})_4\), 70 wt.% in \(n\)-propanol] was obtained from Sigma Aldrich and used as a zirconia (\(\text{ZrO}_2\)) precursor. Acetylacetone (acac, 99.5%) and anhydrous ethanol (99.5%) were obtained from Acros Organics. All of the chemicals were used as received without further purification. The typical preparation of a \(\text{ZrO}_2\) sol can be found in the literature.\(^{72}\)

In our preparation, four \(\text{ZrO}_2\) precursor solutions were prepared by adding 0, 10, 15, and 20 mmol of \(\text{Zr}(\text{O}^n\text{Pr})_4\) into a preformed mixture of anhydrous ethanol (10 mL) and acetylacetone (acac / \(\text{Zr}\) molar ratio = 1.5) under vigorous stirring at room temperature. Acetylacetone was used to stabilize \(\text{Zr}(\text{O}^n\text{Pr})_4\) against fast hydrolysis and condensation to prevent undesirable precipitation.\(^{72}\) After stirring the mixture for 1 h at room temperature, an excess of deionized (DI) water (20 mL) was added dropwise, under vigorous stirring, to the diluted precursor solution for hydrolysis. The obtained solution was stirred for an additional 1 h at room temperature, resulting in the clear and yellow-colored solution. The preparative vial was capped to prevent solvent evaporation and stored in an ice bath until ready to use.

The preparation of resorcinol-formaldehyde solutions containing colloidal silica (\(\text{SiO}_2\)) is described elsewhere.\(^{73}\) We adopted a slightly modified procedure in which the order of addition of reagents was changed. In our typical preparation, pre-determined amount of resorcinol (R, 99%, Sigma Aldrich) was completely dissolved in a quantity 15 mL of DI water first. Formaldehyde (F, 37 wt.% aqueous solution, Sigma Aldrich) was
then added to the aqueous resorcinol solution. After stirring the resulting solution (RF solution) for 30 min at room temperature, 40 mL of Ludox HS-40 (40 wt.% colloidal SiO$_2$ in water, average diameter ~12 nm, Sigma Aldrich) was added dropwise to the RF solution under vigorous stirring. Four SiO$_2$ / RF sol mixtures were prepared using the fixed volume of Ludox HS-40 (40 mL). In all cases, the molar ratio of R to F was 0.5. The amount of R and F to be used for preparation of each SiO$_2$ / RF sol mixture was determined using the calculated volume ratio of SiO$_2$ to (x) ZrO$_2$ · (1-x) RF = 1.3:1, where a volume fraction of x = 0, 0.037, 0.055, and 0.073, which were equivalent to 0, 10, 15, and 20 mmol of ZrO$_2$, respectively. The total volume of ZrO$_2$, R, and F was fixed at 5.94 mL in the calculation.

Next, the inorganic ZrO$_2$ sol was added drop by drop to the organic sol containing colloidal SiO$_2$ particles at room temperature under vigorous and continuous stirring to allow the formation of a homogeneous organic-inorganic composite sol mixture containing both SiO$_2$ and ZrO$_2$. This composite sol mixture was then placed in a sealed vial and aged at 85 °C for 1 week to obtain the ternary gel composite (i.e., SiO$_2$ / ZrO$_2$ / cross-linked RF polymer gel). The resulting gel was dried in open air at 85 °C for 2 days to remove both the residual solvent and the water. Next, the dried gel was subjected to preliminary pyrolysis at 300 °C for 3 h and then carbonized at 1000 °C for another 5 h in flowing argon. The as-carbonized sample was pulverized to a fine powder and then treated with 5 M NaOH at 80 °C for 24 h to selectively remove SiO$_2$ templates, but not ZrO$_2$. The resulting composite material was retrieved by filtration and washed with DI water until the pH of the filtrate became 7. The resulting materials were designated as
CS, ZCS-10, ZCS-15, and ZCS-20, which were prepared using 0, 10, 15, and 20 mmol of the ZrO$_2$ precursor, respectively.

**SCHEME 3.1** Synthetic procedure for mesoporous ZrO$_2$/carbon composites using the colloidal SiO$_2$ template approach.
3.2.2 Characterization of zirconia-carbon nanocomposites

The ZrO₂ content of all samples was determined by thermogravimetric analysis (TGA) combined with elemental analysis using energy dispersive X-ray spectroscopy (EDX). TGA was performed in flowing air with a heating rate of 10 °C·min⁻¹ using a Perkin-Elmer TGA7 thermogravimetric analyzer. EDX was carried out on a field emission scanning electron microscope (FESEM-Hitachi S4800) equipped with an Oxford INCA energy 200 EDX system. The nitrogen adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2010 system. The specific surface areas and pore volumes were determined by BET (Brunauer, Emmett, and Teller) and BJH (Barrett, Joyner, and Halena) methods, respectively. The pore size distribution curve was obtained from an analysis of the adsorption branch of the nitrogen isotherm using the BJH method. The skeleton density was measured using a helium pychnometer (Accupyc 1330, Micromeritics). Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV multipurpose X-ray diffractometer (40 kV and 40 mA) with a Cu Kα radiation at a wavelength (λ) of 1.541 Å. The 2θ angles were scanned from 10 to 70°. The average crystallite sizes (D) were estimated by the Debye-Scherer formula, D = \(0.90\lambda/\beta\cos\theta\), where \(\theta\) is the diffraction angle and \(\beta\) is the full width at half maximum (fwhm). Scanning electron micrographs (SEM) were acquired on a Hitachi SU6600 scanning electron microscope to investigate the composite surfaces, and the embedded ZrO₂ nanoparticles were characterized using a high-resolution transmission electron microscope (Hitachi TM 9500). X-ray photoelectron spectra (XPS) were obtained with a Kratos Analytical Axis UltraDLD spectrometer with monochromatized X-ray Al KR
radiation (1486.6 eV). Powder samples were pressed on indium supports to have a flat surface. With a step size of 1 eV and a pass-energy of 80 eV, survey scans were performed. High-resolution scans were conducted with a step size of 0.1 eV and a pass-energy of 20 eV. The binding energies for detected XPS peaks were referenced to internal C 1s peaks. The acquired spectra were fitted using the Levenberg-Marquardt optimization algorithm, and peak shapes were modeled using an asymmetric Lorentzian line shape convolved with a Gaussian function, using the CASA-XPS processing software. Raman spectra were obtained using an iHR320 imaging spectrometer (Horiba Jobin-Yvon) operating at an excitation wavelength of 514.5 nm with a laser power of 3 mW and a collection time of 30 s per scan. All the samples were in powdered form and were mounted on glass microscope slides.

3.2.3 Modification of zirconia-carbon nanocomposites with phenylphosphonic acid

Phenylphosphonic acid (C\textsubscript{6}H\textsubscript{5}PO\textsubscript{3}H\textsubscript{2}, ≥ 98%) was purchased from Alfa Aesar Chemicals. Modification with C\textsubscript{6}H\textsubscript{5}PO\textsubscript{3}H\textsubscript{2} (aq, 0.07 M) was carried out using all ZCS composite samples (i.e., ZCS-10, ZCS-15, and ZCS-20) and the blank CS. Typically, a 0.2 g quantity of a ZCS powder sample was immersed in an aqueous solution of 0.07 M C\textsubscript{6}H\textsubscript{5}PO\textsubscript{3}H\textsubscript{2} (25 mL) and heated under continuous stirring at 100 °C for 5 h. The treated sample was then separated by filtration on a 0.2 µm nylon membrane. The unreacted acid species were eliminated by repeating centrifugation, filtration, and dispersion in DI water until the pH of filtrate solution became 7. The washed sample was dried overnight at 80 °C under vacuum. In order to investigate the bond formation between the
phosphonates (PO$_3^{2-}$) and ZrO$_2$ surfaces, XPS analyses were performed on all of the acid-treated samples.

3.3 Results and discussion

3.3.1 Preparation of silica / zirconia / RF sol mixtures

The SiO$_2$ / ZrO$_2$ / RF sol mixture was prepared by simply combining a ZrO$_2$ sol solution with a preformed SiO$_2$ / RF binary sol mixture. In doing so, it was critical to achieve a high degree of homogeneity for ZrO$_2$ sol in the preparative solution mixture, while maintaining colloidal SiO$_2$ particles stably dispersed in the mixture. According to our observation in the course of the sol mixture preparation, the pH of the preparative solution seems to determine the dispersion stability of all of the components in the final mixture. The initial pH of the RF solution was around 4 prior to addition of the Ludox-HS-40 colloidal SiO$_2$ sol solution. The addition of the SiO$_2$ sol solution (pH 9.8) increased the pH of the solution to around 8.5. At this pH, the colloidal SiO$_2$ particles remained well dispersed as indicated in the literature.$^{73}$ Upon slow addition of the ZrO$_2$ sol solution to the SiO$_2$ / RF binary mixture, no precipitation or gelation was observed. On the other hand, when the SiO$_2$ / RF sol mixture was added to the ZrO$_2$ sol solution, sudden and severe gelation took place in a short time at the top of the preparative solution, even with the addition of several drops of the SiO$_2$ / RF binary mixture. It seemed that the polycondensation between hydrous zirconia sol particles took place owing to the rapid neutralization (i.e., incorporation of hydroxyl ions into prevalent zirconium species) at a high ratio of ZrO$_2$ sol to SiO$_2$ / RF sol (pH ~8.5, basic), whereas no gelation occurred at a low ratio of ZrO$_2$ sol to SiO$_2$ / RF sol.$^{74}$ The addition of the
ZrO2 sol to the SiO2 / RF sol was found to prevent the formation of a premature gel or precipitate. Another significant observation was that a suitable combination of solvents was another important factor to maintain a stable dispersion of both SiO2 and ZrO2 sols. When a Ludox HS-40 SiO2 sol solution was added dropwise to a preformed ZrO2 / RF sol mixture, abrupt gelation at the top of the preparative mixture and also flocculation of SiO2 particles were observed at the early stage of the addition. We believe that colloidal SiO2 particles were rapidly aggregated because the ratio of water to alcohols was low in the preparative mixture at the early stage of the addition of the colloidal SiO2 sol solution. The SiO2 sol stability is known to decrease significantly in alcoholic media,75,76 and as a result extensive aggregation and/or flocculation can occur. The aggregated SiO2 particles would not be able to serve as templates to generate homogeneously distributed nanopores in the composite. However, upon the slow addition of ZrO2 sol solution to a SiO2 / RF sol mixture, the dispersion stability of SiO2 particles in the preparative mixture was still maintained, probably because the fraction of water was substantially large compared with that of alcohol (the pH of the final mixture was still close to 8). Therefore, the thorough-mixing of the RF sol solution with the Ludox HS-40 SiO2 sol solution is recommended prior to the addition of ZrO2 sol solution.

3.3.2 Thermogravimetric analysis (TGA) for zirconia contents in the composites

The fraction of ZrO2 in the ZCS carbon nanocomposites prepared as described above was determined by using TGA in flowing air followed by EDX analysis on the TGA residues. Figure 3.1 shows the TGA curves for the ZCS composites revealing the total
residual content of each composite material. For comparison, the TGA profile for the blank carbon (CS) is also included in Figure 3.1.

![Thermal gravimetric (TG) curves of (a) CS (solid line), (b) ZCS-10 (dash line), (c) ZCS-15 (dot line), and (d) ZCS-20 (dash-dot line) in air flow at a heating rate of 10 °C·min⁻¹.](image)

Figure 3.1 Thermal gravimetric (TG) curves of (a) CS (solid line), (b) ZCS-10 (dash line), (c) ZCS-15 (dot line), and (d) ZCS-20 (dash-dot line) in air flow at a heating rate of 10 °C·min⁻¹.

The weight loss observed between 300 and 600 °C was due to oxidative carbon decomposition. The residual mass after 700 °C was considered as inorganic solids. The blank carbon (CS) sample exhibited a weight loss of 98 % (2 wt.% SiO₂ residue), which indicates almost complete removal of the SiO₂ template (Prior to SiO₂ removal, the SiO₂ / carbon sample contained ~85 wt.% SiO₂). The overall TG residues remaining from the ZCS-10, ZCS-15, and ZCS-20 composites were 15, 19, and 24 wt.% respectively. Each
residue obtained from the ZCS samples was further analyzed by EDX to evaluate its elemental composition. EDX analyses on the TGA residues revealed that approximately 18, 17, and 15 wt.% of the residues from ZCS-1, ZCS-2, and ZCS-3 composites were composed of SiO₂, respectively. Based on the residue composition found by EDX and the weight% obtained by TGA, the mass fraction of ZrO₂ present in each ZCS composite was estimated to be 12, 16, and 20 wt.%.

These data are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt.% of TG residue a</th>
<th>Elemental composition of TG residue (wt.%) b</th>
<th>wt.% of ZrO₂ c</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS</td>
<td>2</td>
<td>O: 47.53, Si: 52.47</td>
<td>12</td>
</tr>
<tr>
<td>ZCS-10</td>
<td>15</td>
<td>O: 40.02, Si: 7.17, Zr: 52.81</td>
<td>12</td>
</tr>
<tr>
<td>ZCS-15</td>
<td>19</td>
<td>O: 38.04, Si: 7.06, Zr: 54.90</td>
<td>16</td>
</tr>
<tr>
<td>ZCS-20</td>
<td>24</td>
<td>O: 39.97, Si: 6.13, Zr: 53.90</td>
<td>20</td>
</tr>
</tbody>
</table>

All a samples were in powdered form and were dried at 110 °C for 6 h before TGA. Elemental compositions for each TG residue b were obtained from EDX analysis. Weight percent of ZrO₂ c was estimated by subtracting the calculated weight fraction of SiO₂ from the weight percent of TG residue; the weight fraction of SiO₂ was calculated based on the elemental composition (by weight percent) obtained from EDX analysis assuming that only stoichiometric SiO₂ and ZrO₂ were present in the residue.

Other significant information obtained from TGA about these samples relates to the onset temperature of oxidative decomposition. Specifically, decomposition of the CS sample began at around 300 °C, but with the addition of ZrO₂, the onset decomposition temperature increased to above 400 °C. Also, the maximum oxidation rate of the CS was found at around 500 °C, while for the ZCS composites the maximum rates all appeared at temperature higher than 550 °C. In other words, as more ZrO₂ is present in the
composites, higher temperatures are required for complete oxidation of the carbon phase. The reason for this enhanced oxidative stability in the presence of ZrO$_2$ is not yet fully understood; however, it is important for possible application requiring the carbon to have high oxidative stability.

3.3.3 Textural characterization of zirconia-carbon nanocomposites

The pore structures of the nanocomposites (ZCS) were studied by nitrogen sorption measurements. Figure 3.2a–d shows the nitrogen sorption isotherms of CS, ZCS-10, ZCS-15, and ZCS-20 materials along with the pore size distributions derived from the adsorption branches of the isotherms. All isotherms exhibited type IV behavior with a H1 hysteresis loop at high relative pressure, indicating capillary condensation taking place in mesopores. Both adsorption and desorption branches of all the samples were almost vertical and parallel indicating a narrow pore size distribution. However, the hysteresis of the isotherms for the ZCS samples shifted slightly to a lower relative pressure $P/P_0$ of 0.8, revealing mesopores of a smaller dimension compared with the CS sample. The pore size distribution calculated by the BJH method, and shown in the insets of Figure 3.2, reveals that the specific pore volumes of all the ZCS samples are mostly composed of pores in the range of 10 to 30 nm with the maximum pore size at ~15 nm, which is close to the mean size of the silica templates (~12 nm, dia.). This result suggests that individual silica particles acted as templates for most of the pores that were present in the ZCS samples. We believe that silica particles have been stabilized by the interfacial interaction between silica and zirconia sols, e.g., a Si–O–Zr interaction, which could be possibly formed between the silanol groups of silica and the zirconium of
Table 3.2 shows the BET surface areas, pore volumes, and skeleton densities for CS and ZCS samples. The CS sample has a total BET surface area of 983 m$^2\cdot$g$^{-1}$ and a total pore volume of 3.79 cm$^3\cdot$g$^{-1}$, whereas all the ZCS samples exhibited lower surface areas and pore volumes than the CS sample. Also, the specific surface area and the pore volume of the ZCS samples decreased with increasing ZrO$_2$ loading. This decreasing trend is reasonable because these properties are normalized per unit weight (i.e., m$^2\cdot$g$^{-1}$ and cm$^3\cdot$g$^{-1}$) and ZrO$_2$ has a large molar mass and high density relative to carbon. Therefore, a more meaningful comparison was made using a percent porosity (or percent free void) for each sample. The percent porosity was calculated, using the total pore volume obtained from the BET analysis and the skeletal volume evaluated by helium pychnometry. The percent porosity calculation reveals that all of the ZCS samples have nearly identical porosity (~84%), and also the porosity of the ZCS samples was not significantly different from that of the CS sample (~87%). The slightly higher percent
porosity of CS is probably due to a combined effect of higher fractions of micropores and macropores in the CS sample as indicated in Figure 3.2.

**Figure 3.2** Nitrogen adsorption-desorption isotherms and the corresponding pore size distributions (insets) of (a) CS, (b) ZCS-10, (c) ZCS-15, and (d) ZCS-20. (The pore size distribution was calculated using the BJH method for the adsorption branch of the isotherm.)
Table 3.2 BET surface area, total pore volume, pore diameter, and skeleton density data for sample CS, ZCS-10, ZCS-15, and ZCS-20

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{total}}$ (m$^2$·g$^{-1}$)$^a$</th>
<th>$S_{\text{micro}}$ (m$^2$·g$^{-1}$)$^b$</th>
<th>$V_{\text{total}}$ (cm$^3$·g$^{-1}$)$^c$</th>
<th>$V_{\text{micro}}$ (cm$^3$·g$^{-1}$)$^d$</th>
<th>$D_{\text{BET}}$ (nm)$^e$</th>
<th>$\rho_s$ (g·cm$^{-3}$)$^f$</th>
<th>Porosity (%)$^g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS</td>
<td>983</td>
<td>209</td>
<td>3.79</td>
<td>0.11</td>
<td>15.4</td>
<td>1.80</td>
<td>87.2</td>
</tr>
<tr>
<td>ZCS-10</td>
<td>807</td>
<td>137</td>
<td>2.34</td>
<td>0.07</td>
<td>11.5</td>
<td>2.32</td>
<td>84.4</td>
</tr>
<tr>
<td>ZCS-15</td>
<td>778</td>
<td>108</td>
<td>2.22</td>
<td>0.05</td>
<td>11.4</td>
<td>2.48</td>
<td>84.6</td>
</tr>
<tr>
<td>ZCS-20</td>
<td>749</td>
<td>99</td>
<td>1.96</td>
<td>0.04</td>
<td>10.5</td>
<td>2.71</td>
<td>84.2</td>
</tr>
</tbody>
</table>

$S_{\text{total}}^a$ is the total surface area calculated by the BET method. $S_{\text{micro}}^b$ is the micropore area calculated by the BET method. $V_{\text{total}}^c$ is the single-point total pore volume at relative pressure $(P/P_0)$ of 0.99. $V_{\text{micro}}^d$ is the micropore volume of pores less than 3.5 nm. $D_{\text{BET}}^e$ is the average pore size calculated by the equation $4V_{\text{total}}/S_{\text{total}}$. $\rho_s^f$ is the skeletal density measured by helium pycnometry. Percent porosity $^g$ is defined as $V_{\text{total}}/ [V_{\text{total}} + 1/\rho_s] \times 100$, where $1/\rho_s =$ skeletal volume per mass.

3.3.4 X-ray diffraction and Raman analyses

Powder XRD measurements for CS and ZCS samples were performed in order to identify the presence of the crystalline domains of the embedded zirconia. Figure 3.3 shows the XRD patterns of the CS and ZCS samples. The diffractogram of the CS sample (Figure 3.3a) shows only two broad peaks centered at $2\theta = \sim 23^\circ$ and $\sim 43^\circ$, which are characteristics of the carbon phase found in carbon aerogels or xerogels and can be indexed to (002) and (101) diffractions of carbon, respectively.\textsuperscript{79,80} The d-spacing of the (002) plane was 0.38 nm, which is larger than the value (0.34 nm) of typical graphitized carbons that are obtained at high temperatures (e.g., $\geq 2000$ °C)\textsuperscript{81} suggesting that the CS sample can be regarded as partially graphitized carbon. For the ZCS samples, four other diffraction peaks were detected (Figure 3b–d), besides the two peaks associated with the carbon component of the composites. The appearance of these peaks indicates the formation of zirconia nanoparticles in the composites. It was observed that all of the ZCS
samples predominantly contained tetragonal ZrO$_2$ ($2\theta = 30.4^\circ$, 34.9$^\circ$, 50.1$^\circ$, and 59.7$^\circ$). The four diffraction peaks correspond to (111), (200), (220), and (311) lattice planes of tetragonal ZrO$_2$. This result confirms that tetragonal ZrO$_2$ nanoparticles were successfully embedded in the carbon matrix.

![Figure 3.3](image)

**Figure 3.3** Powder XRD patterns of sample (a) CS, (b) ZCS-10, (c) ZCS-15, and (d) ZCS-20 with the indices of carbon (C) and tetragonal ZrO$_2$ (Z).
The diffraction peaks referring to the ZrO$_2$ phase had broad widths indicating that the mean crystallite size was in the nanometer range. Also, this broad feature indirectly proves that ZrO$_2$ nanoparticles have been well dispersed in the carbon framework. The ZCS sample with the higher ZrO$_2$ content exhibited the higher intensity of characteristic peaks of the tetragonal ZrO$_2$ phase relative to the carbon phase peaks. The average sizes of ZrO$_2$ particles for ZCS-10, ZCS-15, and ZCS-20, estimated using the Debye-Scherer formula on the tetragonal ZrO$_2$ (111) peak (i.e. $\theta = 30.4^\circ$), were 3.1, 3.0, and 3.3 nm, respectively. The d-spacing associated with the diffraction peak at $\theta = 30.4^\circ$ was 0.294, 0.295, and 0.293 nm, respectively, which were in good agreement with the expected d-spacing of (111) tetragonal ZrO$_2$ (d = 0.295 nm). \(^8^3\)

As shown in Figure 3.3, the XRD peaks of the ZCS samples at ~23° for the carbonaceous component are not clearly defined enough to estimate the carbon characteristics. Therefore, Raman spectra of the ZCS composites were measured to provide information about the nature of the carbon component in the composites. Raman spectra in the range of 1200–1800 cm$^{-1}$ for the four samples (CS, ZCS-10, ZCS-15, and ZCS-20) analyzed in this study are presented in Figure 3.4a–d. All of the spectra feature two broad peaks centered at ~1350 cm$^{-1}$ and ~1600 cm$^{-1}$, which are characteristics of the D band and the G band of carbon materials, respectively. \(^8^4\) The former peak arises from the vibrational mode of disordered graphene sheets, while the latter peak arises from the vibrational mode of graphite layers. \(^8^4\) In all of these spectra, both peaks are broad and similar in intensity, indicating that the carbon phase is close to disordered amorphous carbon corresponding to small graphitic domains. No clear differences between the ZCS
composite and the CS samples were found in terms of the nature of the carbon phase when comparing their bandwidths and intensity ratios. This suggests that the ZCS samples possess the similar degree of a graphitic or amorphous phase when compared with the CS sample.

Figure 3.4 Raman spectra of (a) CS, (b) ZCS-10, (c) ZCS-15, and (d) ZCS-20.
3.3.5  Electron microscopic analysis for surface and structural morphology

Figure 3.5 shows high resolution SEM images of the CS sample surface before and after NaOH etching (Figure 3.5a and 3.5b, respectively). After removal of the SiO₂ templates, evenly distributed pores were clearly formed onto the entire surface. The pore distribution was broad, ranging roughly from 10 nm to 100 nm as shown in Figure 3.5b, but most pores are in the range of 10-70 nm. These results are consistent with prior nitrogen porosimetry analyses which revealed pores in this size range from a BJH analysis of nitrogen adsorption isotherm data.

![Figure 3.5 SEM photographs of CS (a) before and (b) after removal of SiO₂ templates using 5 M NaOH solution at 80 °C.](image)
The surface morphology of the ZCS samples was also investigated using SEM. In Figure 3.6, the SEM photographs of the ZCS samples present similar surface morphology as compared to the CS sample in terms of well distributed pores onto their surface.

Figure 3.6 SEM photographs of (a) ZCS-10, (b) ZCS-15, and (c) ZCS-20 after removal of SiO$_2$ templates using 5 M NaOH solution at 80 °C.
However, the ZCS samples differ from the CS sample in the average pore size showing that most of the pores possess a diameter smaller than ~20 nm even though a few larger mesopores are also observed (note the different magnification used in Figures 3.5 and 3.6, 300 nm scale vs. 200 nm scale). This value correlates well with the average pore size obtained from nitrogen adsorption data. There are no apparent differences in the porous morphology among the ZCS composites. In the SEM analysis, the ZrO$_2$ domains were not resolved because ZrO$_2$ is not fully electron-conductive and because they are quite small.

Direct evidence of the formation of nanoscale ZrO$_2$ in the carbon matrix is provided by TEM images. Figure 3.7 shows typical TEM images of the ZCS samples with different ZrO$_2$ contents. The nanoparticle sizes estimated from the TEM images are in the range of the values estimated from the XRD measurements. At low magnification, it was difficult to discern individual ZrO$_2$ nanoparticles in the composites because of poor contrast. Therefore, only the related TEM images obtained at high magnification are shown here and clearly reveal the presence of the non-aggregated nanocrystalline ZrO$_2$ particles (roughly 3 to 4 nm in diameter) in all the composites as shown Figure 3.7. This observation proves that no structural damage or dissolution of ZrO$_2$ nanoparticles occurred during the etching process. Combining the TEM observations with the XRD results, it was inferred that ZrO$_2$ nanoparticles with the size of 3 to 4 nm were randomly distributed onto the carbon surface and in the bulk of the carbon body. The HR-TEM images shown in the bottom left insets of Figure 3.7b–d show a clear lattice pattern indicating the high crystallinity of the ZrO$_2$ particles present in the composites. The
lattice spacing values of crystalline ZrO$_2$ nanoparticles were in the range of 0.296–0.298 nm (see the insets), which agree well with the inter-planar spacing (or d-spacing) of the (111) plane in the tetragonal ZrO$_2$ phase. This observation suggests that the embedded crystalline structures represent tetragonal ZrO$_2$ phases, which is in good agreement with the XRD results.

**Figure 3.7** High-resolution TEM images of (a) CS, (b) ZCS-10, (c) ZCS-15, and (d) ZCS-20. (Scale bar = 2 nm. ZrO$_2$ particles are highlighted by circles. The insets of the panel b, c, and d present the magnified TEM image of a ZrO$_2$ particle in each panel.)
3.3.6 Surface analysis by X-ray photoelectron spectroscopy

Surface compositions of ZCS and CS samples were analyzed by XPS technique, which provided information regarding the electronic states and chemical environment of carbon (C), zirconium (Zr), and oxygen (O) atoms in the composite materials. Figure 3.8 shows wide-survey XPS spectra in the full range of the binding energy, scanned from 0 to 1200 eV, which provided both a compositional overview and information about main elemental components in ZCS-10, ZCS-15, and ZCS-20 in comparison with CS. The peak for indium (In) originated from the sample mounting. Therefore, it was excluded from the compositional analysis of the samples. Both ZCS and CS samples produced a strong C 1s peak between 282 and 289 eV. An O 1s peak was also observed at 532 eV on all the samples. A major difference between ZCS and CS samples was Zr 3d and Zr 3p peaks that were found only in the ZCS samples. As shown in Figure 3.8b–d, the peak intensities of O and Zr gradually increase with the increase in the fraction of ZrO₂, indicating an increase in Zr and O surface concentrations. These results prove that ZrO₂ particles have been successfully incorporated into the carbon frameworks and the amount of ZrO₂ moieties can be manipulated by adding a different amount of ZrO₂ precursor.
Figure 3.8 Low-resolution X-ray photoelectron spectra in survey scan mode for (a) CS, (b) ZCS-10, (c) ZCS-15, and (d) ZCS-20. (The powder samples were pressed on indium supports to have a flat surface prior to analyses. Indium peaks originate from the supports. Photoelectron emission peaks of interest are observed at binding energies characteristic for C, O, and Zr. The control experiment using CS that does not have ZrO₂ shows peaks for only C and O.)
To further investigate the states of these atoms, high-resolution XPS spectra of C, O, and Zr were recorded and are shown in Figure 3.9. The C 1s XPS spectra of ZCS and CS samples revealed three carbon components (Figure 3.9a).85 The main carbon peak is found at 284.4 eV, which corresponds to the non-oxygenated carbon. Another peak at 285.1 eV may be assigned to carbon atoms attached to hydroxyl or ether groups, and the other peak at 288.5 eV may be attributed to carbonyl or carboxylate groups. Basically, the C 1s region for both ZCS and CS samples is identical, and no carbon peak associated with zirconium carbide (ZrC, binding energy for C 1s, 282.9 eV) was observed in the spectra for all the ZCS samples, suggesting that no carbothermal reduction took place during the synthesis.86,87 Figure 3.9b shows the O 1s spectra of ZCS-10, ZCS-15, and ZCS-20 in comparison with the spectrum of CS carbon. It was expected that the O 1s spectra for the ZCS composites would contain two primary contributions, one from carbon surface oxygen and the other from oxygen in ZrO₂. Note that the spectra of the powder samples do not allow for a distinction between two types of oxygen. The two components of the O 1s were not resolved probably due to the inhomogeneous charge broadening. However, all the spectra of the CS and ZCS samples exhibited an asymmetric peak. Therefore, the peak deconvolution was performed using a Gaussian function. In the spectrum of CS, the peaks were ascribed to the following oxygen groups: peak 1 to chemisorbed water and/or O₂ (at 536.2 eV), peak 2 to phenol and/or ether groups (at 532.8 eV), and peak 3 to carbonyl groups (at 530.8 eV).88,89
This result suggests that the surface of CS carbon has carbon-oxygen functional groups, which were probably introduced during the strong base etching (e.g., 5 M NaOH). In the spectra of ZCS composites, the peaks were deconvoluted into two primary features related to different surface states of oxygen including one feature at 531.2–531.4 eV, which is consistent with the binding energy of oxygen in ZrO$_2$, and the other at 532.9–533.0 eV, which is close to the binding energy for the phenol and/or ether groups of the carbon phase that was also observed in the CS carbon. As shown in Figure 3.9b, the feature intensity located at the lower binding energy (i.e., ~531 eV) increases with increase in the ZrO$_2$ content, going from ZCS-10 through ZCS-15 to ZCS-20.
20. This peak increase could be due to the increased contribution of the Zr–O bonds. The corresponding area percentages of the components confirm these increases in intensity and are summarized in Table 3.3.

**Table 3.3** Summary of peak area percentages for O 1s peak components shown in Figure 3.9b

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area percentage (%) for individual component of O 1s region</th>
<th>531 eV</th>
<th>533 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZCS-10</td>
<td>60.80</td>
<td>39.20</td>
<td></td>
</tr>
<tr>
<td>ZCS-15</td>
<td>64.19</td>
<td>35.81</td>
<td></td>
</tr>
<tr>
<td>ZCS-20</td>
<td>67.54</td>
<td>32.46</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.10 depicts the Zr 3d spectra for ZCS-10, ZCS-15, and ZCS-20. The spectrum of CS was also acquired in the Zr 3d range as a control experiment. The spectra of all the ZCS samples appear quite similar to one another, showing two primary peaks, with binding energies of ~183 and 185 eV, which can be assigned to Zr 3d_{5/2} and Zr 3d_{3/2}, respectively. The observed Zr 3d_{5/2} binding energies of ~183 eV for all the ZCS samples are higher than those for metallic Zr (binding energy 178.7–180.0 eV), ZrC (binding energy 178.6–179.6 eV), and ZrO\(_x\) \((0 < x < 2, 180.8–181.4 \text{ eV})\), but comparable to that for ZrO\(_2\) \((182.9 \text{ eV})\). Therefore, it can be concluded that the Zr atoms in the ZCS composites primarily have the +4 oxidation state, which represents its oxidation state in ZrO\(_2\).
Figure 3.10 High-resolution XPS spectra of Zr 3d for CS, ZCS-10, ZCS-15, and ZCS-20. (Note that peaks associated with Zr metal or ZrC were not found.)

3.3.7 Modification of zirconia-carbon nanocomposites with phenylphosphonic acid

Covalent grafting of molecular-size phosphonic acids onto ZCS composites was attempted in order to investigate whether the nanometric surface of ZrO$_2$ embedded in the carbon matrix can be used as active sites for anchoring functional groups through well-known Zr–O–P bonds. SCHEME 3.2 presents a graphic representation of a typical anchoring procedure using an organophosphonic acid as grafting molecules onto the surface of ZCS composites. The bonding mode shown in SCHEME 3.2 is just illustrative and may have other possible bonding modes.
Surface modification of ZCS composites was attempted using a commercial organophosphonic acid, phenylphosphonic acid (C$_6$H$_5$PO$_3$H$_2$). In this experiment, all of the as-prepared ZCS samples (i.e., ZCS-10, ZCS-15, and ZCS-20) were treated with a C$_6$H$_5$PO$_3$H$_2$ aqueous solution (0.07 M). C$_6$H$_5$PO$_3$H$_2$ was chosen as the source of anchoring molecules because of its availability, small size, and simplicity to be monitored during XPS analysis. Wide-survey XPS spectra were recorded for all of the ZCS and CS specimens that were identically treated. Prior to XPS analysis, all of the specimens were aggressively rinsed with DI water, sonicated in DI water, and dried overnight under vacuum at 80 °C. In Figure 3.11, survey XPS spectra of the ZCS samples are compared with the CS sample.
Figure 3.11 Low-resolution X-ray photoelectron spectra in survey scan mode of (a) CS, (b) ZCS-10, (c) ZCS-15, and (d) ZCS-20 after treatment with 0.07 M phenylphosphonic acid.
According to XPS results, binding of phenylphosphonates (C₆H₅PO₃−) to the ZCS samples is evident since phosphorous is present in the corresponding spectra (Figure 3.11b–d). However, phosphorus element is absent in the spectrum of the CS specimen (Figure 3.11a). Therefore, the presence of signals for phosphorus confirms the complete grafting of C₆H₅PO₃– onto the ZCS surfaces but not onto the CS surface. The peak binding energies and assignments of the principal features in Figure 3.11b–d are as follows: 134 eV (P 2p), 184 eV (Zr 3d), 285 eV (C 1s), and 532 eV (O 1s). The binding energies are all consistent with the presence of carbon, zirconium, oxygen, and phosphorus on the surface.

Figure 3.12 presents the enlarged low-resolution XPS spectra in the region (110–215 eV binding energy) where Zr 3d, P 2s, and P 2p are clearly observed. The phosphorus binding energies found at 134 eV (P 2p) and 191 eV (P 2s) are all consistent with PO₃ compounds. As seen in Figure 3.12, the peak intensity for phosphorus increases with increase in ZrO₂ content in the composite. This result suggests that the more ZrO₂ sites onto the surface of the materials are available, the more phosphonates can be attached onto these materials. Therefore, it can be confirmed that the attachment of C₆H₅PO₃− moieties onto the composite surface is through the Zr–O–P bonds.
Figure 3.12 Enlarged low-resolution XPS spectra of (a) CS, (b) ZCS-10, (c) ZCS-15, and (d) ZCS-20 after treatment with 0.07 M phenylphosphonic acid in the spectral region of the main peaks for phosphorus and zirconium.

P / Zr atomic ratios on the composite surfaces were evaluated using the atomic percent compositions for Zr 3d and P 2s that were obtained from the corrected signal intensities of the Zr 3d and P 2s peaks in Figure 3.11b-d. The signal intensities were corrected by dividing their intensities by the corresponding relative sensitivity factors (e.g., 2.576 for Zr 3d and 0.344 for P 2s) and normalized over the all of the elements, as provided with the instrument software. It was found that the P / Zr ratios were 0.95 in spectrum (b) for ZCS-10, 1.06 in spectrum (c) for ZCS-15, and 1.00 in spectrum (d) for ZCS-20, of which ratios were approximately close to a 1:1 atomic ratio. In fact, these
atomic percent ratios obtained from XPS analysis were not fully quantitative because all the samples used in the analysis were irregular-shaped, porous powders that had been pressed into an indium substrate foil. A different degree in exposure of the samples in the analyzed layer may contribute some imprecision in the peak integrations. Also, the atom percents were obtained from survey spectra since high-resolution spectra were not available for all samples. This fact may also cause some error to the atomic ratios mentioned above. However, it is believed that the estimation in P / Zr atomic ratios for all the samples should be still in a good approximation and the results strongly support the idea that nanoscale ZrO₂ in the carbon matrix can act as active sites for anchoring compounds that are terminated with phosphonic acid groups.

3.4 Conclusions

The SiO₂-templating method was employed to achieve a high level of control over pore size, pore volume, and interior surface area in the synthesis of the mesoporous carbon nanocomposites containing nanoscale ZrO₂ particles. The resulting nanocomposites possess 1) nanometric ZrO₂ particles embedded in their carbon phase and 2) mesoporous structures produced by selective removal of SiO₂ templates. Our results prove that the ZrO₂ nanoparticles are stable against NaOH etching; therefore selective etching of SiO₂ over ZrO₂ and carbon can successfully produce the mesoporous carbon nanocomposite materials. This approach provides much flexibility for development of novel electrode materials that require porous structures and specific surface properties because the pores and the surface properties can be easily manipulated by using various sized SiO₂ templates and different inorganic functional components,
respectively. Furthermore, this particular type of the composite materials can be modified further to have different surface properties by attaching desirable organic compounds with terminal phosphonic acid groups. Our surface-modification experiments confirmed the successful attachment of phenylphosphonates onto nanoscale ZrO$_2$ surfaces by a 1:1 atomic ratio. From these results, it can be speculated that the addition of nanoparticulate ZrO$_2$ into carbon framework could extend the range of functionalization because, theoretically, any organic compounds having terminal phosphonic acid groups can be chemically attached onto ZrO$_2$-containing surfaces. As an extension, Chapter 4 will demonstrate incorporation of telechelic sulfonated fluoropolymers having terminal phosphonic acid groups onto our ZrO$_2$/carbon nanocomposites. This approach could provide a route to nanocomposite ZrO$_2$/carbon catalyst supports having high ion-exchange capacities of ionomer integrated into electrolyte and/or support pores. Also, it may be able to extend the surface area of the three-phase reaction zone by increasing the chance for ionomer to contact the catalysts present in the support pores. The synthesis of such hybrid nanocomposite materials outfitted with mesoporosity, electrical conductivity, and ionic conductivity could have a potentially important technological impact for PEM fuel cell electrodes.

### 3.5 References


CHAPTER 4
ATTACHMENT OF IONOMER ONTO A NANOSCALE ZIRCONIA-EMBEDDED MESOPOROUS CARBON COMPOSITE

4.1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered as high efficiency energy conversion devices with low to zero pollutant emissions.\textsuperscript{1-3} The key component of the PEM fuel cells is a membrane electrode assembly (MEA). The MEA is a highly integrated system consisting of seven layers. They are a proton exchange membrane, anode and cathode catalytic layers, two gas diffusion layers, and two sealing gaskets.\textsuperscript{4} Even though each layer of the MEA plays its unique role in a PEM fuel cell operation, the catalyst layer at both the cathode and the anode is the active layer where electrochemical reactions occur. More precisely speaking, the electrochemical reactions take place only at the Pt particles for which protons, electrons, and gases converge.\textsuperscript{4-6} The protons, electrons, and gases are each transported in separate phases. Catalyst layer optimization consists of maximizing transport of protons, electrons, and gases, so as to maximize fuel cell activity.

Even though extensive research on PEM fuel cells has been performed in the last few decades, there is still a major issue associated with low catalyst utilization.\textsuperscript{7-9} The low utilization of catalysts results in low energy efficiency, which in turn keeps the cost of commercial PEMFCs high. One way among many others to increase catalyst utilization is to extend the three-phase reaction zone in the catalyst layer.\textsuperscript{10-12} In common practice, a
proton conducting polymer phase is incorporated into the catalyst layer by fabricating the catalyst layer cast from an ink consisting of suspended carbon-supported catalyst and ionomer solution (e.g., Nafion® solution). The ink of carbon-supported Pt and ionomer transforms into a thin composite film with randomly oriented three-phase reaction sites during fabrication. In such morphology, the Pt utilization will be limited because 1) Pt particles are randomly dispersed on a carbon support; 2) carbon supports tend to agglomerate while sheltering Pt particles; and 3) ionomer may not reach Pt particles deep inside pores in the carbon support.

Recently, there have been efforts to circumvent this limitation in Pt utilization. One promising approach is to chemically attach sulfonic acid groups (–SO₃H) onto the carbon supports. Some prior work has been performed in this approach. Xu and co-workers reported the direct attachment of sulfonic acid groups (–SO₃H) onto carbon supports at high temperatures (e.g., 235 °C) through a reaction of C–H groups on carbon surface with SO₃, and these authors observed the enhanced catalyst utilization of the modified catalysts. Several recent reports describe the attachment of molecular sulfonic acid compounds onto carbon supports via a diazonium grafting method, and the grafting of sulfonic groups on the carbon supported catalysts has been shown to enhance the catalyst utilization by extending three phase zones in the catalyst layer. Du et al. reported the use of 4-styrenesulfonate to graft sulfonic groups onto the surface of carbon nanotube supported Pt catalysts (Pt/CNT) via radical polymerization. These authors suggested that the sulfonated Pt/CNT catalysts are more accessible for protons than the unsulfonated counterparts.
In all the attempts of the early work mentioned above, small aryl or aliphatic sulfonic acid compounds were employed as proton conducting agents. In PEMFC technology, fluorinated proton conducting electrolytes are widely used for many reasons, one of which is their greatly enhanced oxidative stability relative to non-fluorinated electrolytes. Therefore, it is important to find methods to attach the fluorinated electrolytes onto carbon supports. Grafting of monomeric fluorinated electrolytes onto carbon has been reported in the literature, but direct covalent attachment of fluorinated polymer electrolytes onto carbonaceous supports for Pt catalysts has not been yet reported to our knowledge. Polymer electrolytes are desirable because they could provide greater ion-exchange capacity in the immobilized electrolyte and they could be more effective in creating pathways for long-range proton transport all the way through a thick composite electrode.

This Chapter presents work on the incorporation of a novel telechelic fluorinated polymer electrolyte (ionomer) into ZrO$_2$-embedded mesoporous carbon composite. The electrolyte is a sulfonated polymer with terminal phosphonic acid groups (–PO$_3$H$_2$). Nanoscale ZrO$_2$ particles exposed at the composite surface can serve as reacting sites for phosphonate groups to anchor. The facile formation and the integrity of Zr–O–P bonds have been proved by many examples reported in the literature and by work described in Chapter 3 of this dissertation. Prior to the attempt to attach the polymer electrolyte onto the composite, covalent attachment of meta-sulfophenylphosphonic acid was performed as a preliminary experiment to study whether proton-exchange capability was able to be introduced into the composite. Then the attachment of ionomer with terminal
PO₃H₂ groups was carried out in the attempt to increase the density of sulfonic acid groups at the composite surface. Elemental analysis (EA), neutralization titration, and energy-dispersive X-ray spectroscopy (EDX) were employed to confirm the incorporation of the ionomer onto the composite support. The attachment of the sulfonated ionomer onto the ZrO₂ / carbon composite onto which Pt catalyst had been deposited was also carried out, and this ionomer-modified catalyst was compared with an unmodified counterpart in terms of the density of sulfonic acid groups (by EA), the electrochemically active surface areas (ECSA), and by electrochemical activity in the oxygen reduction reaction (ORR). The present study demonstrates a simple and effective route to attach a sulfonated fluoropolymer electrolyte onto carbonaceous supports in aqueous media.

4.2 Experimental

4.2.1 Preparation of ZCS-supported Pt electrocatalysts

Nanoscale ZrO₂ (ca. 16 wt.% ZrO₂) - embedded mesoporous carbon composite supports (ZCS) were prepared as described in Chapter 3. The procedure of platinum (Pt) deposition onto carbon-based supports using a combination of EG and NaBH₄ is described in the literature. In our typical preparation, a 0.1 g quantity of the ZCS sample was dispersed with known amount of hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, 37 wt.% Pt, Acros) in 20 mL of ethylene glycol (EG, ≥ 99%, Acros) to prepare a suspended solution. After stirring the solution for 4 h, a solution of sodium borohydride (0.27 g, NaBH₄, ≥ 98%, Acros) prepared in EG (10 mL) was added drop by drop to the suspended solution under vigorous stirring. After stirring for 4 h at room
temperature, a 5 mL quantity of HCl (1.4 M) was added to ensure deposition of Pt nanoparticles on the supports. The solid particles were isolated on a 0.2 µm nylon membrane filter, washed with DI water, and then dried under vacuum at 80 °C overnight. A quantity of 21 wt.% Pt loading on ZCS was achieved (denoted as Pt/ZCS).

4.2.2 Preparation of meta-sulfophenylphosphonic acid solution

meta-sulfophenylphosphonic acid (H$_2$O$_3$PC$_6$H$_4$SO$_3$H, designated as SPPA) was prepared by following a method reported in the literature.$^{28}$ This compound was prepared and provided by our group member, Jiyoung Park. Briefly, SPPA was obtained by sulfonation of phenylphosphonic acid (52.5 mmol, C$_6$H$_5$PO$_3$H$_2$, 98% Alfa Aesar) in chlorosulfonic acid (160.5 mmol, ClSO$_3$H, 99%, Alfa Aesar) at 150 ºC for 3 hours. After cooling it down to room temperature, the excess of ClSO$_3$H was removed by rotary evaporation. The viscous compound was left in a flask. This compound was dissolved in diethyl ether (60 mL, Alfa Aesar). Then DI water (20 mL) was slowly added to it under an ice bath. After three consecutive extractions with diethyl ether, the combined organic phase was dried over anhydrous magnesium sulfate (99%, Strem Chemicals). The organic phase was retrieved by filtration, and the solvent was removed by rotary evaporation and vacuum drying at 80 °C for 1 week. The final product (~7 g) was a white crystalline compound, although it was slightly wet. The crystalline SPPA was so hygroscopic that only the approximate yield (~56%) could be found. An aqueous solution of SPPA (approximately, 0.07 M) was prepared in DI water and stored in a refrigerator until used.
4.2.3 Preparation of sulfonated PFCB ionomer solution

A telechelic sulfonated perfluorocyclobutyl (PFCB) aryl ether ionomer having terminal phosphonic acid groups (MW~10,460 g·mol⁻¹) was designed and synthesized by our group member, Jiyoung Park. In brief, this ionomer was synthesized through the following four steps: 1) step-growth polymerization of perfluorocyclobutyl (PFCB) aryl ether polymer from 4,4´-bis(4-trifluorovinylxyloxy)biphenyl monomer; 2) phosphonation of PFCB polymers via a condensation reaction with diethyl(4-hydroxyphenyl)phosphonate; 3) sulfonation of the phosphonated PFCB using chlorosulfonic acid; and 4) hydrolysis of the phosphonate ester groups using concentrated HCl. The structure of the resulting ionomer compound is illustrated in SCHEME 4.1. The degree of sulfonation was determined to be 0.82 by using ¹H NMR spectra. Because of its high sulfonation level, the ionomer was soluble in water.

\[
\text{SCHEME 4.1 The chemical structure of a telechelic sulfonated PFCB ionomer having phosphonic acid end groups. } \text{ R=} (-\text{CF} \equiv \text{CF} – \text{ or } -\text{CHF} \equiv \text{CF}_2 –). \text{ n} = 20. \text{ MW} = \sim 10,460 \text{ mol} \cdot \text{g}^{-1}, \text{ which was determined from end-group analysis using } \text{¹H NMR spectrometry. Degree of sulfonation } = 0.82.\]
The relative size of the ionomer in salt-free and salt-added aqueous media were investigated by dynamic light scattering (DLS) with a Coulter N4 Plus particle size analyzer equipped with a laser source of 10 mV helium-neon at 632.8 nm. Four salt-added ionomer aqueous solutions were prepared by adding a fixed amount (0.05 g) of the ionomer into sodium sulfate (Na$_2$SO$_4$) aqueous solutions, which contained 0, 2.5, 5.0, and 50 mmol Na$_2$SO$_4$ (99% anhydrous Na$_2$SO$_4$, Mallinckrodt), respectively. The final solution was fixed at 50 mL in a volume. All the DLS measurements were performed at room temperature using a scattering angle of 90°.

4.2.4 Covalent attachment of SPPA onto ZCS

As a preliminary experiment to introduce sulfonic acid (SO$_3$H) groups to ZCS, a 0.2 g quantity of the ZCS powder sample was immersed in an aqueous solution of SPPA (~0.07 M, 25 mL). The suspension was heated at 100 °C for 5 h under continuous stirring. The treated ZCS sample was then separated by filtration on a 0.2 µm nylon membrane. The unreacted SPPA was removed by repeating sonication, centrifugation, filtration, and dispersion in DI water until no acidity was detected in the filtrate. The washed sample was dried overnight at 80 °C under vacuum. The dried sample was then immersed in 0.2 M HCl solution for 5 h at room temperature to assure that only protons were present as counter ions of the sulfonate groups. Finally, the HCl-treated sample was rinsed with 10 mL of DI water and dried for 24 h at 120 °C under vacuum in order to eliminate residual HCl. As a control experiment, the identical treatment with the SPPA solution was also applied to a SiO$_2$-templated mesoporous carbon (blank, CS) without ZrO$_2$. 
4.2.5 Covalent attachment of sulfonated PFCB ionomer onto ZCS and Pt/ZCS

Attachment of the ionomer onto ZCS was performed by immersing 0.2 g of the ZCS powder sample in the ionomer solution with salt (0.05 M Na₂SO₄) or without salt (0 M Na₂SO₄) at 100 °C for 5 h. To remove physically adsorbed ionomer, the treated sample was heated in DI water at 80 °C under continuous stirring for 2 h. The hot suspension was then centrifuged. The supernatant solution was removed by decantation. The precipitated sample was then dispersed again in hot DI water (e.g., 80 °C). These successive washing steps were repeated seven times. The washed sample was dried overnight at 80 °C under vacuum. The dried sample was immersed in a 0.2 M HCl solution for 5 h under stirring. Finally, the HCl-treated sample was centrifuged, rinsed with 10 mL DI water, and vacuum-dried at 120 °C for 24 h. The resulting samples prepared in the salt-free (SF) and salt-added (SA) ionomer solutions were designated as Ionomer-SF/ZCS and Ionomer-SA/ZCS, respectively. In dealing with Pt/ZCS, the identical treatment was applied as described above, except the HCl treatment was left out due to undesired reactivity of Pt nanoparticles with chloride. The resulting materials were referred to as Pt-Ionomer-SF/ZCS and Pt-Ionomer-SA/ZCS, respectively.

4.2.6 Materials characterization

Ion-exchange capacity (IEC) of SPPA-treated or ionomer-treated ZCS samples was determined via a direct neutralization titration method. A known weight of the dried sample was placed in 10 mL of a 2.0 M NaCl solution and mechanically stirred at room temperature for 72 h to allow for complete exchange of Na⁺ ions with H⁺ ions. Only the solution was retrieved by filtration. A 5 mL quantity of the retrieved solution was then
mixed with 5 mL of a standard 0.01 N HCl solution (Fisher Scientific) so that a total 10 mL volume of titration solution was prepared. The resulting solution was titrated with a standard 0.01 N NaOH solution (Fisher Scientific) under a nitrogen blanket. The pH change was monitored to identify the endpoint using a pH meter (accumet AB15, Fisher) with a double-junction pH electrode (Ag/AgCl reference, accumet). The ion-exchange capacity was determined using the following equation:

\[
\text{IEC (mmol·g}^{-1}\text{)} = \frac{2 \times 0.01 \times (V_{\text{NaOH}} - V_{\text{HCl}})}{W} \quad (4.1)
\]

where IEC is the ion-exchange capacity defined as mmol of protons in 1 g of dry sample; \(V_{\text{NaOH}}\) is the volume of titrant (mL); \(V_{\text{HCl}}\) is the volume of a standard HCl added to the titration solution (mL); and \(W\) is the weight of the dry sample (g). As a complementary study, an elemental analysis for sulfur was performed on the SPPA-treated or ionomer-treated ZCS samples at Atlantic Microlab, Inc. (Norcross, GA). Energy-dispersive X-ray spectroscopy (EDX) was also carried out in a parallel analysis. EDX was carried out on a field emission scanning electron microscope (FESEM-Hitachi S4800) equipped with an Oxford INCA energy 200 EDX system or a tabletop scanning electron microscope (Hitachi TM-3000) with EDX analysis. Thermogravimetric analysis of the ionomer-treated ZCS samples was also performed using a Perkin-Elmer TGA7 thermogravimetric analyzer under N\(_2\) environment.

For the Pt catalyst samples, the Pt contents were determined by elemental analysis using EDX. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV multipurpose X-ray diffractometer (40 kV and 40 mA) with a Cu K\(\alpha\) radiation
at a wavelength ($\lambda$) of 1.541 Å. The 2θ angles were scanned from 5 to 90°. The average Pt crystallite size was estimated by the Debye-Scherer formula. The morphologies of Pt nanoparticles supported on the ZCS composite were investigated using a high-resolution transmission electron microscope (Hitachi TM 9500). An elemental analysis for sulfur was performed on the ionomer-treated Pt catalysts at Atlantic Microlab, Inc. (Norcross, GA).

### 4.2.7 Electrochemical characterization

The electrochemical measurements for samples containing Pt nanoparticles were carried out in a three-electrode cell on a CHI 660A electrochemistry workstation, using a Pt wire as a counter electrode and a mercury-mercurous sulfate (Hg / Hg$_2$SO$_4$ / 0.5 M H$_2$SO$_4$) as a reference electrode at room temperature. Electrochemical potentials are reported with respect to the Hg / Hg$_2$SO$_4$ reference electrode in this work. A supporting electrolyte was 0.1 M H$_2$SO$_4$ (aq). The working electrode was a thin layer of the catalyst ink, which was coated on the surface of a glassy carbon disk electrode (CH Instrument, 3 mm diameter). The catalyst ink of Pt/ZCS was prepared by suspending 8.8 mg of the powder catalyst in a solution consisting of 1.6 mL DI water and 0.4 mL 5% Nafion solution (EW 1100, Solution Technology). For ionomer-attached Pt/ZCS, 10 mg of the sample was suspended in a solution of DI water (1.6 mL) and Nafion solution (0.4 mL) in order to account for the weight contribution of the ionomer. The ink suspension was stirred overnight to form a uniform catalyst ink. A 2 μL quantity of the resulting ink was drop cast onto the glassy carbon electrode and subsequently dried in air (Pt loading, ~0.07 mg·cm$^{-2}$).
Before electrochemical measurements were made, working electrodes were activated and cleaned by cycling the potentials between 0.6 V and -0.6 V at a scan rate of 0.1 V·s⁻¹ in a N₂-saturated 0.1 M H₂SO₄ solution until a steady voltammogram was obtained. Cyclic voltammetry (CV) was then carried out to estimate electrochemically active surface areas (ECSA) of Pt catalysts using stripping analysis of adsorbed H and CO (i.e., H adsorption/desorption and CO stripping voltammetric methods). In a hydrogen adsorption/desorption CV, the voltammogram was obtained in 0.1 M H₂SO₄ by cycling the potentials from 0.7 V to -0.7 V at a sweep rate of 0.02 V·s⁻¹. The coulombic charge for hydrogen desorption was used for calculating the active Pt surface area in the following equation:

$$\text{ECSA}_H (\text{m}^2 \cdot \text{g}^{-1} \text{Pt}) = \frac{Q_H}{0.21 \cdot [\text{Pt}]}$$  \hspace{1cm} (4.2)

where $Q_H$ is the charge associated with hydrogen desorption in the electrode (mC·cm⁻²); [Pt] represents the Pt loading (mg·cm⁻²) in the electrode; and a correlation value of 0.21 (mC·cm⁻²) is the charge density required to oxidize a monolayer of hydrogen molecules on Pt. To calculate the charge related to desorption of hydrogen atoms, the anodic peaks between -0.7 V and -0.4 V were integrated. Then the charge associated with the double layer charging was subtracted from the total charge.

In CO stripping cyclic voltammetry, CO adsorption was performed by bubbling CO gas (technical purity 99%, Airgas) into a 0.1 M H₂SO₄ electrolyte for 15 min while the potential was held at -0.25 V. Then, the electrolyte was purged with nitrogen (high purity 99.9%, Airgas) for 15 min to remove dissolved CO from the electrolyte solution. Finally,
the stripping voltammogram was obtained between -0.7 V and 0.7 V at a sweep rate of 0.02 V·s⁻¹. The coulombic charge associated with CO oxidation was used to calculate the active Pt surface area, as described in the following equation:\(^\text{30}\)

\[ \text{ECSA}_{\text{CO}} \left( m^2 \cdot g^{-1} \text{ Pt} \right) = \frac{Q_{\text{CO}}}{0.42 \times [\text{Pt}]} \]  

(4.3)

where \( Q_{\text{CO}} \) is the CO stripping charge (mC·cm⁻²); a correlation value of 0.42 (mC·cm⁻²) corresponds to the charge density (mC·cm⁻²) required to oxidize a monolayer of adsorbed CO on Pt; and [Pt] represents the Pt loading (mg·cm⁻²). To calculate the CO stripping charge, the area under the CO oxidation peak was integrated and corrected by subtracting the charge attributed to the double layer charging and surface platinum oxide formation.

Pt utilization efficiency (%) was estimated using the following equations:\(^\text{31}\)

\[ \text{Utilization (\%) } = \frac{\text{ECSA}}{\text{SSA}} \times 100 \]  

(4.4)

\[ \text{SSA} \left( m^2 \cdot g^{-1} \text{ Pt} \right) = \frac{6000}{\rho \cdot d} \]  

(4.5)

where SSA is a specific surface area, \( \rho \) is the density of Pt (21.4 g cm⁻³), and \( d \) (nm) is the Pt diameter estimated by XRD.

Oxygen reduction reaction (ORR) tests for Pt/ZCS and Pt-Ionomer-SA/ZCS catalysts were performed using linear sweep voltammetry (LSV) with O₂ saturated 0.1 M H₂SO₄ while scanning from 0.35 to -0.15 V (vs. Hg / Hg₂SO₄ reference electrode) at a scan rate of 0.005 V·s⁻¹. The ORR activities of the catalysts were compared in terms of onset and peak potentials observed in linear sweep voltammograms.
4.3 Results and discussion

4.3.1 Attachment of SPPA onto ZCS

**SCHEME 4.2** A schematic illustration of a covalent attachment of SPPA molecules onto nanoscale ZrO$_2$ particles embedded in the carbon matrix.

Modification of a ZrO$_2$ surface with a phosphonate group (−PO$_3^{2-}$) creates the Zr–O–P bond. This bond is known to be very stable.$^{21-26}$ **SCHEME 4.2** presents a graphic representation of a typical anchoring procedure using m-sulfophenylphosphonic acid (SPPA) as a grafting molecule onto the surface of ZCS composite. Although the bonding modes presented in **SCHEME 4.2** are just illustrative, the suggested main bonding modes are bidentate and tridentate.$^{32}$ This multidentate feature allows the stable bonding between a ZrO$_2$ surface and a phosphonate group.$^{26}$

In addition to a phosphonic acid group (−PO$_3$H$_2$), SPPA has a sulfonic acid group (−SO$_3$H). To test whether a sulfonate group (−SO$_3^{-}$) can bind to ZrO$_2$, the ZCS
composite was immersed in a 0.07 M benzenesulfonic acid solution (C₆H₅SO₃H, technical grade, Alfa Aesar) under the identical treatment as with SPPA. EDX was performed on the washed sample to detect element sulfur. The EDX analysis (not shown) proved that there was no trace of sulfur on the sample. This result indicates that the interaction between a SO₃H group and a ZrO₂ surface is not strong probably due to the strong acidic characteristics of −SO₃H; therefore, sulfonyl moieties can be easily removed through the extensive washing process. The supporting result can be found in the literature where pure ZrO₂ particles were covalently grafted with SPPA. They presented that the covalent bonding between ZrO₂ and SPPA was only through the Zr–O–P interactions.³² This is in agreement with our observation.

Figure 4.1a shows a representative EDX spectrum of the SPPA-treated ZCS sample. In the spectrum, sulfur (S) was clearly observed at around 2.30 keV. Sulfur is only element present in the peak at 2.30 keV. Also, unresolved peaks of zirconium (Zr) and phosphorous (P) were found at around 2.05 keV. This result indicates the successful attachment of SPPA molecules onto the ZCS composite surface. The EDX analysis at different locations in the specimen suggested uniform distribution of Zr, P, and S in the sample. An average weight percent of element S was found to 0.80 wt.% throughout the sample. On the other hand, the CS sample (blank, no ZrO₂) that was treated with SPPA under the identical condition did not exhibit any peak associated with phosphorus or sulfur element in the corresponding EDX spectrum (Figure 4.1b). This result proves that SPPA has been attached only onto ZrO₂ and the extensive washing has removed un-reacted SPPA molecules completely from the carbon surface.
To verify the EDX analysis for sulfur, elemental analysis (EA) was carried out using a thermal combustion method. All the CS, pure ZCS (untreated) and SPPA-treated ZCS samples were studied in this analysis. According to the EA results, the SPPA-treated CS and pure ZCS samples did not contain any sulfur. Meanwhile, 0.85 wt.% of sulfur was found in the SPPA-treated ZCS sample. This result indicates that the SPPA attached onto the ZCS surface is the source of the sulfur element since the CS and pure ZCS samples do not possess sulfur. Using the sulfur content values obtained from the EA and EDX analyses, ion-exchange capacity (IEC), which is a measure of proton conductivity, can be derived with assumption that the ion-exchange capacity is dependent only on the extent
of the $\text{SO}_3\text{H}$ groups. The values of the ion-exchange capacity calculated from the sulfur contents which were determined by EA and EDX are listed in Table 4.1. These values may be referred to as theoretical ion exchange capacity.

Practical ion-exchange capacity of the SPPA-treated ZCS sample was determined by a neutralization titration method. From titration, the amount of exchangeable protons ($\text{H}^+$) per unit weight of the sample was measured using NaOH as a titrant. Figure 4.2 presents the titration curve of the SPPA-treated ZCS sample (SPPA-ZCS). For comparison, the titration curves for the SPPA-treated CS (SPPA-CS), untreated ZCS (ZCS), and a blank solution were also included in Figure 4.2.

![Figure 4.2](image_url)

**Figure 4.2** Titration curves of SPPA-ZCS, SPPA-CS, ZCS, and a blank solution (5 mL 2 M NaCl + 5 mL 0.01 M HCl). A fixed sample weight (0.35 g) was used for preparing each analyte solution.
Table 4.1 The amounts of sulfur obtained from elemental analyses (EA and EDX) and the IEC values estimated by EA, EDX, and titration

<table>
<thead>
<tr>
<th></th>
<th>S content (wt %)*</th>
<th>S content (wt %)*</th>
<th>IEC (mmol H⁺·g⁻¹)</th>
<th>IEC (mmol H⁺·g⁻¹)</th>
<th>IEC (mmol H⁺·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPPA-CS</td>
<td>0</td>
<td>0</td>
<td>NA</td>
<td>NA</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>ZCS</td>
<td>0</td>
<td>0</td>
<td>NA</td>
<td>NA</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>SPPA-ZCS</td>
<td>0.85</td>
<td>0.80</td>
<td>0.26</td>
<td>0.25</td>
<td>0.24</td>
</tr>
</tbody>
</table>

S content *a* was the sulfur weight percent obtained from elemental analysis by combustion; S content *b* was the sulfur weight percent estimated by EDX; IEC *c* was calculated using the S content *a*; IEC *d* was calculated using the S content *b*; and IEC *e* was measured by titration.

The blank solution was made up of NaCl (5 mL, 2.0 M) and HCl (5 mL, 0.01 M, a standard HCl solution). The titration curves of a blank solution, SPPA-CS, and ZCS samples almost completely overlapped with one another. This result implies the following facts: 1) SPPA molecules did not anchor onto the carbon surface; 2) The intensive washing successfully removed un-reacted SPPA molecules; 3) HCl, which had been used for re-acidification, was almost completely eliminated from the sample surface after drying at 120 °C under vacuum; and 4) the CS and pure ZCS surfaces did not possess strong acid characteristics (e.g., −SO₃H) of which protons (H⁺ ions) are exchangeable with Na⁺ ions of NaCl. The proton content in the SPPA-ZCS sample was calculated to be 0.24 mmol H⁺·g⁻¹ while subtracting the acid contribution of the blank solution since the pure ZCS exhibited negligible acidity. This value of ion-exchange capacity is in good agreement with those determined by the sulfur contents. This result suggests that the sulfur element detected by the elemental analysis is mainly present in the form of SO₃H because the ion exchange capacity only relies on the amount of SO₃H.
groups; and also the attachment of sulfonated compounds onto ZCS can provide proton exchange capability to ZCS. All the data values are summarized in Table 4.1.

4.3.2 Dynamic light scattering (DLS) studies on the PFCB aqueous ionomer solution

The as-prepared sulfonated PFCB ionomer can be homogeneously dispersed in DI water due to its high degree of sulfonation (e.g., 82%). However, the ionomer chains may form micelles or aggregates in aqueous media because of its amphiphilic (i.e., hydrophobic and hydrophilic) nature. The size of the aggregates should eventually affect the grafting density of the ionomer on the ZCS surface. For instance, the contact between the anchoring sites (–PO₃H₂ groups) of the large ionomer aggregate and the nanoscale ZrO₂ surface should be spatially and statistically limited. Therefore, it is advisable to identify a solution condition for which the ionomer exists as a compact aggregate or as individual solvated polymer molecules so that the bonding interaction between the ZrO₂ surfaces and the PO₃H₂ moieties can be maximized. Reportedly, electrolytes such as NaOH and NaCl suppress the aggregation of Nafion® ionomer in aqueous media.³³,³⁴ In our approach, anhydrous sodium sulfate (Na₂SO₄) was added to the PFCB ionomer solution for that purpose.

The dynamic light scattering (DLS) measurement was performed in order to study the relative size distribution of the PFCB ionomer chains and aggregates in Na₂SO₄-free and Na₂SO₄-added aqueous solutions. Four Na₂SO₄ concentrations (0.00, 0.05, 0.10, and 1.00 M) were considered in this measurement. The DLS studies revealed that the chains and aggregates exist in the ionomer aqueous solution. Figure 4.3 shows that the size of
the ionomer chains and aggregates is influenced by salt concentration at a fixed PFCB ionomer concentration (e.g., 1 mg·mL⁻¹). Figure 4.3a exhibits the particle size distribution of the ionomer in the salt-free aqueous solution. This sample exhibits a bimodal size distribution; one mode is in the range of 100-400 nm and the other in the range of 20-50 nm. One possibility is that the smaller particles consist of individual ionomer chains and the larger particles are aggregates of ionomer chains. The ionomer aggregates could be formed in the aqueous medium either through hydrophobic interactions of fluorocarbon portions or through ionic or H-bonding interactions of acid groups (e.g., sulfonic and phosphonic acid groups).

Figure 4.3b shows the size distribution of the ionomer in the presence of 0.05 M Na₂SO₄. This distribution is dominated by one mode in the size range below 10 nm. This result indicates that the salt has suppressed the formation of larger aggregation while shielding the electrostatic interactions between the ionic groups. Similar speculation has been made in the literature with Nafion aqueous solution. When 0.10 M Na₂SO₄ was added, a similar size distribution was observed even though the mode of the peaks was shifted to a slightly larger size regime (Figure 4.3c), and at an even higher salt concentration of 1.00 M Na₂SO₄ (Figure 4.3d), the DLS was dominated by ionomer aggregates that were even larger than in the absence of salt. At this salt concentration, precipitation of the ionomer was observed approximately 1 h after the ionomer solution was prepared. Figure 4.4 provides the photographic evidence of the ionomer precipitation at 1.00 M Na₂SO₄. It was believed that the precipitating or clustering behavior of the ionomer chains at this high salt concentration resulted from the salting-
out process due to the hydrophobic and van der Waals interactions between the perfluorinated portions of the ionomer chains.

**Figure 4.3** Relative particle size distributions of PFCB ionomer aqueous solutions (1 mg·mL\(^{-1}\)) with a different Na\(_2\)SO\(_4\) concentration: (a) 0.00 M (b) 0.05 M, (c) 0.10 M, and (d) 1.00 M salt concentrations. DLS scattering angle \(\theta = 90^\circ\).

The DLS measurement verifies that the ionomer chains or aggregates of chains become compact in the presence of Na\(_2\)SO\(_4\) at a low concentration (e.g., 0.05 or 0.10 M). The ionomer aggregates appeared to be relatively small when the 0.05 M Na\(_2\)SO\(_4\) was
present in the ionomer solution, compared with the solution having the 0.10 M Na₂SO₄, as shown in Figure 4.3. The compact ionomer would be desired to maximize the number of the ionomer-attached sites on the ZCS surface by maximizing the ability of ionomers to penetrate the ZCS mesopores. Therefore, the ionomer solution containing 0.05 M Na₂SO₄ salt was chosen as an optimal ionomer solution for modifying the ZCS sample in our study.

![Figure 4.4](image)

**Figure 4.4** A photo image of the aqueous ionomer solutions containing different Na₂SO₄ salt concentrations (e.g., 0.00, 0.05, 0.10, and 1.00 M). (Note the yellow precipitate in the 1.0 M salt-added ionomer solution.)

### 4.3.3 Attachment of sulfonated PFCB ionomer onto ZCS

The ZCS composite was subjected to a grafting process that sought to immobilize the PFCB ionomer via chemical covalent bonding between the PO₃H groups of the ionomer
and the ZrO₂ nanoparticles exposed at the surface of the ZCS composite. Both Na₂SO₄ (0.05 M)-present and Na₂SO₄-absent PFCB ionomer solutions were prepared so that each solution contained a 1 mg quantity of the ionomer in 1 mL solution. Then the ZCS sample modified with the salt-added ionomer solution was compared with the ZCS sample modified with the salt-free ionomer solution in terms of the sulfur content for each modified ZCS sample to achieve. Hereinafter, the ionomer-treated ZCS samples in the salt-free and salt-added solutions are referred to as Ionomer-SF/ZCS and Ionomer-SA/ZCS, respectively. The elemental composition of each ionomer-treated ZCS sample was initially studied by EDX analysis.

Figure 4.5 shows a typical EDX spectrum of the ionomer-treated ZCS. All of the expected elements were detected except phosphorus. The phosphorus element did not appear in the EDX spectrum probably due to that fact that its fraction was very small with respect to those of the other elements (e.g., theoretical mole ratio of S to P = 18 to 1). Therefore, its intensity was too low to be extracted from the background for quantification. The trace of fluorine (F) was apparently observed at around 0.70 keV, and peak of zirconium (Zr) was also detected at around 2.05 keV. Sulfur (S) was clearly observed at around 2.30 keV. This result suggests that the ZCS surface has been modified with the ionomer.

For comparison, the CS sample was treated with the ionomer solution under the identical treatment. Figure 4.6 shows representative EDX spectra of the ionomer-treated CS sample prior to washing (Figure 4.6a) and after washing (Figure 4.6b). Prior to washing, the ionomer-treated CS sample exhibited the peaks associated with fluorine
(e.g., 3.45 wt. % F) and sulfur (e.g., 1.74 wt. % S). However, after extensive washing, the CS sample did not exhibit any quantitatively reliable peaks associated with F or S elements in the corresponding EDX spectrum. This result verifies that our washing procedure was effective to remove the un-reacted, physically-adsorbed ionomer from samples containing no ZrO$_2$. It also indirectly proves that the elemental composition of the ionomer-treated ZCS found in the EDX spectrum (Figure 4.5) was almost completely due to the covalent attachment of the ionomer onto the ZrO$_2$ groups on the ZCS surface.

![Figure 4.5](image)

**Figure 4.5** A representative EDX spectrum of the ionomer-treated ZCS in the salt-added condition.
Figure 4.6 Representative EDX spectra of the ionomer-treated CS sample (a) prior to washing and (b) after extended washing, seven times (b). (Note that there is no apparent peak for F or S on the thoroughly washed CS sample.)

To obtain quantitative information regarding the ionomer amount grafted onto the ZCS samples, the percentage of ionomer grafting was estimated from the TGA curves shown in Figure 4.7. For the untreated ZCS sample, the weight loss upon heating was almost negligible, whereas the ionomer-treated samples exhibited weight loss over the
identical temperature range. The amount of the ionomer attached onto the ZCS surface was determined by the weight loss when the ionomer-attached ZCS composite was heated from room temperature to 700 °C under nitrogen. According to the TG analysis for only the ionomer under nitrogen (not shown), ~34 wt.% of mass was left as a residue, probably of carbon. Therefore, the total weight of the attached ionomer should be recalculated considering the residue (ca. 34 wt.%) left from the thermal decomposition of the ionomer. In the calculation, the weight loss in the temperature range between 200 °C and 600 °C was assumed to be attributable to the attached ionomer, and the weight percent of the carbon residue was calculated assuming that 66 wt.% of the ionomer would be burned off and 34 wt.% of the ionomer would be left as a carbon residue. The approximate weight loss percents (wt.%) for Ionomer-SF/ZCS and Ionomer-SA/ZCS were 9 wt.% and 12 wt.%, respectively. Therefore, the weight percents of the carbon residue for Ionomer-SF/ZCS and Ionomer-SA/ZCS were calculated to be approximately 5 wt.% and 6 wt.%, respectively. As a result, the Ionomer-SF/ZCS and the Ionomer-SA/ZCS were covered by ~14 wt.% and ~18 wt.% ionomer, respectively. This calculation implies that higher ionomer coverage can be achieved using the salt-added ionomer solution where the ionomer aggregates become compact.

Based on the ionomer weight percents estimated from the TGA curves, the sulfur contents (wt.%) and the corresponding IEC values for the Ionomer-SF/ZCS and Ionomer-SA/ZCS samples were calculated respectively with assumption that the molecular weight (MW) of the ionomer is 10,460 g·mol⁻¹; the total number of the sulfonated phenyl groups is 44, and its degree of sulfonation is 0.82. According to the calculation, the Ionomer-
SA/ZCS sample exhibited the higher S amount (2.0 wt.%) than did the Ionomer-SF/ZCS (1.5 wt.%). Accordingly, the acid contents (i.e., IEC) for the Ionomer-SF/ZCS and Ionomer-SA/ZCS samples were estimated to be 0.48 and 0.62 mmol H⁺·g⁻¹, respectively. All the calculated results are listed in Table 4.2. These calculated sulfur contents and IEC values will be compared with those obtained by other analytical means such as elemental analysis and titration.

Figure 4.7 TGA curves of an untreated ZCS sample (ZCS, solid line) and the ionomer-treated ZCS samples in the absence of Na₂SO₄ (Ionomer-SF/ZCS, dash dot line) and the presence of 0.05 M Na₂SO₄ (Ionomer-SA/ZCS, dash line).
Table 4.2 The calculated sulfur content (wt.%) and the corresponding proton-exchange capacity for Ionomer-SF/ZCS and Ionomer-SA/ZCS samples by using the TGA data

<table>
<thead>
<tr>
<th>Ionomer wt.%</th>
<th>S content (wt.%)$^a$</th>
<th>IEC (mmol·g$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionomer-SF/ZCS</td>
<td>14</td>
<td>1.5</td>
</tr>
<tr>
<td>Ionomer-SA/ZCS</td>
<td>18</td>
<td>2.0</td>
</tr>
</tbody>
</table>

$^a$ S content (wt.%) was calculated with assumption that the MW of the ionomer is 10,460 g·mol$^{-1}$, the total number of the sulfonated phenyl groups is 44, and the degree of sulfonation is 0.82.  
$^b$ IEC (mmol·g$^{-1}$) was calculated assuming that the sulfur element is derived from SO$_3$H groups.

To validate the IEC values estimated from TGA, titration was carried out as described previously. A 0.10 g quantity of each dried sample was used for this titration. As a control, the ZCS sample, which was only treated with 0.05 M Na$_2$SO$_4$ solution (no ionomer), was also analyzed by titration. The titration curves (Figure 4.8) show that the untreated ZCS sample, which had been immersed in 0.05 M Na$_2$SO$_4$ solution without the ionomer, was almost neutral, having nearly zero ion-exchange capacities; whereas, the ionomer-treated ZCS samples possessed titratable acidic groups. The IEC values for the Ionomer-SF/ZCS and the Ionomer-SA/ZCS were estimated to be 0.45 and 0.55 mmol·g$^{-1}$, respectively. This result clearly indicates that the Ionomer-SA/ZCS sample had the higher number of the SO$_3$H groups than the Ionomer-SF/ZCS sample. This trend is in good agreement with that observed in TGA although the IEC values estimated from TGA were slightly higher than those from titration. This would be probably because various assumption and approximation were made for the calculation with the TGA result.
Figure 4.8 Titration curves for Na$_2$SO$_4$-treated ZCS (dash line), Ionomer-SF/ZCS (dot line), and Ionomer-SA/ZCS (solid line). A 0.10 g sample was used to prepare each analyte solution. All the titration solutions contained 5 mL of a standard 0.01 N HCl.

As a parallel analysis for the IEC determination, both the Ionomer-SF/ZCS and the Ionomer-SA/ZCS samples were further analyzed using EA and EDX to determine their sulfur contents and to calculate their acid group concentrations (i.e., IEC values). The estimated sulfur contents are listed in Table 4.3. Again, the S content and the corresponding IEC value for the Ionomer-SA/ZCS sample were higher than those for the Ionomer-SF/ZCS sample. These results agree well with the results obtained from titration. All the calculated IEC values are also included in Table 4.3. In general, the amount of sulfonic groups (i.e., protons) determined by titration is slightly lower compared with ones by EA and EDX methods. This may be due to the following possible reasons: 1) the titration method detects only the number of accessible sulfonic
acid groups; and 2) some of the sulfonic groups may possess other cations rather than protons. However, all the calculated IEC values from the EA and EDX analyses provided the same trend as that observed from the titration, showing that the ionomer-SA/ZCS sample exhibited the higher IEC value. In conclusion, all the results discussed above suggest that the compact ionomer aggregate experiences less steric hindrance while anchoring to nanoscale ZrO₂ surfaces than the larger counterpart, resulting in increase in the number of the grafted sites, which eventually increases the number of sulfonic groups.

<table>
<thead>
<tr>
<th>Table 4.3</th>
<th>Summary of sulfur analyses (by EA and EDX) and the corresponding IEC values (by EA, EDX, and titration) for Ionomer-SF/ZCS and Ionomer-SA/ZCS samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>S content (wt.%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>S content (wt.%)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;SO₄-ZCS</td>
<td>0</td>
</tr>
<tr>
<td>Ionomer-SF/ZCS</td>
<td>1.58</td>
</tr>
<tr>
<td>Ionomer-SA/ZCS</td>
<td>1.89</td>
</tr>
</tbody>
</table>

S content (wt.%)<sup>a</sup> and S content (wt.%)<sup>b</sup> were obtained from EA and EDX, respectively. IECEA was the ion exchange capacity estimated using the S content (wt.%)<sup>a</sup> while IECEDX using the S content (wt.%)<sup>b</sup>. IECtitration was the ion exchange capacity determined by titration.

4.3.4 Preparation of Pt nanoparticles supported on ZCS composites (prior to ionomer immobilization)

ZCS-supported Pt catalysts (denoted as Pt/ZCS) were prepared as described previously. For comparison, CS-supported Pt catalysts were also prepared, which are referred to as Pt/CS. EDX indicated that the Pt loadings on CS and ZCS were 20 wt.%
and 21 wt.%, respectively. Powder XRD measurements for Pt/CS and Pt/ZCS samples were carried out in order to confirm the presence of crystalline domains (e.g., Pt and ZrO$_2$). Figure 4.9 shows the XRD pattern of Pt/ZCS in comparison with that of Pt/CS. The weak and broad peak at $2\theta \sim 23^\circ$ was observed on both of the samples, which was associated with the (002) plane of carbon.$^{29}$ For the Pt/ZCS sample, the diffraction peaks of Pt and ZrO$_2$ were also detected, indicating their coexistence with carbon. Meanwhile, the Pt/CS sample exhibited only the diffraction peaks of Pt besides the peak for C. Both the Pt/CS and Pt/ZCS samples exhibited diffraction peaks centered at around 39.9°, 46.1°, 67.7°, and 81.3° corresponding to the (111), (200), (220), and (311) face-centered-cubic Pt planes, respectively.$^{35}$ The d-spacing of Pt(111) at $2\theta = 39.9^\circ$ was found to be 0.226 nm for both the Pt/CS and Pt/ZCS samples, which is in good agreement with the d-spacing value found in the literature (e.g., 0.226-0.228 nm).$^{36}$ In addition to the diffraction peaks for Pt, the Pt/ZCS sample also presented the peaks of tetragonal ZrO$_2$ at $2\theta \sim 30.4$, 34.9, 50.1, and 59.7°. These peaks can be assigned to (111), (200), (220), and (311) lattice planes of tetragonal ZrO$_2$.$^{37}$ The d-spacing associated with the diffraction peak at $2\theta = 30.4^\circ$ was 0.293 nm, which agreed well with the expected d-spacing of (111) tetragonal ZrO$_2$ (d = 0.295 nm).$^{38}$ The sizes of Pt nanoparticles on the Pt/CS and Pt/ZCS samples were estimated by using the Scherer equation based on the full-width at half maximum of Pt (220) peak at $2\theta = 67.7^\circ$. The calculated sizes of the Pt nanoparticles for Pt/CS and Pt/ZCS are 2.8 and 3.2 nm, respectively.
The formation of Pt nanoparticles on the surfaces of ZCS and CS supports was also investigated by TEM studies. Figure 4.10 exhibits representative TEM images of Pt/CS and Pt/ZCS samples. The TEM micrographs show that a large majority of Pt nanoparticles were well distributed on the ZCS and CS supports. The average Pt particle size was estimated by measuring the sizes of 50 individual Pt particles. The mean diameters for the CS-supported and ZCS-supported Pt nanoparticles were 3.0 (± 0.3) nm and 3.5 (± 0.5) nm, respectively. For both of the catalysts, the Pt diameters measured on the TEM images were slightly larger than those estimated by XRD. In fact, XRD gives the information about crystallite size information rather than true particle size. Several crystallite grains could form particles. In addition, on XRD, the average size across the
whole sample is estimated; meanwhile, TEM provides particle size analysis from individual particles observed only in localized sample areas where the images are obtained.\textsuperscript{39} These facts would contribute some difference between TEM and XRD measurements for the particle size. Nevertheless, both the TEM and XRD measurements commonly indicate that the Pt diameter of Pt/ZCS is larger than that of Pt/CS.

![Representative TEM micrographs of (a) Pt/CS and (b) Pt/ZCS samples. Scale bar, 20 nm.](image)

**Figure 4.10** Representative TEM micrographs of (a) Pt/CS and (b) Pt/ZCS samples. Scale bar, 20 nm.

Agglomerated Pt particles were observed on both Pt/CS and Pt/ZCS catalysts as shown in Figure 4.10. However, this feature was more pronounced on the Pt/ZCS catalyst. The different behavior of Pt agglomeration on the different supports may be explained as follows. On the CS support, only weak interactions can take place between Pt precursor (e.g., PtCl\textsubscript{6}\textsuperscript{2-}) and carbon surface during impregnation because the CS support does not possess definite functional groups on its surface. Meanwhile, the ZCS
support contains ZrO₂ particles. Reportedly, the pH of point of zero charge for ZrO₂ at room temperature is 7.9.⁵,²⁶,³³,³⁹ Therefore, the surface of ZrO₂ becomes more positively charged at lower pH. Our precursor solution was fairly acidic (e.g., pH~1). Therefore, the negatively charged Pt precursor species may undergo electrostatic interactions with positively charged ZrO₂ surfaces in the acidic condition. During reduction, the Pt crystallites may nucleate and agglomerate near or on some of the positively charged ZrO₂ sites. Figure 4.11 presents an example of this agglomerating behavior of Pt particles near ZrO₂ domains. The lattice spacing values of crystalline ZrO₂ and Pt nanoparticles were estimated to be 0.29 and 0.23 nm, respectively. These values are similar to the inter-planar spacing of the Pt (111) and the ZrO₂ (111) planes, which were obtained from the XRD analysis.

![Image](image.png)

**Figure 4.11** A high resolution TEM image of Pt/ZCS. The dash circle indicates ZrO₂ domains, and the solid circle highlights Pt domains. Scale bar, 2 nm.
4.3.5 Attachment of sulfonated PFCB ionomer onto Pt/ZCS

The Pt/ZCS sample was immersed in the ionomer solution under the identical treatment described previously (section 4.3.3) in attempt to attach the ionomer onto the Pt/ZCS sample. Both Na₂SO₄ (0.05 M)-present and Na₂SO₄-absent ionomer solutions were employed to modify Pt/ZCS samples. Hereinafter, the ionomer-treated Pt/ZCS samples in salt-free and salt added solutions are referred to as Pt-Ionomer-SF/ZCS and Pt-Ionomer-SA/ZCS, respectively.

Figure 4.12 A representative EDX spectrum of the ionomer-attached Pt/ZCS (e.g., Pt-Ionomer-SA/ZCS).

Figure 4.12 shows a representative EDX spectrum of the ionomer-attached Pt/ZCS sample (e.g., Pt-Ionomer-SA/ZCS). It clearly exhibits the presence of all the expected elements such as carbon, oxygen, fluorine, zirconium, platinum, and sulfur, which suggests that the ionomer has been attached on the ZCS support. Elemental combustion analysis (EA) was carried out to estimate the sulfur content for each ionomer-treated Pt/ZCS sample. For the ionomer-treated ZCS samples, it has been seen that the elemental
analysis for sulfur provides a good approximation for ion-exchange capacity (IEC). Therefore, the IEC value of the ionomer-attached Pt/ZCS catalyst was estimated using the sulfur content obtained from EA. Also, the ionomer coverage was estimated based on the sulfur content with the assumption made for the calculation of sulfur content using the ionomer weight percent (refer to Table 4.2). The sulfur content, the corresponding IEC value, and the ionomer weight percent are listed in Table 4.4.

Table 4.4 Summary of the elemental sulfur analysis (by EA) and the corresponding IEC estimation for Pt-Ionomer-SF/ZCS and Pt-Ionomer-SA/ZCS samples

<table>
<thead>
<tr>
<th></th>
<th>S content (wt.%)$^a$</th>
<th>Ionomer (wt.%)$^b$</th>
<th>IEC (mmol·g$^{-1}$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ionomer-SF/ZCS</td>
<td>1.14</td>
<td>10.3</td>
<td>0.36</td>
</tr>
<tr>
<td>Pt-Ionomer-SA/ZCS</td>
<td>1.47</td>
<td>13.3</td>
<td>0.46</td>
</tr>
</tbody>
</table>

S content (wt.%)$^a$ was obtained from EA; Ionomer wt.%$^b$ was calculated based on the sulfur content from EA with assumption that the MW of the ionomer is 10,460 g·mol$^{-1}$, the total number of the phenyl groups is 44, and the degree of sulfonation is 0.82; and IEC (mmol·g$^{-1}$)$^c$ was calculated assuming that all the sulfur element is derived from SO$_3$H groups.

Again, the salt-added ionomer solution introduced the higher amount of SO$_3$H groups onto Pt/ZCS than the salt-free ionomer solution. The EDX analysis showed that the Pt-Ionomer-SF/ZCS and Pt-Ionomer-SA/ZCS contained 19 wt.% and 18 wt.% Pt, respectively. These values are reasonable Pt weight percents considering the ionomer fraction of Pt-Ionomer/ZCS and the Pt content of as-prepared Pt/ZCS (21 wt.% Pt). This result suggests that Pt nanoparticles were stable (e.g., no dissolution of Pt) throughout the grafting process. Further evidence regarding this speculation is given by the following analysis.
Stability of Pt/ZCS against the ionomer solution was investigated by using an X-ray diffractometer. In this investigation, Pt-Ionomer-SA/ZCS was compared with Pt/ZCS. The XRD patterns for Pt/ZCS and Pt-Ionomer-SA/ZCS are presented in Figure 4.13. The broad diffraction peak at $\theta \sim 23^\circ$ shown in both of the XRD patterns relates to the (002) plane of carbon while the peaks at approximately $39.9^\circ$, $46.1^\circ$, $67.7^\circ$, and $81.3^\circ$ corresponding to the (111), (200), (220), and (311) face-centered-cubic Pt planes, respectively. There was no notable change in the Pt crystalline structure. The Pt diameters for Pt/ZCS and Pt-Ionomer-SA/ZCS were estimated to 3.2 and 3.3 nm, respectively, at the Pt (220) peak. This result suggests that the grafting process did not affect the Pt particle size and its XRD pattern. TEM images (Figure 4.14) support this.
suggestion showing that there was no noticeable difference between Pt/ZCS and Pt-Ionomer-SA/ZCS in terms of the morphology and size of the Pt particles.

Figure 4.14 Selected TEM micrographs of Pt-Ionomer-SA/ZCS sample. Scale bars, (a) 20 nm and (b) 5 nm. Note that compared with Figure 4.10b for Pt/ZCS before ionomer immobilization, there was neither noticeable change in the size of Pt nanoparticles nor severe agglomeration after the treatment with the ionomer.

Based on the characterizations discussed above, the Pt-Ionomer-SA/ZCS catalyst was considered as the optimal Pt catalyst in our study since one of the goals in this study was to achieve many proton exchange sites on carbon-supported Pt catalysts using the sulfonated ionomer. Therefore, we focused only on the Pt-Ionomer-SA/ZCS catalyst for following electrochemical characterization in order to investigate the electrocatalytic activity of the ionomer-incorporated Pt catalyst.
4.3.6 Electrochemical characterization of Pt/ZCS electrocatalysts before and after ionomer immobilization

The electrochemical active surface area (ECSA) of the as-synthesized catalyst was estimated using hydrogen adsorption/desorption and CO stripping methods over the potential range of -0.7 to 0.7 V (V vs. Hg/HgSO₄). The electrolyte solution was 0.1 M H₂SO₄. Figure 4.15 presents the cyclic voltammograms (CV) of Pt-Ionomer-SA/ZCS. For comparison, the CVs of Pt/CS and Pt/ZCS electrocatalysts were also included. In Figure 4.15a, all of the electrocatalysts exhibit typical voltammetric features of Pt electrode with adsorption and desorption of hydrogen peaks in the voltammograms at potentials from -0.4 to -0.7 V. The Pt oxide formation was also observed at around 0.1 V in the forward scan and the Pt oxide reduction between 0.1 and -0.3 V in the backward scan. Among the three electrocatalysts, the Pt/CS catalyst exhibited larger hydrogen desorption peaks than the Pt/ZCS and Pt-Ionomer-SA/ZCS catalysts. The electrochemical active surface areas for Pt/CS, Pt/ZCS, and Pt-Ionomer-SA/ZCS electrocatalysts were calculated to be 62, 50, and 51 m²·g⁻¹, respectively. The ZCS-supported Pt catalysts (Pt/ZCS and Pt-Ionomer-SA/ZCS) exhibited almost identical electrochemical surface areas. This result suggests that Pt nanoparticles supported on the ionomer-attached ZCS retained their electrochemical activity. And it also shows that, under these conditions where electrodes are flooded by aqueous H₂SO₄ electrolytes, addition of grafted ionomer to the electrodes has had no detectable effect on the ECSA of Pt electrocatalysts.
Figure 4.15b shows the CO-stripping voltammograms of Pt/CS, Pt/ZCS, and Pt-Ionomer-SA/ZCS catalysts. The adsorption of CO was performed in CO-saturated 0.1 M H$_2$SO$_4$ solution at -0.25 V for 15 min. All of the catalysts presented the typical CO-stripping voltammetric behavior. Commonly, the hydrogen desorption peaks were not observed under the first positive scan starting at -0.7 V. The disappearance of the desorption peaks proves that the Pt surface had been completely covered by CO species. The single peak centered at around 0.1 V in the first forward scan represents the electrochemical oxidation of the adsorbed CO species. CO oxidation was not observed in the second forward scan, verifying the complete CO oxidation in the first forward scan.

As seen in Figure 4.15b, the stripping peak intensity and area of Pt/CS catalyst is larger than those of Pt/ZCS and Pt-Ionomer-SA/ZCS catalysts. The calculated specific surface areas for Pt/CS, Pt/ZCS, and Pt-Ionomer-SA/ZCS catalysts were 63, 49, and 50 m$^2$ g$^{-1}$, respectively. The CO-stripping method provided similar ECSA values to those obtained in the hydrogen adsorption/desorption method. The surface areas estimated using the two different methods were reasonably consistent with each other. The higher electrochemical active surface area of Pt/CS may be attributed to the smaller Pt size and better Pt dispersion over the carbon support. Also, in the case of Pt nanoparticles supported on ZCS, some Pt nanoparticles can possibly exist directly on ZrO$_2$ surfaces, which are electrically insulating. These Pt particles would be electrochemically inactive unless they were in contact with other electrical conductors (e.g., the carbon domain or Pt particles on the carbon domain of other Pt/ZCS particles). As a result, such inactive Pt particles may lead to the smaller ECSA than it should be.
Figure 4.15 (a) H-adsorption/desorption and (b) CO-stripping voltammograms of Pt/CS (dot line), Pt/ZCS (dash line), and Pt-lonomer-SA/ZCS (solid line) with a scan rate of 0.02 V·s⁻¹ in 0.1 M H₂SO₄ as supporting electrolyte.
The efficiency of Pt utilization was estimated using equation 4.4 and the ECSA estimated from the CO-stripping method. The specific surface area was calculated using equation 4.5 with the average Pt size obtained from XRD. As observed in the ECSA estimation, the same trend was indicated in the Pt utilization calculation. The calculated percent efficiency values for Pt/CS, Pt/ZCS, and Pt-Ionomer-SA/ZCS were 63, 56, and 57%, respectively. The Pt/CS catalyst exhibited a slightly higher Pt utilization efficiency probably because of the reasons discussed above. No significant difference in the Pt utilization was found between Pt/ZCS and Pt-Ionomer-SA/ZCS in a liquid electrolyte system (e.g., H₂SO₄).

4.3.7 Oxygen reduction reactions (ORR) of modified and unmodified Pt/ZCS catalysts with ionomer

Oxygen reduction measurements were performed on Pt/ZCS and Pt-Ionomer-SA/ZCS catalysts at room temperature. The electrode prepared with Pt/ZCS or Pt-Ionomer-SA/ZCS catalyst was immersed in 0.1 M H₂SO₄ solution and purged with nitrogen (N₂) gas for 15 min to deaerate the solution. Linear sweep voltammetry (LSV) was then carried out to obtain a baseline linear sweep voltammogram.

To investigate the electrocatalytic activity of each catalyst toward the oxygen reduction reaction (ORR), LSV was performed in O₂-saturated H₂SO₄ solution. Figure 4.16a shows the linear sweep voltammograms of Pt/ZCS and Pt-Ionomer-SA/ZCS catalysts in 0.1 M H₂SO₄ solution saturated with O₂. For comparison, the voltammograms obtained in N₂-saturated H₂SO₄ solution were included in Figure 4.16a. In the N₂-saturated solution, no definable reduction peak was observed at either Pt/ZCS
or Pt-Ionomer-SA/ZCS, which indicates that the solution was almost completely O₂-free; and the contribution of PtO reduction was minimal in our measurement. In the O₂-saturated solution, however, a remarkable reduction peak centered at ~0.11 V was observed at both of the catalysts. Therefore, it can be concluded that only oxygen reduction contributed to the reduction current in the O₂-saturated solution. As seen in Figure 4.16a, the oxygen reduction at both of the catalysts was diffusion controlled when the potential was below ~0.11 V. Meanwhile, it was under a mixed diffusion-kinetic control in the potential range between ~0.11 V and 0.35 V. Both of the catalysts exhibited the almost identical voltammograms. This result indicates that their catalytic activities toward O₂ reduction were almost identical.

Figure 4.16b presents LSV curves, which were recorded with O₂ being bubbled in 0.1 M H₂SO₄. In this case, the diffusion-controlled behavior below ~0.11 V was not observed because O₂ was continuously supplied to the electrode surface. The half-way potential for both Pt/ZCS and Pt-Ionomer/ZCS was 0.152 V, proving that their activities toward O₂ reduction were not significantly different. This result is complementary to that shown in Figure 4.16a.
Figure 4.16 (a) Linear sweep voltammograms of Pt/ZCS (dash line) and Pt-Ionomer-SA/ZCS (solid line) in O\textsubscript{2}-saturated H\textsubscript{2}SO\textsubscript{4} and those of Pt/ZCS (dash dot line) and Pt-Ionomer-SA/ZCS (dot line) in N\textsubscript{2}-saturated H\textsubscript{2}SO\textsubscript{4} solutions. (b) Linear sweep voltammograms of Pt/ZCS (dash line) and Pt-Ionomer-SA/ZCS (solid line) in H\textsubscript{2}SO\textsubscript{4} solution continuously purged with O\textsubscript{2}. The LSVs were performed in the range between 0.35 V and -0.15 V with a scan rate of 0.005 V·s\textsuperscript{-1}.
4.4 Conclusions

This study has presented a convenient route to modify a mesoporous carbonaceous composite material with sulfonic acid electrolyte compounds. The mesoporous carbon composite where ZrO\textsubscript{2} nanoparticles were embedded was prepared as described previously (Chapter 3) and modified by chemically attaching the sulfonated electrolytes with PO\textsubscript{3}H\textsubscript{2} groups for the purpose of introducing a high SO\textsubscript{3}H concentration onto / into the composite surface. This particularly designed hybrid composite was able to act as a Pt catalyst support and have proton exchange ability on its surface.

The main goal of this study was to demonstrate the covalent attachment of sulfonated ionomer onto the composite support so that a large SO\textsubscript{3}H concentration was able to exist on the support surface while providing high proton exchange capacity. The preliminary experiment with SPPA exhibited that nanoscale ZrO\textsubscript{2} embedded in the carbon matrix showed a high reactivity toward grafting of SPPA through Zr–O–P bonding. The comparative study with benzenesulfonic acid indirectly suggested that the PO\textsubscript{3}H\textsubscript{2} group was strongly bound to the ZrO\textsubscript{2} surface while the SO\textsubscript{3}H group was weakly bound to the ZrO\textsubscript{2} surface and therefore easily removed by washing. The elemental analyses and titration revealed that the treatment of the ZCS composite support with SPPA allowed the support to have the proton exchange capability (e.g., 0.24 mmol H\textsuperscript{+}·g\textsuperscript{-1} by titration) derived from the SO\textsubscript{3}H groups of the anchored SPPA molecules.

The characterization confirmed the attachment of both the SPPA model compound and an oligomeric sulfonated ionomer onto the ZCS surface. In the case of ionomers, the presence and concentration of salt (e.g., Na\textsubscript{2}SO\textsubscript{4}) in the ionomer solution influenced the
amount of the ionomer grafted onto the composite surface. A relatively high surface coverage of the ionomer was achieved when the ionomer solution containing 0.05 M Na₂SO₄ salt was used, compared with that obtained using a salt-free ionomer solution. This finding is thought to be due to the decreased aggregation of the ionomer chains in the presence of salt, which were caused by screening on the ionomer charges by the added salt. As a result, the higher concentration of SO₃H groups on the composite was able to achieve with the salt-added ionomer solution than with the salt-free ionomer solution, evidenced by elemental analysis and titration. Compared with the composite modified with SPPA molecules, the modification with the ionomer allowed the increased proton exchange capacity (e.g., 0.55 mmol H⁺·g⁻¹ with the salt-added ionomer solution vs. 0.24 mmol H⁺·g⁻¹ for SPPA-modified ZCS) because of the higher SO₃H concentration possessed by the ionomer.

Pt nanoparticles were successfully deposited onto the ZCS composite (e.g., Pt/ZCS) using a Na₂BH₄-ethylene glycol reduction method. Interestingly, the nanoscale ZrO₂ sites seemed to undergo electrostatic interactions with negatively charged Pt precursors probably due to the positively charged surface in the preparative solution, resulting in the assembly of Pt particles locally around the ZrO₂ sites. The ionomer was able to be attached onto Pt/ZCS catalysts through Zr–O–P bonding between the ZrO₂ exposed at the ZCS surface and the PO₃H₂ groups of the ionomer while the Pt crystalline structure and size were retained. Again, the higher SO₃H concentration was observed when the salt-added solution was used during the modification process. The Pt catalysts were examined for their electrocatalytic performance in promoting oxygen reduction by
voltammetric techniques in aqueous acid media. The electrochemical measurements indicated that the ionomer-modified Pt/ZCS and unmodified Pt/ZCS possessed the similar electrochemical active surface area and the electrocatalytic activity toward $O_2$ reduction in an aqueous solution. The aqueous solution facilitates proton conduction. Therefore, protons can undergo facile transport across the electrode layer and easily contact Pt surfaces. This fact seems to result in no significant difference in the ECSA and ORR measurements between the ionomer-modified Pt/ZCS catalyst and -unmodified Pt/ZCS catalyst when these catalysts are studied under conditions where they are flooded by aqueous acid electrolyte. However, we expect that the ionomer-modified Pt/ZCS would exhibit the increased ECSA and the enhanced catalytic activity under a real operational condition of PEM fuel cells where no aqueous electrolyte media are present to assist the proton conduction. It is expected that under these circumstances the sulfonated ionomer chemically attached to the support would be able to extend the three-phase-boundary in the catalytic layer.

4.5 References


CHAPTER 5
INCORPORATION OF LITHIATED IONOMER INTO LITHIUM-ION BATTERY CATHODES

5.1 Introduction

Lithium-ion batteries are being aggressively developed for hybrid electric vehicle (HEV), plug-in hybrid electric vehicle (PHEV), and electric vehicle (EV) applications. For many of these applications, a high-rate performance (e.g., fast charge and discharge reactions) is essential.\textsuperscript{1-3} Typical lithium-ion battery electrodes are composite mixtures obtained by blending electroactive material particles with non-electroactive additives such as carbon black and a polymeric binder. Lithium-ion transfer at the interface between the electrode and the electrolyte, as well as lithium transport inside the active materials and in the porous spaces of the electrode, are essential processes during battery charging and discharging, and the rates of these processes in part determine the overall battery performance. Therefore, it is important for the battery electrodes to possess high lithium ion and electron conductivity in order to efficiently transport lithium ions and electrons to and from each active material particle and the current collector, respectively.\textsuperscript{4}

In a typical lithium ion battery electrode, the binder provides structural integrity at relatively low mass fractions (e.g. < 10 wt.%), bringing together the electroactive material and the carbon black which (usually) provides electronic conductivity. Nonionic polymers such as Teflon (PTFE) or poly-vinylidene difluoride (PVDF) which do not have any intrinsic ionic functionality are commonly used as electrode binders. Rapid and full
penetration of liquid electrolyte into the accessible pores of the composite electrodes, and rapid transport of lithium ions into and out of the pores via the liquid electrolyte, are necessary in such electrodes to access the available capacity at reasonable rates. Modeling studies suggest that salt concentration polarization and/or electrolyte depletion from the porous space in the electrodes are important factors limiting the performance of lithium ion batteries during high-rate charging / discharging.\(^5\) Salt concentration polarization and/or depletion from the electrode void space occur because the salt concentration in the liquid electrolyte is low and also because anions in the electrolyte are mobile and may be ejected from the electrode void space as lithium cations are consumed in electrode reactions. If this happens, the lithium availability inside the electrode becomes limited and the electrode becomes a poor lithium ion conductor, and battery performance is compromised.

We hypothesize that the use of lithiated ionomers as binders might offer a route forward to achieving high performance (i.e., high power and high capacity utilization) by providing ionic functionality within the battery electrodes. By incorporating ionic binders with immobile anionic groups into the electrodes, we hope to compensate for and possibly prevent the loss of electrolyte from electrodes during rapid charging and discharging, thereby allowing for more rapid charging / discharging while maintaining adequate cell voltages and capacities.

Some prior work has been performed in this area. Early work on the use of ionic binders employed lithium-exchanged Nafion\(^\circledR\) as a component of the binder for battery electrodes. Yang et al prepared a composite of Birnessite-type lithium manganese oxide
electrode with Nafion binder by co-precipitation. These authors suggested that addition of Nafion to Birnessite improves cycleability and utilization of the active material even at a high rate in a LiPF$_6$/organic carbonate electrolyte because of the enhanced ionic conductivity.$^6$ Liang et al studied LiCoO$_2$/carbon black/Nafion using a lithiated Nafion membrane swollen with a propylene carbonate/ethylene carbonate (PC:EC) mixture as electrolyte in a half-cell configuration that also used lithium metal as both a counter and a reference electrode.$^7$ A high irreversible capacity loss due to solid electrolyte interface (SEI) formation at the lithium metal electrode was observed although reversible charge-discharge was achieved. Riley and co-workers tested lithiated Nafion and also lithiated clays as components of composite LiCoO$_2$ cathodes in cells that utilized solvent-wetted lithiated clay as electrolyte.$^8$ Reversible charge and discharge were demonstrated but improvements over standard cells were not noted. In this case, limitations on performance may have been attributed to the utilization of lithiated clays as electrolyte. In all these attempts of the early work, however, explicit quantitative comparisons of cathodes with and without ionic binder, and with simultaneous use of a conventional liquid electrolyte, were not made.

We present here the results of our study using a short-side-chain perfluorosulfonate ionomer in lithium form as a cathode binder material. This particular ionomer is simply a short-side-chain analog of lithiated Nafion$^6$, having a poly-tetrafluoroethylene (PTFE)-like backbone and simpler $\text{OCF}_2\text{CF}_2\text{SO}_3\text{Li}$ pendant side chains.$^9$ A structure for the ionomer is given in SCHEME 5.1. This ionomer is well matched for our approach for the following reasons. First, it is easily prepared at various compositions as dispersions in N-
methyl-2-pyrrolidone (NMP) solvent. Second, it is assumed to be able to hold many lithium ions after exchanging its protons with lithium ions because it has a high cation exchange capacity (approximately, 1.2 meq·g⁻¹). Third, fluoro-ionomers in general exhibit a high oxidative stability which should help the cathode to retain full capacity under highly oxidizing conditions following multiple deep charge-discharge cycles.

\[
\begin{array}{c}
\text{SCHEME 5.1 Structure of the lithiated ionomer used as a battery cathode binder.}
\end{array}
\]

\[m = 3.6 - 10\]

The work described herein is focused on direct, explicit comparisons of cells with ionic and nonionic binders in the cathode, using a conventional liquid electrolyte (e.g., LiPF₆-EC/DEC). In our system, part of the active material particle surface is in direct contact with the ionic binder; therefore, the lithium-ion exchange / intercalation can take place not only between the liquid electrolyte and the active material but also between the binder and the active material. In this regard, the use of ionomer as an electrode binder should be advantageous for performance of lithium-ion batteries at high rates. The
ionomer binder also provides additional ion-exchange capacity to the cathode via a salt for which the macroscopic anion mobility is zero, which should help to minimize and possibly prevent salt depletion from cathodes during charge/discharge cycling. Improvements in composite cathode performance, in terms of accessible capacities at a particular cutoff voltage at different discharge rates, were realized through the use of an ionic binder in the cathode and standard salt-in-solvent electrolytes.

5.2 Experimental

5.2.1 Preparation of ionic and nonionic binder solutions

Perfluorosulfonic acid ionomer was obtained in acid form, as 3 wt.% dispersion in water. The ionomer dispersion was originally obtained as a donation from the Dow Chemical Company, which at the time had an active program in fluorinated ionomers that has since been discontinued. To prepare ionic binder solutions, water was first removed from the dispersion by evaporation, then an approximately 5 wt.% solution of the acid ionomer in absolute ethanol was prepared and employed to make thin films by a solution-cast method. Films were cast onto a Petri dish, air-dried at 110 °C for 3 h, and then vacuum-dried at 140 °C for another 2 h to completely remove the solvent and stabilize the film. To convert the dried cast ionomer film to a lithium sulfonate (–SO₃Li) form, the film was cleaned with concentrated nitric acid (70%, Acros) at 80 °C overnight, followed by thorough rinsing with boiling de-ionized (DI) water. Then a lithium ion exchange procedure was carried out using a solution of 2.0 M lithium hydroxide (Alfa Aesar) in DI water for 12 h at 80 °C under vigorous stirring. The resulting lithium sulfonate form of the ionomer film was then rinsed in boiling DI water to remove the remaining salt and
vacuum-dried at 120 °C overnight. Attenuated total reflection (ATR) FT-IR spectroscopy measurements were performed to verify the chemical conversion of the membranes. The ionomer film in lithium form was then dissolved at 70 °C in 1-methyl-2-pyrrolidone (anhydrous solvent, NMP, 95%, Sigma Aldrich) and stirred over 4 h to form the ionic binder solution having 5 wt.% of the lithium-form ionomer in NMP. The ionic binder solution was stored in an inert-atmosphere glove box. For comparison with a nonionic binder, poly-vinylidene difluoride (PVDF, MW = 523,000 g·mol⁻¹, Sigma Aldrich) was used as a baseline binder. PVDF was dried at 120 °C under vacuum, overnight, prior to dissolution in NMP to obtain a 5 wt.% solution which was stored in the glove box prior to use.

5.2.2 Preparation of composite cathodes

Carbon-coated LiFePO₄ (C-LiFePO₄, 2.1 ± 0.2 wt.% carbon) was provided by Hydro-Québec. Acetylene carbon black (99.99%, 100% compressed) was purchased from Strem Chemicals, Inc. Composite cathodes were prepared by casting slurries of 60% LiFePO₄ (by weight), 20% acetylene carbon black, and 20% polymer binder in NMP solvent onto stainless-steel current collectors (alloy 20, diameter 0.5 in, 1.27 cm). The weight percents of LiFePO₄ and acetylene carbon black were adjusted by the weight of the carbon present in the active material. The slurry preparation was as follows. The binder solution was diluted in additional NMP solvent to achieve a proper thickness of slurry on the current collector (approximately 0.5 mm). Acetylene carbon black was stirred into the diluted binder solution for 12 h. Carbon-coated LiFePO₄ (C-LiFePO₄) was then added to the homogenized ionomer / acetylene carbon black mixture and the resultant
mixture blended for another 12 h. After homogenization, slurries were cast on the end of current collector rods using PTFE tubing fitted around the rods to keep the slurry from running down the side, and dried first for 12 h at 110 °C in air then in a vacuum oven at 110 °C for another 12 h. The dried composite electrodes typically had mass loadings of 2.4 - 2.5 mg·cm⁻² with the nominal electrode thickness of 40 µm.

5.2.3 Electrochemical characterization

The composite LiFePO₄ cathodes were assembled into Swagelok-style cells with Li₄Ti₅O₁₂ anodes (Hydro Québec) supported on aluminum foil current collectors and Celgard 2320 separators in an Ar-filled glove box. Cells were filled with a 100 µL volume of a 1.0 M or 0.1 M LiPF₆ (Battery grade, Sigma Aldrich) electrolyte in a solvent mixture of 1:1 (v/v) ethylene carbonate (EC) / diethyl carbonate (DEC). After aging for 12 h in the glove box to ensure full wetting of the cathodes, cell testing was accomplished outside of the glove box using an Arbin BT 2000 cycler. Prior to each measurement, for activation, each full cell was first constant current (CC) charged at C/5 rate from the open-circuit voltage (OCV) to 2.5 V and then constant voltage (CV) charged at 2.5 V until the current reached C/60. The rate capability was measured by charging the cells to 2.5 V at C/5 rate and then discharging to 1.0 V at discharge rates varying from C/5 to 5C. All specific capacities discussed in this paper were calculated from the weight of the cathode active material because cells were always fabricated so that the cathode capacity limited the overall cell capacity.
5.3 Results and discussion

5.3.1 Electrode integrity testing

Electrode binders must exhibit low solubility when in contact with liquid electrolytes so that the composite electrodes can maintain their mechanical and structural integrity under battery operation and storage.\textsuperscript{10} Therefore, it is essential to test whether a combination of C-LiFePO\textsubscript{4}, acetylene carbon black, and the lithiated perfluorosulfonate ionomer would give electrodes that hold together under exposure to a particular solvent-electrolyte combination (e.g., LiPF\textsubscript{6} in organic carbonates). In this regard, a high-throughput method for testing electrode integrity was developed. In this method, composite electrodes, which were prepared on aluminum foil using various combinations of C-LiFePO\textsubscript{4}, acetylene carbon black, and the lithiated perfluorosulfonate ionomer, were immersed in 1.0 M and 0.1 M LiPF\textsubscript{6}–EC/DEC electrolyte solutions for one week at room temperature while the solution was agitated occasionally. The degree of darkening of the LiPF\textsubscript{6} solution and the loss of internal contact of the composite electrode with the foil were monitored. It was observed that for all combinations involving the ionomer binder, the electrolyte solution remained colorless and the electrodes on the aluminum foil stayed intact. No visible change in the electrode integrity was detected. All the formulations involving the lithiated perfluorosulfonate ionomer resulted in stable electrodes suitable for battery testing. For the sake of comparison, this method was also applied to electrode formulations including PVDF, which also presented stable electrodes.
5.3.2 FT-IR characterization of the lithiated perfluorosulfonate ionomer

In order to confirm completion of perfluorosulfonic acid ionomer lithiation, the infrared spectra of solvent-cast ionomer membranes in H⁺ and Li⁺ forms were acquired using ATR FT-IR spectroscopy. Figure 5.1 compares the IR spectrum of the acid form (H⁺ form) with that of the lithium salt form (Li⁺ form). The dashed line represents the absorption bands characteristic for the H⁺ form while the solid one corresponds to the absorption characteristics of the Li⁺ form.

![ATR FT-IR spectra of the perfluorosulfonic acid ionomer (dash line) and the perfluorosulfonate lithium form ionomer (solid line).](image)

**Figure 5.1** ATR FT-IR spectra of the perfluorosulfonic acid ionomer (dash line) and the perfluorosulfonate lithium form ionomer (solid line).
The evidence for completed lithiation was in part found from the symmetric stretching of the sulfonate group that was observed in the region between 1000 and 1100 cm\(^{-1}\), although the spectrum obtained from the ionomer in the H\(^+\) form is not consistent with that of the complete H\(^+\) form.\(^{11}\) As shown in Figure 5.1, the stretching band appeared at around 1050 cm\(^{-1}\) in the case of the ionomer in the H\(^+\) form (dash line). In contrast, the corresponding band of the lithiated ionomer (solid line) was located at a higher frequency, which is known to be due to the interaction between lithium ion and oxygen.\(^{7,12,13}\) One more evidence was observed from the broad absorption near 1700 cm\(^{-1}\) in the spectrum for the acid form (dashed line), which is caused by the bending of protonated water in the acid form of the ionomer. However, this band is absent in the spectrum of the lithium salt form, and only O-H stretching vibration of the absorbed water molecule was present at about 1640 cm\(^{-1}\).\(^{14-16}\) These spectral changes indicate that lithium-ion exchange was complete.

5.3.3 Microstructure and porosity of composite cathode films

Figure 5.2 shows SEM images of a cross section of the ionomer-based composite electrode (right side) in comparison with that of the PVDF-based composite electrode (left side). C-LiFePO\(_4\) and carbon black particles appear embedded within the binder matrix for both binders (Figure 5.2a-d). Both PVDF-based and ionomer-based composite electrodes exhibited an identical nominal thickness of ca. 40 µm. C-LiFePO\(_4\) particles were mostly elliptical in shape as shown in Figure 5.2e-f. The diameter of C-LiFePO\(_4\) particles was in the range of several tens of nanometers while they were several hundreds of nanometers in length. In general, it was observed that aggregated carbon black
particles (average particle size, ca. 40 nm) were interspersed among C-LiFePO₄ particles, forming electrical networking in the composite electrode (Figure 5.2e-f). The fractured cross section of the ionomer-based electrode revealed a similar porous morphology with submicron-sized pores. TEM images (Figure 5.3a-b) also showed evidence of pore formation in the composite electrodes.

The capacity of ionomer binders to augment the liquid electrolyte contained within electrode pores depends in part upon the electrode porosity. Therefore, the porosity of each composite electrode was estimated from the difference between the theoretical density of close-packed composite materials calculated from the density and mass fraction of the individual electrode components, and the apparent density calculated from the thickness, diameter and weight of the composite electrode disk film. In the theoretical density calculation, we employed density values of 3.6 g·cm⁻³ for LiFePO₄, 0.2 g·cm⁻³ for carbon black, and 1.74 g·cm⁻³ for PVDF, respectively, as in Zaghib’s recent report. A density value of 2.1 g·cm⁻³ was used for the ionomer (i.e. short-side-chain perfluorosulfonic acid). The calculated porosity values for each of the composite electrodes are listed in Table 5.1. From the porosity evaluation, it was found that both of the composite electrodes had similar porosities, indicating that the electrode architecture was approximately independent of the ionic property of the binders.
Figure 5.2 SEM micrographs of cross-sectional areas of (a, c, e) the PVDF-based and (b, d, f) ionomer-based composite cathodes. The images (e) and (f) are fractured cross-sectional areas. The other images were obtained from the polished cross-sectional areas of the electrode films embedded in the resin.
Figure 5.3 Representative TEM images showing pore formation in the configuration of C-LiFePO₄, carbon black, and binder polymer: (a) PVDF-based composite electrode; and (b) ionomer-based composite electrode.
Table 5.1 Porosity in composite electrode

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composite film weight (mg)</th>
<th>Apparent density (g·cm⁻³)</th>
<th>Theoretical density (g·cm⁻³)</th>
<th>Porosity (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-based composite</td>
<td>3.0</td>
<td>0.59</td>
<td>0.78</td>
<td>24</td>
</tr>
<tr>
<td>Ionomer-based composite</td>
<td>3.1</td>
<td>0.61</td>
<td>0.79</td>
<td>23</td>
</tr>
</tbody>
</table>

Porosity<sup>a</sup> = (1 - apparent density of composite electrode / theoretical density of close-packed composite materials) x 100

5.3.4 Electrochemical characterization

All the electrochemical measurements presented here were performed in a full-cell configuration with a Li₄Ti₅O₁₂ anode for which the capacity always exceeded the cathode capacity. Two types of Li₄Ti₅O₁₂/C-LiFePO₄ full cells were tested, one in which the cathode was formulated using the lithium form of perfluorosulfonate ionomer as binder and another one with PVDF as binder. Hereinafter, the testing cells are referred to as Li₄Ti₅O₁₂/C-LiFePO₄-Li⁺ ionomer or –PVDF (by the type of cathode binder).

Figure 5.4 shows initial charging voltage profiles at C/5 for Li₄Ti₅O₁₂/C-LiFePO₄–Li⁺ ionomer and Li₄Ti₅O₁₂/C-LiFePO₄–PVDF cells in the voltage range of OCV - 2.5 V for 1.0 M (Figure 5.4a) and 0.1 M (Figure 5.4b) LiPF₆–EC/DEC electrolytes. The cell voltage quickly increased from OCV to about 1.9 V and then showed a plateau at around 1.9 V corresponding to the two-phase reaction between LiFePO₄ and FePO₄, which is consistent with published literature. The initial charging curves for both cells were almost identical in terms of voltage profile and charge capacity at C/5, even though slightly more capacity was accommodated during charging of the Li₄Ti₅O₁₂/C-LiFePO₄–Li⁺ ionomer cell. In 1.0 M electrolyte (Figure 5.4a), specific capacities for Li₄Ti₅O₁₂/C–
LiFePO$_4$–Li$^+$ ionomer and Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–PVDF based cells were 147 mAh·g$^{-1}$ and 146 mAh·g$^{-1}$, respectively which is close to the estimated specific capacity of the C-LiFePO$_4$ of 154 ± 3 mAh·g$^{-1}$, provided by Hydro-Québec. At low electrolyte concentration (Figure 5.4b), both cells also attained similar capacities (e.g., 145 mAh·g$^{-1}$, Li$^+$ ionomer; and 143 mAh·g$^{-1}$, PVDF) although capacities slightly lower than those in 1.0 M electrolyte were observed, which might be attributable to the lower free lithium ion concentration and ohmic losses during charging.

Using identical cells, the charge-discharge behavior at room temperature was investigated with a galvanostatic protocol at C/5 in the voltage range of 1.0 to 2.5 V. In Figure 5.5, a flat voltage plateau at around 1.85 V was observed on discharge from all of the cells. The voltage difference between the charge and discharge plateaus was small (e.g., ~0.05 V), indicating that polarization losses were small within the cells at this rate.

In 1.0 M electrolyte (Fig. 5.5a), the charge and discharge capacities of the Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–Li$^+$ ionomer cell were 138 and 135 mAh·g$^{-1}$, respectively, differing by only about 2% showing high coulombic efficiency for the redox process. The Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–PVDF cell in the identical electrolyte also exhibited high coulombic efficiency with very similar charge and discharge capacities (137 and 134 mAh·g$^{-1}$, respectively).

In 0.1 M electrolyte (Fig. 5.5b), similar coulombic efficiencies and charge-discharge capacities from both cell types were obtained when compared with those observed in the 1.0 M electrolyte. From these results, it was concluded that the effect of the ionic functionality in the cathode binder in the Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–Li$^+$ ionomer cell was not very significant at this slow charge/discharge rate of C/5.
Figure 5.4 Initial voltage profiles for Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–Li$^+$ Ionomer full cells in comparison of Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–PVDF in (a) 1.0 M and (b) 0.1 M LiPF$_6$-EC/DEC at C/5-rate, with a top-off at 2.5 V. The cathode loading of LiFePO$_4$ was 2.4 - 2.5 mg·cm$^{-2}$ for each cathode.
Figure 5.5 Comparisons in coulombic efficiency between charging and discharging of full cells having different binders (e.g., Li⁺ ionomer and PVDF) in (a) 1.0 M and (b) 0.1 M LiPF₆-EC/DEC, respectively. Depicted are the 2nd charge and the 2nd discharge. Rate, C/5, Cutoff voltages, 1.0 to 2.5 V.
The results presented in Figures 5.4 and 5.5 were obtained with cathodes that were prepared using high carbon black (20 wt.%) and binder (20 wt.%) content. Even though such high carbon and binder loadings are inappropriate for real lithium ion batteries, those loading amounts were optimized for testing purpose, and the results proved that the cathodes having high carbon and binder contents exhibited the typical behavior expected of lithium ion batteries. These sample cathodes were therefore accepted as suitable cathodes to study the effect of ionomer binder on discharge rate capabilities at higher discharge rates.

Figure 5.6 compares discharge curves for cells with Li$^+$ ionomer and PVDF as the cathode binder at C/5, 1C, 3C, and 5C discharge rates. Prior to each discharge, the cells were slowly charged to 2.5 V at a rate of C/5. Cells with and without ionomer in the cathode presented generally similar characteristics in discharging at different C rates; that is, specific capacity gradually decreases with increase in C rate. Interestingly, the cells with ionomer binder show a smaller decrease in capacity at higher rates (i.e. rates above 3C) than cells with PVDF binder. For example, in 1.0 M electrolyte (Figure 5.6a), the discharge capacity of the cell with PVDF binder at 3C was 102 mAh·g$^{-1}$, approximately 76% of that at C/5, whereas the cell with the ionomer binder yielded a discharge capacity of 107 mAh·g$^{-1}$ at 3C, about 80% of that at C/5. Even at 5C, the capacity of the cell with ionomer binder still amounted to 87 mAh·g$^{-1}$, whereas 78 mAh·g$^{-1}$ was obtained from the cell with PVDF binder. This behavior corresponds to generally better performance at high rates for cells having ionomer binder relative to cells having PVDF binder.
Figure 5.6 Discharge curves of Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–Li$^+$ ionomer and Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–PVDF full cells at different C rates after a slow charge at C/5 in (a) 1.0 M and (b) 0.1M LiPF$_6$ electrolytes.
This behavior is much more pronounced when the salt concentration in the electrolyte is low (Fig. 5.6b). For the combination of high rate (5C) and low salt concentration (e.g., 0.1 M LiPF₆) the difference between ionomer binder and PVDF binder is particularly striking; for the ionomer-binder electrode the discharge capacity at 5C is 75 mAh·g⁻¹, whereas for the PVDF binder electrode the capacity is only 57 mAh·g⁻¹. These results indicate that the discharge capacity and rate capability of a battery electrode are enhanced by use of Li⁺ ionomer as the electrode binder and that the effect is particularly strong when the liquid electrolyte salt concentration is low. It is believed that because the ionomer can accommodate lithium ions, the loss of lithium ions in the electrolyte due to consumption via electrode reactions can be compensated. Poorer high-rate performance in cells with PVDF binder is consistent with their lack of ionic functionality which in turn allows for salt concentration polarization and/or salt depletion to occur more readily within electrodes during rapid discharging. The amount of lithium ions available for uptake by active materials is restricted at high discharge rates which limits battery performance.

Figure 5.7 presents the results for Li₄Ti₅O₁₂/C-LiFePO₄–Li⁺ ionomer and Li₄Ti₅O₁₂/C-LiFePO₄–PVDF cells in the form of a modified Peukert plot, which shows the discharge capacity as a function of discharge C rates on a log scale for 1.0 M and 0.1 M LiPF₆-EC/DEC electrolyte solutions. This plot includes all the data in Figure 5.6 and also data at rates of C/2, 2C, and 4C. The general features observed in Figure 5.7 are summarized as follows. First, discharge capacity always decreased with increasing discharge rate. Second, the discharge capacity of the Li₄Ti₅O₁₂/LiFePO₄–Li⁺ ionomer
cell was always larger than that of the counterpart cell with PVDF binder, with the difference being greatest at rates higher than 1C in identical salt concentration solutions. Third, the discharge capacity in 0.1 M electrolyte was always smaller than that in 1.0 M electrolyte, with the difference being greatest at the highest discharge rate. We note in particular that the discharge capacity of the Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–Li$^+$ ionomer cell at 5C rate in 0.1 M electrolyte was marginally similar to that of the Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–PVDF cell at the same rate in 1.0 M electrolyte. These observations suggest that the practical lithium ion concentration around active materials can be considered as one of the important factors affecting rate capability.

Figure 5.7 A modified Peukert plot for the Li$_4$Ti$_5$O$_{12}$/C-LiFePO$_4$–Li$^+$ ionomer and PVDF full cells. The data were collected by discharging at various rates after charging at C/5.
To support this observation, the practical amount (in moles) of lithium ions present in the electrode from the liquid electrolyte in the pores, and also from the binder, was calculated and is given in Table 5.2 for each electrode / electrolyte combination. The calculations were performed assuming that the amount of lithium ions depends on the pore volume to be filled with the liquid electrolyte (calculated from the electrode volumes and porosities in Table 5.1), the salt concentration in the liquid electrolyte, and the amount and ion exchange capacity of the binder. According to the calculation, when 1.0 M LiPF₆-EC/DEC electrolyte is used, the lithium ion content contributed by the liquid electrolyte in each composite electrode is approximately 1.2 x 10⁻⁶ moles (similar for both composite electrodes because they have similar pore volumes; see Table 5.1). The ionomer present in the ionomer-based composite electrodes contributes additional 7.3 x 10⁻⁷ moles of lithium ions, which is approximately 60 percent of the amount contributed by the liquid electrolyte. Meanwhile, it is assumed that PVDF binder does not have any capacity to hold lithium ions, such that lithium ions accessible to the active materials in the PVDF-based composite electrode are derived solely from the liquid electrolyte. We see from this calculation that, by incorporating the ionic binder into the electrode, the practical amount of lithium ions available to the active materials was increased by 60% compared to the case when the nonionic binder was used. When the 0.1 M LiPF₆-EC/DEC electrolyte is used, the effect of ionomer is even more pronounced, such that the ionomer contribution prevails over the liquid electrolyte contribution to the total lithium ion “budget” (see Table 5.2). The active material in the ionomer-composite electrode has access to approximately six times more lithium ions than in the PVDF-
composite electrode when using the electrolyte having the lower salt concentration. These calculations strongly support the electrochemical measurements in which it was shown that ionomer incorporation into electrodes enabled discharge to occur with minimal voltage loss at much higher rates than was possible without ionomer in the electrode.

Table 5.2 Calculated amounts (moles) of Li\(^+\) in composite electrodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>1.0 M LiPF(_6)-EC/DEC</th>
<th>0.1 M LiPF(_6)-EC/DEC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li(^+) content in liquid electrolyte (mol)(^a)</td>
<td>Li(^+) content in binder (mol)(^b)</td>
</tr>
<tr>
<td>PVDF-based composite</td>
<td>1.2 x 10(^{-6})</td>
<td>0</td>
</tr>
<tr>
<td>Ionomer-based composite</td>
<td>1.2 x 10(^{-6})</td>
<td>7.3 x 10(^{-7})</td>
</tr>
</tbody>
</table>

Li\(^+\) content in liquid electrolyte \(^a\) was calculated assuming the all the pores were filled with the liquid electrolyte, and Li\(^+\) content in binder \(^b\) was estimated assuming that EW of the ionomer is 850 g / eq. mol and PVDF does not have any capacity to hold free lithium ions.

At least one other significant aspect of the effect of ionomer binders warrants mention. Because the macroscopic anion mobility in the ionomer binder is zero, it is impossible for electrodes containing ionomer binder to ever become fully depleted of electrolyte. This situation is in contrast to that for electrodes with conventional, non-ionic binders. Anions in liquid electrolytes are mobile and can become expelled from electrode pores as lithium ions are consumed, for example by intercalation into lithium-deficient LiFePO\(_4\) particles during discharge. This process can fully deplete the electrode of all free salt, which in turn can limit further discharge by requiring more lithium salt to diffuse into the electrode from the bulk electrolyte solution for discharge to occur. This
type of salt depletion will not happen, at least not to full depletion, in electrodes containing ionomer binder for which the anions are immobile. When lithium cations associated with these immobile anions are consumed in electrode reactions, more lithium is forced to migrate into the electrode to maintain electroneutrality inside the electrode. These lithium ions are then available to support further discharge of electrode active components. The net effect would be to allow for discharge at higher rates with lower voltage losses than would be possible in electrodes without ionic binders. We note that it should be possible to address this effect more quantitatively via mathematical modeling of electron and ion transport rates in porous electroactive electrodes, considering the motions of lithium cations and both mobile and immobile anions. Such a study would be quite interesting though to be done properly it may require more detailed knowledge than is currently available on the nanoscale spatial distribution and ionic conductivity of lithiated ionomer in the electrode. Such a study is beyond the scope of the present work.

5.4 Conclusions

We have shown the effect of a lithiated perfluorosulfonate ionomer on the discharge rate capabilities when it is used as a cathode binder. To focus our investigation on ionic functionality in the battery cathode, a high binder content (20 wt.%) was employed in the preparation of cathodes for which possible limitations from electronic conduction were removed by also using a high carbon black content (20 wt.%). Our results have proved that the ionic functionality present in the cathode binder helps to enhance the rate capability of lithium ion batteries, particularly when using a relatively low salt concentration. The improved discharge rate capability of the ionomer composite cathode
is thought to be due to an increase in the amount of lithium ions available in the composite electrode, which can be increased by use of a lithium-containing ionomer binder. The presence of more lithium ions in ionomer-based cathodes improves lithium availability to active particles and prevents salt depletion in the electrode void space as a consequence of migration of mobile anions out of electrode void space, as would occur in non-ionomer-based cathodes. Our results suggest that fluorinated ionomers which can transport lithium ions fast from the bulk electrolyte to the surface of the active material and help prevent salt depletion inside electrode void spaces may be promising as cathode binders to further enhance the rate capability of lithium ion batteries, particularly in electrodes for which liquid electrolyte penetration is impaired.

5.5 References


CHAPTER 6
SUMMARY AND CONCLUSIONS

6.1 Electrospun carbon nanofibers as a Pt catalyst support

Carbon nanofibers were prepared for use as Pt electrocatalyst supports through stabilization and carbonization of electrospun acrylic fibers. Pt particles were successfully supported on the carbon fibers using a combination of EG and NaBH₄ as a reducing agent for the Pt precursor. It seemed that electrospun carbon nanofibers were adequate as Pt catalyst supports since nano-size Pt particles were able to be deposited on their surface. However, the electrochemical measurement showed that their performance in the electrode layer required large pore structure. To obtain a high Pt activity toward protons, protons must be accessible to large number of Pt nanoparticles on the supports. To do that, the electrode layer must possess mesopores through which protons can easily transport. It is difficult to create mesoporosity in the electrode layer while using microporous materials. Initially, the unwoven carbon nanofiber mat possessed substantially large pore structures (e.g., macropore and mesopore). However, after pulverizing, the pulverized carbon fibers had mainly microporous characteristics. Mesoporosity for the pulverized electrospun carbon fibers was found to be low. It is not a good approach to use the pulverized carbon nanofibers-supported Pt catalysts in preparation of the electrode layer. When they pack in the electrode layer, the randomly packed Pt/carbon nanofibers would form pores only by interconnection of the individual Pt/carbon fibers. In this randomly formed packing configuration, it would be very difficult to control porosity in the resulting electrode layer. Therefore, it seemed to be
appropriate to use carbon nanofibers in the form of mat as Pt supports in order to retain large pore structures.

6.2 Nanoscale ZrO$_2$-embedded mesoporous carbon composites

Mesoporous carbon nanocomposites containing zirconia nanoparticles were successfully prepared using colloidal SiO$_2$ as templates. The mesoporous structures were created by removing SiO$_2$ templates by NaOH, but not ZrO$_2$. Therefore, only ZrO$_2$ nanoparticles were embedded in the carbon phase after etching. This approach presented a facile route to introduce not only ZrO$_2$ but also mesoporous structure into the carbon matrix. Because the embedded ZrO$_2$ particles in the mesoporous carbon matrix are accessible for other molecules, this carbon nanocomposite can be further modified to have different surface properties by attaching desirable organic compounds with terminal phosphonic acid groups. Organophosphonates are able to anchor onto nanoscale ZrO$_2$ surfaces exposed at the composite surface. Therefore, any organic compounds having terminal phosphonic acid groups should be chemically attached onto the ZrO$_2$ surfaces. This approach provides a flexible way for fabricating novel electrode materials that need porous structure and specific surface properties because the pores and the surface properties can be tuned by applying various sized SiO$_2$ templates and different inorganic functional components, respectively. It is believed that the modified mesoporous carbon materials with various metal oxide nanoparticles and/or other organic functional groups can be used as a promising support for Pt catalysts.
6.3 Attachment of electrolyte onto a nanoscale zirconia-embedded mesoporous carbon composite

As an extension of the surface modification for the ZrO₂-carbon composite, the composite was modified with telechelic sulfonated PFCB ionomers having terminal PO₃H₂ groups. This is one simple method of producing the material that can possess mixed properties of electrical and ionic conductivities. This intimate integration would be necessary for high activity and long life in the PEM cell electrode. Through the chemical interactions between ZrO₂ and PO₃H₂ groups, the ionomer was able to anchor onto the ZrO₂ surface. As expected, the modification with the ionomer allowed for increased proton exchange capacity (IEC), compared with supports modified with sulfophenylphosphonic acid, because of the higher SO₃H group concentration possessed by the ionomer. Using the salt (e.g., Na₂SO₄)-added ionomer solution, the even higher IEC on the composite was achieved because the ionomer became compact in the presence of salt and therefore the more ionomer was able to penetrate mesopores and interact with ZrO₂ surface. The sulfonated ionomer was also able to be attached onto the platinized composite (e.g., Pt/ZCS) via the identical chemical interaction between ZrO₂ surfaces and PO₃H₂ groups. Pt particles were stable against the ionomer treatment and retained their crystalline structure and size during the treatment. By incorporating the sulfonated ionomer into Pt/ZCS catalysts, we obtained the carbon composite-supported Pt catalysts, which were outfitted with mesoporosity, electrical conductivity, and ionic conductivity. We expect that this particular Pt catalyst material will have a potentially significant technological impact for PEM fuel cell electrodes. Under an aqueous solution system,
the electrochemical catalytic enhancement was not observed on the ionomer-attached Pt/ZCS catalysts. Nevertheless, the catalytic improvement derived from the chemically attached ionomer onto the Pt support is still expected under a real operational condition of PEM fuel cells where no aqueous media assist the proton conduction because the ionomer may be able to extend the surface area of the three-phase reaction zone.

6.4 Incorporation of lithiated ionomer into a cathode electrode in lithium-ion batteries

In this study, a lithiated perfluorinated ionomer was incorporated as binder into the cathode layer. The use of a lithiated ionomer affected the discharge rate capabilities when it was used as a cathode binder. Our results proved that the ionic functionality present in the cathode binder helps to improve the rate capability of lithium ion batteries. This enhanced rate capability was pronounced when a relatively low salt concentration was used. The enhanced discharge rate capability of the ionomer composite cathode is believed to be due to an increased amount of lithium ions available in the composite electrode. The presence of extra lithium ions in ionomer-based cathodes helps active particles to be able to utilize more lithium ions and prevents salt depletion in the electrode void space. We note that, while the effect of ionomer binder was found to be relatively modest in the present work when salt concentration in the liquid electrolyte was high, it could be much more important in electrodes that have low porosity and/or for which liquid electrolyte penetration into the electrode void space was somehow restricted. Such may be the case in electrodes fabricated using nano-sized active materials at high loading densities, or in polymer or solid-state battery electrodes. The
present work provides valuable insight into how ionomer binders could contribute to improving high-rate performance in cells made using such electrodes.