CHARACTERIZATION OF CATALYST COATED MEMBRANES USING ELECTRON AND X-RAY MICROSCOPY

CHARACTERIZATION OF CATALYST COATED MEMBRANES USING ELECTRON AND X-RAY MICROSCOPY

Ву

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ABSTRACT

Proton-Exchange Membrane Fuel Cells are an alternative source of electricity generation for automobiles and stationary power plants. With increasing concerns on environmental issues, recent research has focused on maximizing the efficiency and durability as well as minimizing the costs of fuel cells. One of the main areas of research is optimizing the structure of the cathode catalyst layer. The main driving force of this thesis was the effective visualization of nanostructure of the ionomer, which is responsible for proton conduction in the cathode catalyst layer. However, challenges regarding sample preparation and radiation damage still need to be well understood. Different sample preparation techniques of catalyst inks and catalyst coated membranes were used for Scanning and Transmission Electron Microscopy, such as freeze fracturing, ultramicrotomy and Focused Ion Beam. Comparisons of the microstructure and chemical differences of all components, especially the ionomer, prepared by ultramicrotomy and Focused Ion Beam, was done with Transmission Electron Microscopy and Scanning Transmission X-ray Microscopy applied to the same catalyst coated membrane sample. Detailed spectroscopic information regarding components in both specimens was compared with C 1s and F 1s near edge X-ray absorption spectra recorded in a Scanning Transmission X-ray Microscope. Focused Ion Beam causes extensive damage to the carbon support and ionomer but prepares thinner sections than ultramicrotomy. This work makes it possible to understand the limitations of each sample preparation and compositional analysis technique in order to later apply one of them to image the ionomer in the catalyst layer at the nanoscale, hopefully using tomography techniques.

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LIST OF ABBREVIATIONS

- AFCC Automotive Fuel Cell Centre
- AFM- atomic force microscopy
- APM Atomic Probe Microscopy
- ART algebraic reconstruction technique
- BSE backscattered electrons
- CCEM Canadian Centre of Electron Microscopy
- CCM catalyst coated membrane
- CL catalyst layer
- ECSA electrochemical active surface area
- EDX Energy Dispersive X-ray Spectrometry
- EELS Electron Energy Loss Spectroscopy
- EFTEM Energy-Filtered Transmission Electron Microscopy
- FEG Field Emission Gun
- FIB Focused Ion Beam
- GIF Gatan Imaging Filter
- HAADF High Annular Angular Dark Field
- MEA membrane electrode assembly
- NEXAFS near edge X-ray absorption spectroscopy
- OD Optical density
- OD1 Optical density per nanometer
- **ORR Oxygen Reduction Reaction**
- PAAm polyacrylamide
- PEMFC Proton-Exchange Membrane Fuel Cell
- PET poly(ethylene terephthalate)
- PFSA perfluorosulfonated or perfluorosulfonic acid
- PS polystyrene
- PSS-PMB poly(styrene sulfonate)-block-poly(methyl butylene)
- PTFE Polytetrafluoroethylene
- SE secondary electrons
- SEM Scanning Electron Microscopy
- SIRT simultaneous iterative reconstruction technique
- STEM- Scanning Transmission Electron Microscopy
- STXM Scanning Transmission X-Ray Microscopy

TEM - Transmission Electron Microscopy

WBP - weighted back projection

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1 Introduction

Fuel cells have gained a lot of attention due to the promise of converting chemical energy into electricity with higher efficiency than fossil fuels and, in general, with water as the only product. In the commercial market since the 1990s, several types of fuel cells have been developed and share a common structure: an electrolyte membrane sandwiched between two electrodes. The electrolyte of the Polymer Electrolyte Membrane or Proton-Exchange Membrane Fuel Cell (PEMFC) consists of a thin film of perfluorosulfonated acid (PFSA) polymer, an ionomer generally with the trade name of Nafion®, that conducts protons from the anode to the cathode. As shown in Figure 1.1, the anode is fed with hydrogen gas that oxidizes into 2 electrons and 2 protons (H^{+}) while the cathode is fed with oxygen gas or air which reduces according to the Oxygen Reduction Reaction (ORR). The electrodes are composed of a gas diffusion layer and a catalyst layer. The catalyst layer, made up of an electrically conductive porous carbon support framework with Pt/alloy nanoparticles and a proton conductive ionomer phase, shares an interface with the membrane. This structure results in two main types of PEMFC samples, membrane electrode assembly (MEA) and catalyst coated membrane (CCM). The difference is the fabrication method and presence of the gas diffusion layers in the MEA, which are absent in the CCM samples. The porosity of the carbon support enables the gas transport through the gas diffusion layer to the membrane interface and water flow away from the reaction sites to avoid flooding of the fuel cell. Electrons flow through the electrodes, current collectors and the outside circuit until the other electrode is reached, with a net result of direct electrical current (Barbir 2005).

The rate limiting reaction to the performance of a PEMFC is the ORR. This reaction occurs in the complex structure of the cathode catalyst layer, in a triple-phase boundary between two electron conductive phases (carbon support and Pt/Pt alloy nanoparticles), a proton conductor phase (PFSA ionomer) and gaseous phases available through a nano to microscale porous structure of the carbon support. Basically, protons and electrons meet O_2 at this interface with

water and electricity being produced (Barbir 2005). Therefore, this electrochemical reaction depends on the structure of these materials and the relationship between each material and consequently on the transport properties of the different components. One of the main challenges in this field is to clearly understand what influences the transport of the reactants to the catalytic reaction sites as well as the removal of water from the pores. It is believed that optimization of the structure of these transport media can help maximize fuel cell performance and durability.



Figure 1.1 Schematic of the Proton-exchange membrane fuel cell (PEMFC) (Barbir 2005). See text for explanation.

Therefore, different microscopy techniques are needed to explore the structural relationship of the catalyst layer components. The objective of this thesis is to explore different sample preparation and electron and x-ray microscopy techniques, in order to identify their strengths and limitations with respect to visualizing and quantitatively mapping the PFSA ionomer component in the cathode catalyst layer. The interest in the effective visualization of this component is that a consolidated structural-property relationship can optimize the performance of the fuel cell. However, issues such as choosing appropriate sample preparation method and overcoming radiation damage of the electron/photon beam becomes essential for the successful visualization of this component and are treated in subsequent sections.

2 Literature Review

2.1 Structure, properties and performance of PEMFC

Effective modeling of the transport properties of the electrodes rely on accurate microstructural characterization of the catalyst layer (Kim & Pitsch 2009), which can then be used with suitable modeling approaches to predict and optimize the performance of the fuel cell (Ziegler et al. 2011). There is no technique currently available that enables the simultaneous visualization of all components in the catalyst layer (Scheiba et al. 2008; Bessarabov & Hitchcock 2009), specially the nanoscale morphology of the ionomer (Yakovlev & Downing 2012). Thus, modeling has played an important role in the understanding of the major transport processes and electrochemistry occurring in the cathode catalyst layer (Kim & Pitsch 2009; Lange et al. 2010; Thiele et al. 2013) and in improving the design of the cell stack, flow fields, and thus the performance of fuel cells. The 3-D structure of this layer - porosity, distribution of pore size, catalyst particle size, ionomer and catalyst loading and distributions, and accessibility of protons and O_2 to the reaction site – is correlated to the performance of the fuel cell and thus all of these aspects are crucial areas of research (Thiele et al. 2013; Ziegler et al. 2011).

Simulations to effectively predict the transport properties of the catalyst layer are currently limited by information on the structure of the ionomer (Kim & Pitsch 2009). Parameters such as pore size distribution, size of the primary carbon support particles and the volume fraction of each phase in the catalyst layer have been successfully determined from simulations of the transport properties of the electrode (Kim & Pitsch 2009). However, the structure of the ionomer, membrane swelling and liquid water were not considered in these calculations. In simulations of a reconstructured nanoscale catalyst layer with the objective of studying transportation processes and electrochemical reactions, it was seen that the effective oxygen diffusivity and proton conductivity is increased if larger carbon support particles are used (Lange et al. 2010). Nonetheless, the effects of the humidification of the membrane, which

depend on the volume fraction and thickness of the electrolyte phase, the presence of liquid water in the electrodes, which affect the transportation of the reactants to the reactive sites, and the ionomer structure are still not well modeled (Kim & Pitsch 2009).

Optimizing the nanostructure of the catalyst layer such that the conduction paths are not blocked can be directly related to a high performance of the fuel cell. A high Pt utilization can be achieved with an homogenous distribution of all the components in the catalyst layer, specially the dispersion of the Pt nanoparticles (Wang et al. 2010), which depend on the type of carbon support and ionomer content. For example, a highly graphitic carbon support deters carbon corrosion but the Pt nanoparticles are not homogenously distributed over the surface (Wang et al. 2010).

With Transmission Electron Microscopy (TEM) analysis, Nafion® loading was seen to influence the porosity of the catalyst layers (Sun et al. 2010) and the ratio of the ionomer and carbon content yielded different performances of the CCM (Suzuki et al. 2010). The highest performance was achieved with a Nafion® to carbon black weight content ratio of 1.0, where sufficient transport paths were available for the electrochemical reaction to occur. Xie *et.al.* (Xie et al. 2010) studied catalyst layers with different Nafion® loadings and observed a performance and structural relationship within the samples. An optimal amount of Nafion® in the catalyst layer yielded a highly dispersed carbon-support phase with the highest electrochemical performance. In a computational simulation of a catalyst layer, a more uniform Nafion® film surrounding the catalyst particles resulted in a higher utilization of the precious Pt nanoparticles (Hattori et al. 2008).

As seen in the examples above, the perfluorosulfonic acid (PFSA) ionomer plays an important role in the catalyst layer. It is not only responsible for proton conductivity, but it also influences the electrochemical active surface area (ECSA), mass transport, the electronic resistance, porosity of the carbon support and acts as a binding agent of the different components in the catalyst layer. The membrane of the PEMFC is chemically similar to the PFSA ionomer. Both consist of copolymers with a hydrophobic tetrafluoroethylene (or

polytetrafluoroethylene, PTFE) backbone with good mechanical properties and hydrophilic ionic side chains responsible for the proton conduction. The membrane and PFSA ionomer are sensitive to water and swell when exposed to aqueous solutions (Yakovlev & Downing 2012). The structure of the PFSA ionomer in the catalyst layer depends on the preparation and formulation of the catalyst ink as well as the solvents used. Optimizing this structure is critical to improving the performance of the fuel cell and can also help minimize costs by maximizing the fraction of the Pt catalyst that can be accessed by protons and O₂, thereby allowing Pt content to be minimized (Ngo, Yu & H.-L. Lin 2013; Ngo, Yu & H. Lin 2013; Therdthianwong et al. 2010). The main PFSA ionomer used in PEMFC is Nafion[®] and is available with varying size of the side chains, molecular weight and chain termination. Paul et al. (2011) suggested that there may be a difference between proton conductivity of bulk PFSA membrane and PFSA ionomer present in the catalyst layer, due to the nanostructural nature of the latter. To date, it is unknown exactly how the nanoscale morphology of the PFSA ionomer is related to proton and O₂ transport (Yakovlev & Downing 2012). This implies that there is a strong need to visualize and quantitatively map the nanostructure of the PFSA ionomer in the cathode catalyst layer.

2.2 Measuring the performance of the fuel cell

One of the key parameters of the performance of a fuel cell is related to the available surface area of the Pt nanoparticles for the reaction to occur. Unfortunately, if the structure of the catalyst layer is not optimized, meaning that the available Pt surface area is not in contact with the other phases (gas and protons), then this measured surface area has no value (Saha et al. 2011). Therefore, the area measured with cyclic voltammetry of the MEA ($A_{Pt,MEA}$) can be smaller than the surface area of the catalyst ($A_{Pt,cat}$). The ratio of both areas is defined as the MEA catalyst utilization, u_{Pt} , and is the maximum accessible fraction of the total catalyst area (Saha et al. 2011). $A_{Pt,MEA}$ is measured in the presence of a membrane (solid electrolyte) and $A_{Pt,cat}$ is measured with the catalyst immersed in a liquid electrolyte (Saha et al. 2011). The most used evaluation criteria for a new CCM is to consider the polarization behavior in a single-cell with H_2 /air atmosphere, yielding the overall electrochemical fuel cell performance (Saha et al. 2011). However, the peak power density can be related to the amount of Pt used, and is an important performance value that is linked to costs of the fuel cell.

2.3 Degradation effects on the durability of PEMFCs

Another main challenge PEMFC face for commercialization in stationary and transportation applications is durability (Xie et al. 2005; Liu et al. 2010; Wang et al. 2010; Artyushkova et al. 2012). As electrochemical reactions occur generating electricity, the different components present in the MEA suffer structural and chemical transformations, being responsible for the degradation of the fuel cell. The cathode catalyst layer must withstand a strong oxidizing environment in the presence of water and high humidity during operation of the PEMFC. Gradual morphological change due to the degradation processes occurs (Xie et al. 2005) that is not necessarily uniform across the MEA, specially under load cycling conditions (Guetaz et al. 2012).

The most commonly used carbon support is carbon black, usually a high surface area material, which provides the structural framework of the electrode and porosity for mass transportation and electrical conductivity. A consequence of the electrochemical reaction is a change in the size of the carbon particles and Pt dispersion, which results in a loss of surface area as well as a decrease in porosity (Liu et al. 2010; Wang et al. 2010). The corrosion rate of the carbon support particles strongly depends on the morphology and structure of the aggregates in thermal and electrochemical conditions (Liu et al. 2010), which determine if the corrosion starts from the surface or bulk of the particle (Wang et al. 2010). Graphitic carbon is known to be more resistant to carbon corrosion than amorphous carbon due to lower amounts of defect sites, location of oxidation initiation (Vinod Selvaganesh et al. 2011; Artyushkova et al. 2012). However, the Pt nanoparticles are not homogenously distributed on its surface, as they tend to bond to defect sites.

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Numerous research activities on the different degradation mechanisms were explored and microscopic techniques have been widely used to visualize morphological and chemical transformations (Xie et al. 2005; Guetaz et al. 2012). In a particular study, Xie *et.al.* (2005) submitted several identical MEAs to harsh environments (1000 hours of constant current testing) and found that there is a loss of 30% of the electrochemical active surface area due to morphological changes in the cathode: Pt alloy individual particles grew in size and agglomerated, generating more densely packed Pt particle clusters. The anode had both Pt and Pt alloy nanoparticles and it was found that the smaller Pt nanoparticles migrated more easily to the membrane than the larger Pt alloy nanoparticles during performance testing, possibly due to a stronger bond between the Pt alloy nanoparticles and carbon support particle (Xie et al. 2005).

2.4 Microscopy and its limitations

Over the last few decades, the Transmission Electron Microscope (TEM) has become a routine analysis technique with numerous applications in metallurgy, semiconductors, structural biology, catalysis, and many other fields. Recent hardware innovations have led to the acquirement of true atomic lattice images and atomic compositional mappings (Batson et al. 2002; Krivanek et al. 2010). TEM is therefore an essential tool to visualize the morphology and to assess chemical transformations occurring inside the electrochemical cell at the nano and atomic-scale, as well as to visualize the geometry and distribution of the different components within the electrodes and membrane. Although there have been many TEM studies of CCM samples, there is limited work in visualizing the PFSA ionomer in the cathode catalyst layer (Schulenburg et al. 2012). This limitation is mostly due to the radiation damage this material suffers under an electron beam (Rieberer & Norian 1992) and X-ray beam (Almeida & Kawano 1998), the low contrast and the limited sampling known to TEM, which is not a bulk technique but site-specific (Yakovlev & Downing 2012). Therefore, the challenges to overcome include (1) contrast enhancement for TEM images and (2) radiation damage induced by electron beam (Yakovlev & Downing 2012).

The main strategy used nowadays to overcome the radiation damage is limiting the dose. The challenge is that the images become a lot noisier, and this is the opposite of ideal condition for analytical measurements. Radiation damage is not limited to the PFSA ionomer, but also occurs to the carbon nanostructure of graphite in the form of knock-on displacement of the carbon atoms (Banhart 1999), present in the carbon black (carbon support).

Xie et al. (2004) published images of the cathode catalyst layer and assumed that the PFSA ionomer surrounds the carbon support particles. However, this conclusion was not supported by elemental analysis demonstrating the presence of fluorine. In addition, the sample was prepared with ultramicrotomy using an epoxy to infiltrate the porous structure, making it possible that what is assumed to be PFSA ionomer is actually epoxy, due to their similar contrast in TEM images.

Since PFSA ionomer is made up of mobile side chains with sulfonate or sulfonic acid end groups in a crystalline Teflon-like backbone, the approach to increase contrast is to stain the polymer with heavy metal ions which will react with the ionic side chains (Yakovlev & Downing 2012; Xue et al. 1989). Ag⁺ ion-exchange has been applied to visualize the PFSA ionomer in the Pt/C-support catalyst particles (Uchida et al. 2006; Song et al. 2006). The low magnification TEM images make it difficult to actually visualize the enhanced contrast due to Ag⁺ ions. Although the authors compare the catalyst layer preparation method and use the staining to visualize the PFSA ionomer distribution, it is questionable whether the new contrast is due to the ionomer. Without spectroscopic analysis, the clusters seen could just be due to inhomogenous Pt distributions.

The challenge of using staining techniques is finding the ideal metal salt to ion-exchange with the sulfonic groups of the PFSA ionomer without causing additional artefacts. While this may enhance the contrast in TEM images, it is possible that the observed morphology of the ionomer depends on the heavy ions being used (Yakovlev & Downing 2012). Nafion® membranes stained with

RuO₄ for different time lengths had different morphologies: for 20 and 60 mins staining contrast was not sufficient, but for 40 mins, the 3-phase model believed to be present in Nafion® was distinguished (ionic clusters, interfacial and organic matrix phase) (Xue et al. 1989). The staining process also requires the immersion of the sample into a solution, which can cause swelling of the membrane of the CCM sample and result in "inhomogenous drying and redistribution of the staining agent" as demonstrated by (Scheiba et al. 2008).

An alternative to staining is to use elemental analysis such as Energy Dispersive X-ray Spectrometry (EDX) and Energy-Filtered TEM (EFTEM), which are less prone to artifacts (Scheiba et al. 2008). EDX mapping is usually not reliable due to the low fluorescence yield for elements with low atomic number, inefficient detectors and thus, long acquisition times are required. EFTEM is an alternative technique that uses lower acquisitions times. However, nearly 2.5% fluorine loss per minute was calculated in an EFTEM analysis, and the images published do not show nanoscale ionomer distribution (Scheiba et al. 2008). Also, these techniques essentially change the structural arrangement of the PFSA ionomer (staining) or are susceptible to radiation damage (elemental composition) (Scheiba et al. 2008). In addition, EDX and basic EFTEM methods only provide elemental composition and do not give insight into the chemical structure.

Scanning Transmission X-Ray Microscopy (STXM) is an alternative microscopy technique that has been successfully applied to visualize the PFSA ionomer in CCM by spectroscopically mapping and differentiating it from other carbon components, such as carbon support and embedding epoxy, through the C 1s and F 1s NEXAFS signals (Susac et al. 2011). The advantage of using STXM to access the chemical structure of the catalyst layer and changes to its components caused by ion and electron radiation damage is the relatively lower radiation damage caused by X-ray photons in comparison to electrons when using Electron Energy Loss Spectroscopy (EELS), a complementary technique that is widely available in the TEM. It has been shown that there is a ~500 fold advantage in using soft x-rays in a STXM at room temperature to assess fine structural information on a soft material [poly(ethylene terephthalate) (PET)] if

compared to EELS-STEM in cryo-conditions (used a 500 nm probe size STXM) (Rightor et al. 1997; Wang et al. 2009). In X-ray absorption, each absorbed X-ray provides analytically useful spectral information, whereas deposition of the equivalent energy through inelastic electron scattering results in a very large number of valence ionization events, which break bonds but do not provide the analytically useful core loss information (Hitchcock et al. 2008). However, the critical dose for chemical change in PET using a 30 nm STXM probe beam, which achieves sufficient spatial resolution, is the same with EELS, which results in bond breaking that is tracked by spectral features (Hitchcock et al. 2008; Wang et al. 2009). For the same absorbed dose, mass loss caused in PET is larger when induced by an electron beam in vacuum rather than by a x-ray beam in He environment (Wang et al. 2009). This means that if STXM is to be used routinely to assess the PFSA ionomer distribution in a catalyst layer, it is essential that the radiation damage caused is better understood.

Another serious limitation these microscopy techniques impose in the visualization of structure of materials is sample preparation artefacts. In order to understand the structural information given by microscopy, it is of crucial importance to be aware of different artefacts imposed on the sample during its preparation, as well as from damage suffered during the analysis. Since the material suffers radiation damage, to be able to <u>distinguish</u> morphological and chemical features intrinsic to the sample from radiation damage inflicted on the sample in either sample preparation or analytical microscopy, it is necessary to understand the mechanism of the radiation damage.

2.5 Sample preparation for TEM/STXM

The samples analyzed by the TEM and STXM have to be thin enough to transmit electrons; consequently, the third dimension (Z axis) is usually considered constant throughout the sample allowing for correct interpretation of 2D projection images. Microtomy techniques have been successfully used to prepare uniformly thin sections of CCMs (Blom et al. 2003). However, parts of the sample can be dragged over the section, therefore smeared, during slicing

(Kuroda & Yamazaki 2007) and structural alterations due to mechanical stresses can occur (Bassim et al. 2012) leading to deformations in the morphology and phase transformation of the PFSA ionomer (Yakovlev & Downing 2012). Combining hard materials (such as the carbon support/Pt particles) with a soft material (in this case, the PFSA ionomer) may result in cutting artefacts at the interface between these two components (Michler 2008b). The pressure that is built up at the tip of the knife can reach 200 MPa and possibly deform the morphology of the material due to friction between the polymer chains and induce phase transformation of the PFSA ionomer (Yakovlev & Downing 2012). This is not a problem for TEM projection images, but to correctly visualize the 3-D interface, it can lead to misinterpretations of the images. Another disadvantage is the need to embed the material, as the contrast of all carbon containing materials becomes similar. Finding the ideal embedding material is not trivial either (Blom et al. 2003; More & Reeves 2005). A partial penetration of the cathode by the embedding material is ideal. Although partial penetration of the cathode has been attempted with different embedding materials (More & Reeves 2005), the penetration probably depends on the porosity of the sample and it is not always reproducible.

The partial penetration of the embedding material can lead to erroneous interpretation of the microstructure with TEM. While TEM bright-field images indicate that the alternative embedding material (Polystyrene or PS) has not fully penetrated in the catalyst layer (**Figure 2.1a**), spectroscopic STXM composite maps indicate otherwise (**Figure 2.1b**). Since the contrast seen with TEM bright-field images is solely due to mass and thickness differences, the 'holes' seen in **Figure 2.1** could also be interpreted as a non-uniform section from the microtome sample or could be clean areas of the cathode material. On the other hand, with spectroscopic contrast, STXM C 1s edge stacks distinguishes C-containing materials that have different fine structures and maps the different components (**Figure 2.1b**). In the composite map shown in **Figure 2.1b**, PS (in red) penetrated through the catalyst layer; regions in black are holes and could be due to imperfect cut with the microtome knife.



Figure 2.1 Microscopy images of cathode catalyst layer in a CCM sample prepared by microtomy (a) TEM bright-field image indicates that embedding material has not fully penetrated into the cathode due to presence of 'holes' (indicated in circles). (b) STXM composite maps of the different carbon containing materials show that there are indeed holes in the section (seen as black) and PS (in red) penetrated all the way through the carbon support (in blue) and into the membrane (in green).

Another technique used to prepare thin specimens for TEM analysis is Focused Ion Beam (FIB), which is also a microscopic technique (Scanning Ion Microscopy). Specific areas of organic, inorganic (minerals and ceramics), metals, composites, biological materials and even frozen liquids samples have been prepared for TEM analysis with an accuracy of 20 nm (Mayer et al. 2007). More recently, geometry-specific samples for Atom Probe Tomography and 360° degrees electron tomography was also achieved. If catalyst pillars from CCMs could be successfully prepared without beam damage and bending, our understanding on the carbon corrosion could be improved and it could be extremely useful for simulations on mass transport (Schulenburg et al. 2012).

Most FIB systems nowadays also have an electron beam, which facilitates the visualization of the sample preparation. These systems are also used for tomography studies, where the ion beam sputters the sample every 10 nm while the electron beam takes images. Reconstruction of the 3-D volume can be achieved with the combination of these images, resulting in 3-D structural information down to a 10 nm scale (Möbus & Inkson 2007). Pore size distribution and connectivity of the carbon support can be achieved with this technique (Ziegler et al. 2011) and can be related to the performance: a

homogenous pore structure and Pt distribution yielded high performance of the PEMFC (Zils et al. 2010). In a degradation study, morphological changes of the 3-D pore structure of pristine and cycled catalyst coated membrane samples were compared using FIB-SEM (Scanning Electron Microscopy). The severe loss of performance was attributed to the collapse of the catalyst support pore structure (porosity decreased from 40% to 5% with a decrease in average pore size) and the interconnected pore structure of the pristine samples was transformed into isolated pores in the cycled sample (start/stop cycling) (Schulenburg et al. 2011). This is valuable information that can improve modeling of the mass transport in the electrodes (Schulenburg et al. 2012). The porosity of carbon support is paramount for the transport of both gases (H2 in the anode and O2 in the cathode) and water out of the cathode. Although gas adsorption and porosimetry techniques yield information about the pore size distribution and volume of pores of a catalyst layer, it does not provide details about the position of the pores or pore elongation, which is only available through tomography methods such as FIB-SEM. Three-dimensional imaging is achieved through other tomography techniques, such as Scanning X-ray Microscopy (STXM) (Berejnov et al. 2013) and Atomic Probe Microscopy (APM). Nonetheless, each of these techniques have their own drawback, such as limited resolution (FIB/SEM and STXM) or sample restrictions (APM).

There is limited resolution of FIB-SEM in the Z direction of 10 nm due to the ion beam diameter while the resolution is 1 nm in the X and Y direction due to the beam diameter of the electron beam in state of the art Field Emission Gun (FEG)-SEM (Möbus & Inkson 2007). This implies limitations to distinguish the carbon support, PFSA ionomer and the smaller Pt nanoparticles. TEM Tomography, or simply electron tomography, has nanoscale resolution and a diversity of imaging modes that can be applied in the analysis of beam-sensitive (commonly found in biology or polymers) to crystalline materials (Midgley & Dunin-Borkowski 2009). The combination of both tomographic techniques was done in a scale-up approach of CCM samples without, however, assessing the PFSA ionomer structural information (Thiele et al. 2013). Another issue is the limited applicability of FIB to polymers due to radiation damage (Michler 2008b). Nonetheless, FIB has been applied to patterning of different polymeric systems that suffer cross-linking or chain scission damage (Orthacker et al. 2014). Specific technical details such as changing the way the beam is scanned (Orthacker et al. 2014) or beam features such as overlapping (Bassim et al. 2012) can reduce damage on polymeric samples.

2.6 Electron tomography

The mathematical principles for tomography reconstruction were developed decades before it found one of its most well known applications in the 1960s: Computerized Automatic Tomography Scan (CAT-scan) used for medical imaging. Around the same time, tomography was also being applied to the TEM in structural biology and later became a routine technique among biologists. Nowadays tomography comprises a vast subject area with diverse applications also in the physical sciences and makes use of many different detected signals such as x-rays, electrons, positrons, ultrasound and nuclear magnetic resonance (Midgley & Weyland 2003). Furthermore, the basic mathematical theory behind it is the same for any signal used: from a 3-D object, a series of 2-D images is generated from which the volume must be reconstructed to allow the visualization of the original 3-D object of interest.

In electron tomography, the reconstruction problem is to determine the 3-D structure object that generated the 2-D projection images acquired over a large range of tilt angles. Therefore, it is important to take into account all aspects of the sample interaction with the electron beam, including radiation damage. This means that the accelerating voltage, beam current, camera length of the detector and electron source of the microscope must be considered before acquiring the tilt series along with the correct imaging mode. The projection requirement must be satisfied, which depends on the thickness of the sample and the nature and position of the atoms. After determining which parameters will be used, the acquired tilt series must then be aligned and reconstructed with the selected algorithm (Carazo et al. 2006).

There are diverse imaging modes available in the TEM/STEM, but for tomography the sample must satisfy 'the projection requirement' as defined by Hawkes (2005) as: "the 'projection' need not necessarily be a (weighted) sum or integral through the structure of some physical property of the latter; in principle, a monotonically varying function would be acceptable". For amorphous samples, the contrast or intensity seen in images is due solely to differences in mass and/or thickness, satisfying the projection requirement. However, diffraction contrast will play an important role in the images of crystalline samples as the intensity of the projection image will depend on the orientation of the sample (Midgley & Weyland 2003). To satisfy the projection requirement and overcome the diffraction contrast, the use of incoherent signals such as High Annular Angular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) and EFTEM have been successfully applied to determine the 3-D structure of crystalline materials such as catalysts, semiconductors, glassceramic composites, and nanocomposites. These techniques were also used to visualize the faceting and morphology of crystals and the distribution of precipitates and dislocations in steels or alloys (Koguchi et al. 2001; Midgley et al. 2001; Midgley & Weyland 2003; Midgley & Dunin-Borkowski 2009; Möbus & Inkson 2007; Möbus et al. 2003). These imaging signals have also been complemented with 3-D elemental composition maps/linescans using EDX and information on electromagnetic properties using holography (Koguchi et al. 2001; Möbus et al. 2003; Midgley & Dunin-Borkowski 2009; Lepinay et al. 2013; Saghi et al. 2007). It has also been shown that beam-sensitive materials can withstand prolonged acquisition times without suffering beam-induced damage with HAADF-STEM tomography due to the dissipation of energy in areas not illuminated (Midgley et al. 2001).

Therefore, electron tomography can help correlate structural information with the performance of the fuel cell, such as where and how the Pt particles bond with the carbon support and possibly the 3-D distribution of the PFSA ionomer in the catalyst layer. The information gathered by FIB-SEM and TEM tomography was used as the first step necessary to model the reaction transport properties to create 'a microstructural model of the Pt catalyst particles

embedded in a porous matrix' (Thiele et al. 2013). The main advantage of using 3-D imaging in these systems is that determining the connectivity of the different components is possible and the statistics is improved, for each 3-D image is made up of approximately 100 projection images (Schulenburg et al. 2010).

Schulenburg et al. (2011) used electron tomography to understand why performance degradation after start/stop cycling was not severe considering: 1) large decrease in porosity of the carbon support seen with FIB tomography and 2) Pt particle size distribution doubled compared to pristine CCM. Since FIB tomography is not able to resolve pores smaller than 20 nm, electron tomography showed that the carbon support used in this study was highly porous, as Pt particles were seen inside these structures. The degraded sample after start/stop operating cycles showed isolated pores between 5-20 nm, indicating that the larger Pt particles were isolated from the gas supply.

The position of the Pt nanoparticles on the carbon support can be inferred with electron tomography (Ito et al. 2011), and can be related to the performance of the fuel cell (Banham et al. 2011). Pt loaded-carbon support with high surface area had higher activity compared to the lowest surface area carbon support due to the smaller and more uniform Pt particle size distribution (Banham et al. 2011). The carbon support with highest activity at all potentials was the colloid-imprinted, in comparison to Vulcan[™] and ordered mesoporous carbon, due to the larger, thicker and more crystalline walls of the support. Electron tomography permitted the determination of the localization of the Pt nanoparticles on the carbon support. It was shown that in mesoporous structures smaller Pt nanoparticles were deposited inside the pores of the carbon support, whereas in microporous Vulcan[™] carbon the Pt nanoparticles were larger and were deposited on the outside surface (Banham et al. 2011).

Precise tomographic reconstruction of Pt nanoparticles is only achieved with HAADF-STEM, as diffraction contrast plays a strong role in Annular Dark Field and Bright Field images. HAADF-STEM tomography was used to determine the shapes, orientation and faceting of Pt and PtCr catalyst nanoparticles and their position relative to the carbon support (Gontard et al. 2008). In order to resolve details of the weakly scattering carbon support the

camera length of the detector was increased to a suitable value, such that the diffraction contrast of the Pt particles was not dominant. Together with High Resolution TEM (HRTEM), tomography helped establish the nature and role of the surfaces of the Pt nanoparticles which can be used to quantity the fraction of catalyst particles available for reaction (Gontard et al. 2008).

Indeed, the selected sample preparation method affects the kind of information obtained. In a particular study, catalyst powders with and without Pt were analyzed and the surface of the Pt nanoparticles available for the interfacial formation with PFSA ionomer or gases was determined for different carbon supports (Jankovic et al. 2013). However, it is possible that the physical properties determined in this study could have changed after the catalyst powder was hot-pressed onto the membrane and tested electrochemically.

2.7 Damage of polymers by radiation/ion beams

The ability of the FIB to mill, image and deposit material makes it highly sensitive to the nature of the ion-beam interaction and consequently the damage done on the sample (Giannuzzi et al. 2005). The sputtering of atoms occurs when enough kinetic energy is transferred from the ions to the target atoms to overcome the surface binding energy (Giannuzzi et al. 2005). As the material is sputtered by the gallium ion beam, the surface of the sample is modified. This may result in complete amorphization in semi-conductor materials to formation of defects or intermetallic phases for certain metals (Mayer et al. 2007). Effects such as swelling, sample redeposition, ion implantation and defect generation were demonstrated in Si single crystal samples (Lehrer et al. 2000). On the other hand, heating damage, sample redeposition and the so called "curtain" effect have been seen in polymer composites (Olea-Mejía et al. 2012). Since the different nature of materials imply different interaction with ion beams, it is imperative to understand the interaction of the components of the cathode catalyst layer with the ion beam and to minimize the damage if FIB is to be considered a non-invasive technique in this field of research.

Radiation damage has been a concern for soft materials for decades. For these materials, FIB has the potential to cause even greater chemical and physical transformation of the sample, such as heating, knock-on damage and radiolysis (Bassim et al. 2012). Structural changes such as chain scission, cross linking, chain shrinkage can cause transformation in the surface and crystallinity of polymers. Structural transformations of polymeric samples have been analyzed using STXM C 1s edge and the utilization of the electron beam from the imaging process was found to be the major cause of damage (Bassim et al. 2012). FIB final polishing at lower kV minimized the damage, but STXM C edge spectra still showed some modifications when compared to a microtome prepared section. Cryo-FIB was used in the final polishing for refractory lignite coal (aromatic bonds) and it was found to cause less structural chemical changes when used at 2 and 5 kV (Bassim et al. 2012).

In another study, FIB damage in polycarbonate was assessed by phase contrast atomic force microscopy (AFM) (Bailey et al. 2013). The higher ion beam energy (above 25 kV) caused scission of the main polymeric chain, reducing the molecular weight and the elastic modulus of the polymer. Cross-linking of the chains occurred with a 10 keV ion beam energy, which promoted surface stiffening possibly due to embedding of Ga ions. Therefore, smooth surfaces comparable to bulk material were seen at ion energies between 15 and 25 keV. Simulation results indicated that the higher energy Ga ions penetrated deeply into the surface leaving less ions in the surface, opposed to lower ion beam energies that penetrated less deeply, which the authors argue could result in high concentration at the surface. The authors claim that the sputter yield for polycarbonate at low energies is such that the Ga ions do not have enough energy to displace atoms and therefore are embedded within the sample.

These studies show that FIB damage can be assessed with different techniques and the extension of damage depends on the structure of the polymer. With such a complex structure, it can be challenging to predict the damage to the different cathode components in the fuel cell, especially considering the porosity. Due to the porous nature of the carbon support in the

cathode catalyst layer, simulating the penetration of Ga is a challenge. This also means that the damage to the different components is not as straightforward as if the analysis was done on the pure, non-porous, isolated materials.

The interaction of the sample with the ion beam can result in heating. This is due to the absorption of kinetic energy transferred from ions to atoms of the sample and depends on the beam current, voltage and thermal conductivity of the sample. Furthermore, a small portion of that kinetic energy is responsible for breaking the bonds and milling the sample (Bassim et al. 2012; Olea-Mejía et al. 2012). Therefore, for thermally conductive materials heating is usually not an issue. However, since soft materials have low thermal conductivities, this makes them more sensitive to temperature increases and leads to softening and reduction of rigidity during the final polishing steps (Bassim et al. 2012). PFSA ionomer membranes have a low thermal conductivity (Vie & Kjelstrup 2004) which decreases with thickness and increases up to 40% with its hydration or water content (Burheim et al. 2010). Measured thermal conductivities of a single PEMFC also indicated a low thermal conductivity (Burheim et al. 2010), if compared to silicon. Therefore, it is reasonable to expect damage to the different components in a catalyst layer during FIB processing, as it is not thermally conductive if compared with semiconductors or metals.

FIB milling damage in fuel cell samples has been assessed with SEM by other groups. However, the use of SEM only allowed to see surface differences, and structural alterations have not been acknowledged to date. The membrane material was seen to deteriorate with the FIB milling during a FIB-SEM serial tomography study (Ziegler et al. 2011). Thermal damage caused by using a 30 kV FIB milling in a MEA sample has been observed at different temperatures (Kuroda & Yamazaki 2007). The surface of the carbon support and the membrane of a MEA section FIB milled at cryogenic conditions was better preserved than the section milled at room temperature (Kuroda & Yamazaki 2007). This is probably due to reduced local sample heating induced by operating the FIB in cryogenic conditions (Bassim et al. 2012). However, cryostages do not necessarily reduce damage if the sample is an insulator or if the heat generated by the ion beam is not transported away from the target area

(Schmied et al. 2012). It has been shown that utilizing an alternative patterning strategy (interlacing instead of serpentine) eliminates heating at room temperature and is comparable to results obtained with serpentine scanning in cryo-conditions (Schmied et al. 2012).

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3 Experimental procedures

All of the samples analyzed in this thesis were related to the cathode catalyst layer of PEMFC samples. The samples consisted of 1) original catalyst inks 2) cycled and pristine CCMs on which the cathode was fabricated by inkjet-printing catalyst inks on commercial half-CCMs; all of these samples were obtained through a collaboration with Queen's University and 3) commercial CCM provided through collaboration with Automotive Fuel Cell Cooperation (AFCC).

3.1 Printed catalyst layers on half-CCMs (Queen's University)

Since one of the main goals to successfully commercialize fuel cells is to decrease manufacturing and fabrication costs, increasing Pt utilization has been a major area of research as Pt is the most expensive component. Two major areas of research focus on accomplishing this: alternative Pt catalysts and optimization of the structure of the catalyst layer, including the PFSA ionomer.

A set of CCM samples was obtained through a collaboration with Queen's University RMC Fuel cell Research Centre. The objective of this collaboration was to follow-up a published study with a more detailed structural analysis. The main objective of the study was to fabricate thinner catalyst layers with ultra-low Pt loadings and high electrochemical performance (Saha et al. 2011). They applied a relatively new technique called piezo-electric printing to deposit catalyst layers directly onto the membrane. Other printing processes to fabricate the electrodes from catalyst ink solutions include: screen printing (Bonifácio et al. 2011) and flexography (Bois et al. 2012). The difference is that the Pt loading in these electrodes are in the order of 10 times higher than in the samples provided by Queen's University.

The provided samples consisted of commercial half CCMs with $50\pm2 \mu m$ thick PFSA ionomer® NRE-212 membrane and a 10 μm anode with a Pt-loadings of 0.3 mgPt/cm² supplied by Ion Power, Inc. A commercially available piezo-electric printer Dimatix Materials Printer, DMP-2800 series, Fujifilm) was

used to fabricate the cathode catalyst layers on the half CCMs with different thicknesses (1, 2, 5, 7 and 10 layers) (See Table 3.1). The ink cartridge filled with the catalyst ink was loaded into the printer and ink was applied to the blank side of the half-CCM. In order to achieve different cathode thicknesses, the CCM was printed on more times for thicker layers. The CCM was then subjected to drying for 60 min at 80°C. Further, the CCMs were boiled in de-ionized water for 2 h and dried again overnight at 60°C. Dry CCMs were hot-pressed at 100°C for 5 min with the intention of improving the integrity and adhesion of the CLs to the electrolyte membrane (Saha et al. 2011).

The Pt surface area in the Pt/C was measured in liquid electrolyte at 25°C whereas the MEA Pt surface area was measured at 60°C. Although this temperature difference could introduce discrepancy, it is expected to be negligible (Saha et al. 2011). The catalyst inks used in the cathode-printing were prepared by mixing 40 wt % Pt on Vulcan XC-72 (E-TEK, USA) with 5 wt % solubilized PFSA ionomer (Ion Power, USA), isopropanol, water and glycerol.

Electrode	Cathode Pt loading ^a (mg _{Pt} /cm ²)	A _{Pt,MEA(ca)} ^b (m²/g _{Pt})	<i>u</i> Pt ^c (%)
Printed CCM (2 layers)	0.02	45.7	~100
Printed CCM (5 layers)	0.06	42.6	~100
Printed CCM (7 layers)	0.08	40.5	94
Printed CCM (10 layers)	0.12	33.9	79

^aPt at anode: 0.3 mg/cm2.

^bSpecific Pt surface areas for the MEA cathodes

^cMEA catalyst utilization, uPt, is defined as the ratio of the MEA cathodes' specific Pt surface area ($A_{Pt,MEA(ca)}$) to that of the catalyst ($A_{Pt,cat}$ = 42.8 m²/ g_{Pt})

Pristine samples with one and five cathode layers were provided. Some of these samples were tested for electrochemical performance for approximately
500, 200 and 900 hours, and had 2, 7 and 10 layers, respectively, under different conditions and gases.

The objective of this collaboration was to investigate structural differences between the samples to understand the relationship between the microstructure and the Pt content. The sample preparation and conditions for the SEM analysis are described in section 3.4.

3.2 Catalyst inks

As the collaboration with Queen's University evolved, the original catalyst inks were provided to understand differences occurring within the fabrication process. One composition was used, but two batches were made in different days and sent to us. They consisted of 40% Pt/C (0.05g, PEMAS), 5% PFSA ionomer solution (Ion Power. Liquion [™] Solution LQ-1105 EW, 0.332g), glycerol (0.332g, Sigma Aldrich >=99.5% ACS reagent), and mixture of isopropyl alcohol (Fisher Scientific, PHLC Grade) and water (18 MOhm) with 4 mL.

3.3 Commercial CCM sample from AFCC

This is a specific sample prepared with a Gore Select membrane to allow STXM study of the catalyst layers prepared without N-based Pt precursor. It has an 18 microns thick Gore-SELECTA® ePTFE micro-reinforced membrane. The cathode has 0.4 mg/cm² Pt loading on a graphitized carbon catalyst support. The Pt deposition process involved a hexa-chloro Pt acid precursor.

3.4 Sample preparation for Scanning Electron Microscopy

In previous work done by the collaborators (Saha et al. 2011), it was seen that the Pt utilization increased with thinner cathode catalyst layers (section 3.1). This means that the thicker the cathode catalyst layer, the more isolated the Pt particles are, contributing to a higher cost of the fuel cells. However, the thicker cathode catalyst layers had a higher overall electrochemical performance (electrode area specific current density at any given cell potential) and peak power density than the samples with thinner layers. The authors were unable explain the reason for this, and therefore the nature of the collaboration was to understand microstructural differences between these samples. The objective of analyzing these samples with SEM was to visualize defects such as thickness variations, delamination between cathode and membrane and clusters of Pt or PFSA ionomer so that there could be a better understanding of their performance.

The pristine and cycled printed catalyst inks on commercial half-CCMs provided by Queen's University were freeze-fractured for SEM visualization. This technique is known to cause few artifacts on the surface of PEMFC (Kundu et al. 2006). Freeze-fracturing consists of fracturing the sample in liquid nitrogen. A small part of the sample sized around 0.5 cm x 1 cm is cut from the original sample with a razor blade. Tweezers were used to submerse the sample and fracture them while in the liquid nitrogen, held in a Styrofoam cup. Silver paste was used to mark the cathode side. The fractured sample is then put on carbon tape in a cross-section stub with silver paste on the sides to ensure conductivity.

The original catalyst inks used to fabricate the cathode layer were also analyzed with SEM. The inks were sonicated (for 10 minutes) or analyzed aswas-received. The diluted ink was mixed with isopropanol available in the Sample Prep Room in the Canadian Centre of Electron Microscopy (CCEM). For SEM analysis: the diluted ink sample consisted of 5 droplets of isopropanol to 1 droplet of catalyst ink; the pure ink sample consisted of one droplet of ink on an Al polished stub. The stubs were stored in a desiccator under vacuum for a couple of days before the analysis. A special sample holder was used for imaging the catalyst ink in liquid state: QX-101 WETCELL® from Electron Sciences Microscopes. A droplet of the liquid was put into the specified orifice and then sealed. Conditions of the SEM were similar, except for the higher voltage (15 kV) and current needed to image through the polymer window of the holder.

Two SEM microscopes from the CCEM at McMaster University were used in this work. The JEOL JSM-7000F is equipped with a Schottky Field Emission

Gun (FEG) filament with an Oxford Synergy INCA X-ray micro-analysis system. This instrument was operated at 1 and 2 kV for higher resolution images and 10-15 kV for backscattered and EDX analysis. The current chosen for 1 and 2 kV was between 3 and 5 while for higher voltages a higher current was used. For higher resolution surface analysis, the FEI Magellan 400, an extreme highresolution SEM (XHR-SEM) was used. Novel detectors such as the high collection efficiency in-lens detector (TLD) and a unique low voltage, high contrast solid state detector combined with a two mode objective lens with beam deceleration and immersion capabilities combine to provide high surface sensitivity, high resolution and enhanced contrast at low voltages, specially for beam-sensitive materials.

3.5 Sample preparation for Transmission microscopy

Two sample preparation techniques were applied to the same commercial CCM sample provided by AFCC (see section 3.3) ultramicrotoming and Focused Ion Beam (FIB) milling. In order to reduce penetration of the embedding material in ultramicrotomy, we attempted an alternative method using polystyrene (PS). The CCM was sandwiched between two polystyrene beads gently softened with toluene. The composite was dried overnight at 60°C. The microtomed slices were cut with a Leica Ultracut UCT at a thickness of approximately 100 nm with a DiATOME diamond knife. Sections were transferred from a water surface to holey carbon coated 200 mesh Cu grids from Electron Microscopy Sciences. This procedure was done in the Electron Microscopy Facility at the Faculty of Health Sciences, McMaster University.

For the FIB preparation, a small slice of the CCM was cut with a razor blade and was glued with carbon tape and silver paste on a stub with the cathode side up. The region of interest was the cathode material and a W strip was applied to the top surface to prevent further damage (**Figure 3.1**). The Zeiss Nvision40 FIB available in the CCEM was operated at 30 kV, with final polishing at 10 kV and 80 pA. A lower polishing ion beam energy of 10 keV was used with the intention of lowering sample damage. The use of lower ion beam

energy is known to reduce the thickness of the amorphous layer in Si (Mayer et al. 2007).







Figure 3.1 FIB preparation of the CCM sample (a) W strip is applied on the top of the cathode to protect the material from further damage (b) inhomogenous cathode material seen as features of different contrast underneath the W strip and (c) final FIB sample.

3.6 Scanning Transmission X-ray Microscopy (STXM)

STXM is the combination of X-ray absorption spectroscopy with microscopy, also known as spectromicroscopy. A high brightness x-ray beam from a synchrotron light source is monochromatized and focused with a zone plate on a raster scanned sample and at each point the transmitted photons are detected (Bessarabov & Hitchcock 2009). At each energy of the photon beam, an image is acquired, making up an image sequence. Due to the high energy resolution achieved (comparable to monochromated EELS), different components that contain the same elements can be distinguished due to

differences in the fine structural features that result in the X-ray absorption spectra. For example, in CCMs that are prepared with ultramicrotomy, the expected C-containing components are: PS from the embedding material, the PFSA, the carbon support and holey carbon from the grid. The components present in the cathode region of the sample are carbon support, which for the AFCC sample is graphitic, PFSA ionomer and also Pt. The Pt will absorb X-ray photons at all energies and is seen as an offset of the overall spectrum (**Figure 3.2a**).

The transmitted signal measured in STXM is converted to optical density, OD = $\ln(I/I_0)$, where I is the signal transmitted through the sample and I_0 is the incident photon intensity, measured from the transmitted signal without the sample, but with all other components in the path (e.g. holey carbon or formvar substrate). The OD can then be quantitatively related to the type, density and thickness of the sample, through $OD(E) = \Sigma \mu_i(E)\rho_i t_i$ where $\mu_i(E)$ is the massabsorption coefficient, ρ_i is the density and t_i is the thickness of the ith component present at a specific point in the sample. If the density of each component is known and a spectrum of the pure component is available, the absolute thickness of each component of a sample can be determined. If external reference spectra are not available, internal reference spectra may be used. Ideally these should be extracted from regions within the sample that are pure components. However, one can often get valid spectra of single components from a mixed region, if the spectra of other components present in that same region are known. For example, the C 1s spectrum of the carbon support can be derived from Pt decorated carbon support particles by subtracting the structure-less signal of the Pt. In the case of the microtomy sections of a commercial CCM, the internal reference spectra generated from Figure 3.2c are shown in Figure 3.2b. As with other additive analytical methods, one must account for each component present. In practice, that is done by carefully evaluating the suitability of internal or external reference spectra and checking that the statistical guality of a least squares fit procedure is within that expected from the overall statistical quality of the data (Hitchcock 2012).

The approach used to quantify the components prepared with FIB and ultramicrotomy consisted of starting with the PS reference spectrum from a region without any material in the microtomed section (shown in Figure 3.2c). After that, a region with holey carbon and PS was chosen. The PS component was subtracted to generate the holey carbon internal reference spectra. The next component to be isolated was the membrane. As shown in Figure 2.1, the PS penetrates into the membrane and also has to be subtracted. Since the PFSA ionomer does not have a peak at 285 eV, generating the reference spectra was somewhat straightforward. The last and most challenging was generating the internal reference spectra for the carbon support (see Figure 3.2c). Contributions of the PFSA ionomer and the PS were subtracted, as well as a constant which corresponds to the signal from the Pt catalyst. Previous knowledge of the expected carbon support (graphite) C-edge spectrum as well as the fit to the elemental response were used to guide the amounts of PFSA ionomer, PS and constant signals that were subtracted to generate the internal, pure carbon support spectrum.

The FIB and ultramicrotomed specimens of the AFCC sample were measured using the STXM on beamline 10ID1 at the Canadian Light Source (CLS) (Kaznatcheev et al. 2007). The C and F 1s edge were of particular interest as the PFSA ionomer is made up of carbon, fluorine, oxygen and sulfur. The F 1s signal is unique to the PFSA ionomer and membrane components while the C 1s signal distinguishes the PFSA ionomer from the carbon support, the PS and the holey carbon (**Figure 3.2**). Image sequences, also called stacks (Jacobsen et al. 2000), were acquired at the C 1s and F 1s edges for the cathode region of the microtome and FIB sections.

After generating internal reference spectra of each component, they are converted to a quantitative intensity scale (optical density per nm, OD1) by scaling the intensity of the so-isolated internal reference spectrum so that it matched the intensity of the X-ray absorption predicted from the elemental composition, standard density and elemental absorption coefficients of the material (Henke et al. 1993). The OD1 reference spectra were then used to fit the spectrum at each pixel of the C-1s edge stack in order to generate

quantitative components maps as shown in **Figure 3.3**, with intensity being represented in a thickness scale.



Figure 3.2 STXM C 1s edge (a) overall spectrum of the cathode and (b) of all the components in the cathode region of a commercial CCM sample from AFCC. For the generation of each spectrum in (b), internal reference spectra were taken from the sample as explained in the text (c) explanation of how the internal reference spectra were generated.

The relative quantification of the fluorine content in both samples was done by first selecting internal reference spectra for the PFSA ionomer from the membrane of the microtome sample or generating an internal F 1s reference spectrum from the cathode in the FIB section. The outcome in this case did not alter the relative amount of PFSA (damaged) ionomer. These spectra were set to quantitative OD1 intensity scale by scaling to match the elemental response for PFSA ionomer. Another approach was used and will be treated in Chapter 4. A pixel-by-pixel fit to the F 1s image sequence yielded quantitative component maps for the PFSA ionomer and non-fluorinated components (as the constant in the stack fit). The relative fractional amount of PFSA ionomer was calculated by dividing the PFSA ionomer component map by the sum of the PFSA ionomer and non-fluorinated maps. Since we don't have reference spectra of nonfluoronated components, the value is not absolute, but still relevant.



Figure 3.3 Component maps of all carbon containing materials in a commercial CCM sample prepared with microtomy were derived from C 1s STXM. The maps are in thickness scale (nm), with the lightest color corresponding to regions of most material. RGB composite maps showing PS, membrane and C support are also shown.

3.7 Transmission Electron Microscopy

All micrographs used in this thesis were taken from instruments available in the CCEM at McMaster University. Three different TEM instruments were used: Philips CM12 with a LaB_6 electron source operated at 120 kV was used for low magnification images of the TEM samples. The JEOL 2010F TEM/STEM is a field emission TEM operated at 200keV with an EDX detector of low solid angle of 0.1Sr, scanning, scanning-transmission and a Gatan imaging filter (GIF) for energy filtered imaging and electron energy loss spectroscopy (EELS). The Titan 80-300LB, a high resolution HRTEM/STEM made by FEI Company equipped with a CEOS-designed hexapole based aberration corrector for the image forming lens, was operated at 80 and 300 keV. The operation at 300 kV was used for electron tomography in a specialized holder from Fischione.

3.8 Electron tomography

The acquisition procedure of TEM/STEM images for tomographic reconstruction can be done in several different ways (DeRosier & Moore 1970; Carazo et al. 2006). In most cases, the sample is tilted over the largest possible angles with specialized goniometers in which the tilt angle of the projected images is known. Single-axis tilt, the most commonly used in electron tomography, consists of tilting the sample in small increments in a fixed axis from approximately $-70-80^{\circ}$ to $+70-80^{\circ}$ and taking an image for each tilt angle. The sample geometry must be taken into consideration since the specimen thickness usually increases at high tilt angles. Double-axis tilt, which consists of imaging the sample in two perpendicular axis, and conical tilt, which consists in tilting the sample to the maximum angle and then rotating in small increments, limit the 'missing wedge' information but are less implemented due to increased difficulties during reconstruction of the volume (Carazo et al. 2006). Recently developed holders allow a 360° rotation in the objective pole piece minimizing the 'missing wedge', but the required needle-like specimen geometry prepared with a FIB limits the application of this holder to specific materials (Midgley & Dunin-Borkowski 2009).

The projection images acquired during the tilt series are, however, imperfect data sets with high levels of noise corrupting the gray level scale and are limited in number and angular coverage since the acquisition is not taken in continuous tilt angles. Therefore, the reconstruction algorithm must deal with

this imperfect data and the collection geometry to regenerate the object as faithfully as possible (Carazo et al. 2006).

The mathematical basis of reconstruction started with The Radon Transform, formulated in the 1910s. It described the object by a function f(x,y) in real space which is transformed to a series of projections (or transmitted signal) in Radon space and each projection is described by a perpendicular line *I* at an angle Θ . The transform is the summation of all the lines, L, with unit *d*s through $f(x,y) : Rf = \int_L f(x,y)ds$. In other words, when the transform is applied, the object described in real space will correspond to a series of projections or lines in Radon space. Therefore, the original object f(x,y) can be reconstructed when the inverse transform is applied on the projections Rf; this concept is the basis of all reconstruction algorithms used nowadays. However, since the projections are imperfect, the inversion will also result in an imperfect object and so the reconstruction problem evolves into the determination of the most faithful object given the deficient data (Midgley & Weyland 2011; Midgley & Weyland 2003).

An instructive insight on how the finite number of projections affects the reconstruction volume is given by the Fourier Space description. The image or projection from real space is now considered to be a plane, instead of a line, in Fourier Space. The 'central slice theorem' states that different projections in real space [Figure 3.4(a)] actually correspond to planes tilted with different angles in Fourier Space intersecting each other at their centers, which pass through a common origin [Figure 3.4 (b)] (Carazo et al. 2006; Crowther et al. 1970a). The empty spaces seen between the planes in the Fourier space (projections in real space) correspond to information that was not imaged due to the limited number of images taken during the acquisition. This description clearly indicates the higher concentration of information closer to the centre of the slices, whereas further away from the origin, the opposite is true [Figure 3.4 (c)]. Figure 3.4 (c) also illustrates 'the missing wedge' due to the limitation of tilting the goniometer at high angles in the objective pole piece or due to the higher thickness of the sample in high tilt angles. In principle, the inverse Fourier Transform of the projections would result in the original object; however, the missing gaps of information have led to complicated calculations that have made this method

disused and substituted by the back-projection reconstruction (Midgley & Weyland 2011; Carazo et al. 2006).

The principle behind Direct Backprojection is similar to the Randon Transform, with the difference being that the description is still in real space: the object is described as rays that pass through it describing the object in that direction. More rays are needed to describe the object as its complexity increases. Midgley & Weyland (2003) state that "a projection of the object is an inverse of such a ray, and *backprojection* is inverting the projection to generate a ray that describes uniquely the object in that direction". The reconstruction, therefore, consists of "the superposition of all the back-projected rays from a sufficient number of projections from different angles" (Midgley & Weyland 2003). The application of the same filter function for all projections to make up for the lost information between projection images, except for the first and last due to the missing wedge, results in the Filtered Back-projection. However, as shown in **Figure 3.4 (c)**, since there is a higher concentration of information closer to the central part of the Fourier space and lower concentration of information away, the reconstruction will be blurred without fine details of the 3-D object even if each projection is taken at evenly spaced tilt angles (Carazo et al. 2006). Improved reconstructions are achieved when a weighted filter is applied to each projection, compensating for the difference in concentration of information in relation to the origin in Fourier Space. The weighted backprojection (WBP) reconstruction improves the distribution of information or frequency between the projections by enhancing high frequency information and reducing low frequency information and avoids the blurry backprojection reconstructed object (Carazo et al. 2006). The WBP is the most widely used reconstruction nowadays with numerous applications in life and physical science (Möbus & Inkson 2007).

If a projection from the reconstructed volume is compared with a projection from the original tilt series at the same tilt angle, in general, they will not be the same. It is possible to generate a difference reconstructed volume by backprojecting the difference into the reconstruction space and this can be seen as a measure of the imperfection of the method used. This difference

reconstruction can be used to improve the quality of the original backprojections, thus better fitting the reconstruction with the original projections images. This is done by using iterative algorithms, with the most common being the algebraic reconstruction technique (ART) and the simultaneous iterative reconstruction technique (SIRT). ART compares the reconstruction with each single projection and corrects only in one direction at a time, whereas SIRT compares all projections simultaneously. Midgley & Weyland (2011) state that "SIRT does not improve the resolution of the reconstructed volume when comparing to WBP, but it reproduces the object more faithfully because it doesn't lose the higher frequency information."



Figure 3.4 The central slice theorem, (a) real space representation of an object near the origin of coordinate axes (x, y, z) and its projection image g, formed by integrals of orthogonal parallel lines to the x-axis tilted by Θ on z-axis, (b) the Fourier space representation G of the projection, g, is a plane which passes through the origin of the Fourier space (a central section) with coordinate axes (X, Y, Z) and tilted by Θ . The image on the bottom right represents the Fourier representation of several projections with a common origin (Carazo et al. 2006), which results in the missing wedge, shown in (c), where Θ is the tilt increment, and α is the maximum tilt angle (Midgley & Weyland 2011).

The resolution of electron tomographic reconstructions is anisotropic because of the 'missing wedge' [**Figure 3.4c**]. The resolution in the x axis, that is parallel to the tilt axis, should be the same as in 2-D TEM/STEM images, but in the z and y axis the resolution will depend on the number of images taken over the whole tilt range and the volume to be reconstructed. Crowther et al. (1970) established that the resolution, d, is $d = \frac{\pi D}{N}$, where D is the diameter of

the reconstructed volume and N is the number of projections evenly spread over π radians. Because of the limited space between the upper and lower pole piece of the objective lens, in general, tomography holders have a limited tilting angle of ~70°. Due to increased thickness of the samples in high tilt angles, this angle is usually limited to ~60°. This results in an even higher loss of resolution in the z axis, by an elongation factor (Midgley & Weyland 2011).

With the availability of computers with increased processing speeds and memory, the acquisition of the tilt series is now totally automatic. The FEI software Xplore3D was used for the STEM tomography calibration and acquisition. The STEM tomography calibration consisted of calibrations of: magnification, stage shift, image shift, focus scale and eucentric focus, and should be done with a copper grid and carbon film with sputtered Au nanoparticles (Voigt & Kubel 2010). Since the imperfections of the tilting movement of the specimen stage (CompuStage) are reproducible, part of the calibration is to measure this movement and then compensate it automatically to predict the shifts of the image and focus. The change in focus occurs because of a misalignment between the optical axis and the tilt axis and must also be compensated (FEI COMPANY 2003a). Accordingly, a new calibration sample.

The sample of interest and the calibration file were then loaded. The STEM tomography acquisition consisted of tilting by the increment determined, shifting onto the area of interest, focusing and taking the image (Kubel & Voigt 2009). Image shifts were minimized with the use of cross-correlation between every two images and are important because only the areas that appear in all images can be successfully reconstructed. Cross-correlation compares an image with the previous one taken in the tilt series, and compensates for the shift between them. Filters were used to enhance dominating features. Fourier filters are commonly used and reduce low frequency components and high frequency components; the latter consists mostly of noise (see **Figure 3.5**) (Midgley & Weyland 2011; FEI COMPANY 2003b). Automatic focus was done

with algorithms that chose the maximum gray-level difference in the STEM tomography images.

Electron tomography was performed on the FIB prepared CCM sample provided by AFCC. The first tomography tilt series was acquired with a <u>'thicker'</u> <u>specimen</u> [see **Figure 3.6(a)**] on the FEI Titan 80-300 LB over -70 to 70° with 1° increment at 300 kV in HAADF-STEM mode with a convergence angle of 8.1 mrad. The acquisition started at 0° and tilted to negative angles until -70° was reached, then restarted at 1° and finished at +70°. Due to specimen artifacts discussed in subsequent sections, a second tilt series was taken with the same specimen after further <u>thinning</u> with FIB [see **Figure 3.6 (b)**] over 0° to -64° and then from 1° to 65° with a 2° increment. The convergence angle was 5.5 mrad and a lower current of 0.055 nA was used. The advantage of using a low convergence angle is that the depth of field is increased, which helps keep the image in focus in thicker specimens. Dynamic focus was used in all HAADF-STEM images. The camera length used for the acquisition of both tilt series was 115 mm.



Figure 3.5 Correction of image shift and filtering of lower and higher frequencies and its effect on the crosscorrelation: (a) and (b) are two images of block copolymer from a HAADF-STEM tilt series taken at different angles (c) cross-correlation between the two images. The centre has a broad intensity peak. (d) and (e) are high pass filtered images of a) and b) (f) cross correlation of d) and f), with a fine intensity peak at the centre which easily permits the calculation of the image shift (Midgley & Weyland 2011).



Figure 3.6 SEM images of the **(a)** 'thicker and **(b)** 'thinner' CCM PEMFC FIB prepared sample used for electron tomography. The porous structure of the carbon support is more obvious in the thinner sample.

Even though the tilt series acquisition is automatic, it is necessary to align the images with sub-pixel accuracy as part of the post-processing. This can be done using cross correlations, as described above (Figure 3.5), or by using landmarks. During this process the tilt axis has to be corrected. The use of landmarks also determines the tilt axis, but does not use the entire image as it uses fiducial makers in some points on the image and the software tracks their positions automatically through the entire tilt series. This method is mostly used in biology applications with spherical Au particles. On the other hand, cross correlation utilizes information from the entire projection image, but does not determine the tilt axis and this has to be done with additional techniques. In materials science applications, cross correlation is more widely accepted to align the images (Midgley & Weyland 2011). Therefore, cross-correlation with Fourier Filters and manual alignment of the tilt axis were used to align the images of both tilt series using the software Inspect3D by FEI COMPANY[™]. Both WBP and SIRT reconstruction (25 iterations) algorithms were used in Inspect3D. Amira was used to visualize the reconstructed volume.

4 Results and Discussion

4.1 Structural features of the cathode catalyst layer of cycled and pristine CCM samples (Queen's University)

All five samples (see section 3.1) were analyzed with SEM. The decreased Pt utilization with higher Pt loadings (thicker cathode layers) indicated that "significant amounts of Pt surface area are either ionically or electronically isolated" (Saha et al. 2011). Nonetheless, the thicker cathode layers yielded higher overall electrochemical performance of the fuel cell compared with the thinner and lowest Pt loading layers. However, if the peak power density was considered instead, the thinnest cathode layer yielded the highest performance/amount of Pt used (Saha et al. 2011). Therefore, the objective of this section is to study the structural differences of these samples.

Although Pt and carbon support distribution in the cathode are usually seen with TEM projection images, high resolution SEM can also be used with the advantage of seeing the surface topography (**Figure 4.1** and **Figure 4.2**). In most regions of the cathode layer of pristine CCMs, the Pt seems to be evenly distributed over the carbon support particles (the small white particles are Pt and larger gray particles are carbon support particles in **Figure 4.1a**). An advantage of the secondary electron (SE) image is that the location of the Pt particles can be correctly interpreted and are visible on top of the carbon support particles. However, back-scattered electron (BSE) images, which show compositional contrast, indicate that some regions extended over several hundred nanometers have agglomerations of Pt particles (**Figure 4.1b**). It is likely that these regions contribute to a lower Pt utilization in the electrochemical reaction as only electrons are being transported and are probably electronically isolated regions. It is possible that the samples with thicker cathode layers had higher Pt agglomerations, which would explain the decreased Pt utilization.

The cycled samples had a different Pt distribution, as shown in **Figure 4.1c** and d. Although some regions have a homogenous distribution (**Figure 4.1c**), there are regions of 50-100 nm with Pt agglomerations that could have

been caused by Ostwald Ripening. Ostwald ripening is a known effect observed in Pt catalysts after MEA degradation and consists of the growth of the larger particles at the expense of the smaller particles (Guetaz et al. 2012). In regions



Figure 4.1 Pt distribution with HRSEM images of pristine sample with one catalyst layer **(a)** SE image from the top surface of the CCM image indicates that Pt nanoparticles are evenly distributed on top of the carbon support particles although some regions have high agglomerations of Pt, as seen with the BSE image shown in **(b)**.



Figure 4.1 continued - Pt distribution with HRSEM images of and cycled sample with 10 catalyst layers. A somewhat even distribution of Pt nanoparticles close to the membrane interface after cycling is seen in (c) and regions of where the Pt probably detached from the carbon support particles during cycling (d).

further from the membrane interface, holes in the carbon support are clearly visible (**Figure 4.1d**) and are probably regions of carbon corrosion and Pt detachment and migration to form agglomerates. One of the known effects of carbon corrosion is the loss of surface area and porosity needed for supporting Pt catalysts and mass transport, respectively (Liu et al. 2010). The corrosion

also results in the loss of graphitic character of the carbon support particles (Wang et al. 2010). This change in chemical structure is probably what results in the Pt detachment.

Qualitatively, the carbon support size distribution looks similar between a pristine and cycled sample (with different cathode layer thickness) as shown with SE images in **Figure 4.2**. Quantitative analysis is difficult to perform in SE images due to minimum contrast between different particles, which is the reason TEM projection images are preferred (ASTM 2014). However, for porosity differences caused by different electrochemical testing, FIB/SEM serial tomography is the ideal technique as mentioned in section 2.5. A start/stop cycling caused severe porosity changes in the carbon support framework when compared to potential cycling (Schulenburg et al. 2011). A qualitative comparison between SE images of the pristine and cycled samples from our work showed that the performance testing on these samples was not severe as the carbon support framework did not drastically change.

The residual gas diffusion layers used for the performance testing were found on top of the cathode catalyst layers of the cycled CCMs, as shown in **Figure 4.3**. Although the gas diffusion layers usually consist of carbon fibers or paper, this feature could also be PFSA ionomer (see section 4.1.2) due to the 'viscous' nature of its structure.



Figure 4.2 Carbon support close to membrane interface of **(a)** pristine sample with 5 cathode catalyst layers and **(b)** cycled sample with 10 cathode catalyst layers is qualitatively similar.



Figure 4.3 SEM images of the cathode catalyst layer of a sample with 7 layers. The structure found on top of the layer is probably residual gas diffusion layers, used for the cycling performance testing.

The pristine samples had an uneven distribution of the cathode catalyst layer on top of the membrane (**Figure 4.4**). On a top surface view of a sample with only one cathode catalyst layer, 'cracks' are seen all over the surface and are probably due to the heat treatment the samples undergo after the printing process to ensure good adhesion between the membrane and cathode. The membrane is sensitive to the heat treatments and probably expands and then contracts resulting in an uneven distribution of the catalyst particles. The presence of the cracks or uneven distribution of the catalyst on the membrane could also be related to the solvents used in the catalyst ink solution and the

membrane swelling effect (Therdthianwong et al. 2010). However, the catalyst inks investigated in this thesis contained isopropanol. In Therdthianwong's study (Therdthianwong et al. 2010), the isopropanol catalyst ink yielded the CCM with highest performance when compared with other solvents used. They also found that this solvent caused a high swelling ratio in the membrane, with high absorption capacities, and therefore the ink adhered and covered the surface of the membrane.



Figure 4.4 Top surface of pristine sample with one catalyst layer and thickness of approximately 500 nm. Cracks on the cathode are probably due the heat to treatment the sample undergoes after the printing process to ensure good adhesion with the membrane.

4.1.1 Thickness variation

The thickness of the cathode varied within a pristine CCM sample of 5 L of cathode material (**Figure 4.5**). In previous work (Saha et al. 2011), it was seen that each layer was approximately 0.5 μ m thick and therefore, for 5 layers, the cathode layer thickness should be 2.5 μ m. However, measurements done on SEM images indicate that the layer thickness varied from 0.7 to 4 μ m.

a)

Region 1 Region 2 cathode membrane membrane anode JSM-7000F 3 SEI 1.0kV X1.400 WD 6.0mm 10µm

b)



Figure 4.5 Thickness variation of ink-jet printed cathode catalyst layers on half CCMs. The sample has **(a)** 5 layers and should have a thickness of 2.5 μ m, but the thickness varied from 0.7 to 4 μ m in region 2 and 1 respectively and **(b)** had 1 layer with area shown 1.5 μ m thick.

The thickness variation of the cathode catalyst layer is related to the manufacturing process of the sample: the catalyst ink mixture or the deposition process of each layer onto the membrane. There are many possible causes for this thickness variation which can result in: variable resistance through the MEA, areas susceptible to degradation by heat and mechanical weakness (Kundu et al. 2006). Although the piezo-electric printing "permits the generation of droplets at pico-litre resolution and offers fine control of the position at which the ink can be dispensed" (Saha et al. 2011), **Figure 4.5** demonstrates that this technique does not always print perfectly uniform cathode layers. It is possible that this is related to the ink's solution and stability, rather than the printing process. For this reason, we also analyzed the original ink used for the catalyst layer deposition process in section 4.2.

One of the known effects of MEA degradation is that the electrode thickness reduction results in the collapse of the carbon support framework (Liu et al. 2010; Vinod Selvaganesh et al. 2011). This effect can be seen in **Figure 4.6**, which demonstrates that a ten-layer cathode is only 2.5 μ m in size, same thickness as the pristine 5 L sample (**Figure 4.5**).



Figure 4.6 SEM image demonstrating the cathode layer thickness of a cycled sample with 10 layers. Theoretically, the thickness of the cathode should be approximately 5 μ m. The average thickness was ~2 μ m instead, indicating cathode thickness loss during performance testing.

4.1.2 PFSA ionomer morphology

The main challenge in visualizing the PFSA ionomer in the catalyst layer is overcoming radiation damage, mentioned in section 2.7. The 'viscous' features imaged in Figure 4.7 are probably PFSA ionomer, as only carbon support, Pt nanoparticles and PFSA ionomer are present in the pristine samples. Since it is believed that the PFSA ionomer forms a thin film covering the catalyst particles, it is highly likely that this 'sticky' film is PFSA ionomer. In order to confirm the presence of fluorine, element present only in PFSA ionomer in this system, it is necessary to measure the composition of this feature. However, EDX analysis does not provide information about the surface, posing a limitation of this technique in characterizing the ionomer in CCMs. In studies where the PFSA ionomer morphology in catalyst layers was explored and related to the performance of the fuel cell, it was seen that higher concentrations of the solvents used in PFSA ionomer solution lead to less un-shielded or visible Pt particles (Ngo, Yu & H.-L. Lin 2013; Ngo, Yu & H. Lin 2013). This means that the more diluted PFSA ionomer solution yielded more visible Pt particles, as the PFSA ionomer didn't cover the surfaces of these particles. In this case, it is possible to have SEM-SE images taken at different voltages and relate to surface features. However, the authors used HRSEM with much higher voltages, which leads to less surface sensitive images (Ngo, Yu & H.-L. Lin 2013; Ngo, Yu & H. Lin 2013).

The membrane morphology of all samples (pristine or cycled) consisted of a rough surface, probably caused by imperfect fracture at cryogenic conditions, and small features were seen with darker contrast (**Figure 4.8**). Due to sensitivity to radiation damage, the voltage used for generating these images was low (700 V – 1 kV). The image is actually a sum of several images taken with frame integration. It is possible that the dark features are holes, or could be precipitation of a different phase within the membrane. In literature, as a result of several techniques used to analyze the PFSA ionomer morphology, it was shown to consist of "a phase segregated structure, with a series of internal ion channels, accounting for its high conductivity" (Hobson et al. 2002).



Figure 4.7 PFSA ionomer morphology in pristine samples (a) and (b) with 5 layers and (c) with 1 layer. The PFSA ionomer is seen as a 'viscous' feature on top of the catalyst particles of the cathode. In further investigation with the catalyst inks, shown in subsequent sections, similar features were observed and fluorine was detected in the thin film with compositional analysis done with EDX, confirming the presence of ionomer.

The brighter particles seen in **Figure 4.8b** were also imaged with TEM, as shown in **Figure 4.9b** and **c**, and are composed of Si as demonstrated in **Figure 4.10**. The sizes of these particles are of approximately 20 nm. The presence of Si in this sample is probably due to contamination during the electrochemical performance testing, as Si gaskets were used. These particles

were well bonded to the membrane, as they are seen in both the freeze fractured surfaces with SEM and microtomed samples at room temperature with TEM.







c)



Figure 4.8 Membrane morphology using SE images at a HRSEM and low voltage. Rough surface and small features with darker contrast are seen in all samples (**a**) pristine with 5 layers imaged at 700 V (**b**) cycled with 10 layers at 1 kV and (**c**) cycled with 7 layers at 1 kV. An additional feature was seen in the sample with 10 layers (b), that consisted of smaller white particles of approximately 15-30 nm in size, and are composed of Si as seen in Figure 4.10.

TEM images of the cycled sample with 10 cathode layers are shown in **Figure 4.9**. We expected that the bright particles seen in **Figure 8.b** were Pt and migrated to the membrane during electrochemical testing. However, the particles in **Figure 4.9a** and **b** are quite different; the ~5 nm black particles in the bright-field image in **Figure 4.9a** are Pt and correspond to the bright white particles in the HAADF image in **Figure 4.10**, while the ~20 nm gray particles in the bright-field image in **Figure 4.9b** are actually Si, as shown in the HAADF image in **Figure 4.10** with the corresponding EDX spectrum.







Figure 4.9 (a) and **(b)** TEM Bright-field and **(c)** HAADF image of cycled sample with 10 cathode layers, demonstrating membrane morphology (a) close to the anode (b) middle of CCM sample and (c) close to the cathode region. The black particles in (a) are Pt, and the gray particles are part of the membrane morphology. Bigger particles are seen in (b) which correspond to the particles seen in (c) of approximately 15-20 nm.



Figure 4.10 Membrane morphology and elemental point analysis of cycled sample with 10 catalyst layers. The regions indicated in the image correspond to the EDX point analysis spectra shown. Region one consists of Pt particles, region 2 consists of Si particles while region 3 does not contain Si.

4.2 Structural features of the catalyst ink

The catalyst ink was imaged in the SEM and was prepared in several different ways: diluted, pure and in liquid state. The morphology of the diluted ink is shown in **Figure 4.11** and is very similar to the morphology of the printed ink in the CCM (**Figure 4.2**), where individual carbon support particles are visible. The solvents have clearly evaporated and the ink is shown in complete solid state.



Figure 4.11 SEM image indicating that the morphology of the diluted catalyst ink is very similar to the printed ink in a CCM, as shown in Figure 4.2.

When the catalyst ink is prepared without dilution, a completely different morphology is visible (**Figure 4.12**). BSE and SE images of the same region indicate nearly identical features, meaning that the features present in the surface are similar to that of the bulk. The solvents have not completely evaporated and individual carbon support particles are not visible. The dispersion of the ink is relatively homogenous as in the scale seen there are not visible agglomerations of microns in size.



Figure 4.12 Morphology of the catalyst ink without dilution (a) BSE and (b) SE SEM images of the same area. There are no surface features visible, as the same morphology is seen in both images. The bright areas are Pt agglomerates.

The catalyst ink was also imaged in the liquid state (**Figure 4.13**) in a special "liquid cell" holder that seals the sample environment in the high vacuum chamber of the SEM (see section 3.4). Since the electrons generated in the sample have to escape a thin polymer film (part of the holder), a high voltage was used (15 kV). Similar to the images of the catalyst ink without dilution (**Figure 4.12**), the dispersion of the ink is homogenous. The features observed in the liquid ink are a lot bigger than in the ink that was imaged without dilution, meaning that some of the solvents evaporated in the latter case. This, however, did not affect the distribution of the agglomerates, as the particles are still homogenously dispersed. The similarity between the SE and BSE images indicate that the surface features are the same as the bulk features, although regions of higher agglomerations in the BSE are due to the in-depth information gathered.

The PFSA ionomer in the catalyst layer can be imaged in the SEM if different voltages are used, as shown in **Figure 4.14.** Consider the region in the white circle: in the 2kV image, what seems to be a 'viscous' thin film is seen on top of the particles and surface features seem to be obscured by this film. In the corresponding region in the 10 kV image, small particles are seen more clearly and there are features present in greater depth or beneath the 'viscous' film. The BSE image indicates the compositional contrast in the area imaged.



Figure 4.13 Liquid cell SEM (a) SE and (b) BSE images of the catalyst ink, indicating a state where there is practically no solvent evaporation and is therefore, the most reproducible state of the ink. The different phases are homogenously distributed within the imaged region.

The 'viscous' film seen in the CCM (**Figure 4.7**) had a similar morphology as seen in the catalyst ink (**Figure 4.14**). To confirm if this component is PFSA ionomer, EDX analysis was done in regions of distinct morphology in the catalyst ink (**Figure 4.15**). Since the catalyst ink consists of a thin film on the stub, the interaction volume of the electron beam with the sample is much smaller than in a CCM. EDX spectra from regions with and without the 'viscous' film indicate that the presence of this film is related to a higher F content (region selected in a pink square in **Figure 4.15**) than in a region without this feature (region selected in blue square in **Figure 4.15**). A comparison between the BSE images of the two regions show that a higher atomic number element is present in more regions in the blue squared region, with corresponding spectrum indicating higher concentration of Pt.



c)



Figure 4.14 The PFSA ionomer morphology is seen as a 'viscous' thin film on top of the catalyst particles if (a) SE at 2 kV, (b) SE at 10 kV and (c) BSE at 10 kV images are compared. Since lower kV is more surface sensitive, a comparison between the image at this voltage and at 10 kV, indicates more Pt particles and more carbon support particles are visible, without the presence of a film over these particles. The Pt distribution is seen in the BSE image.



Figure 4.15 Morphology difference in an ink with corresponding EDX spectra indicating that the 'viscous' feature seen (squared region in pink) can be associated with higher F content if compared to region shown in blue and is probably composed of PFSA ionomer agglomeration. The selected regions are shown in higher magnification SE and BSE images. A comparison between the BSE images indicates that there is more higher atomic weight elements in the bottom region, selected in a blue square.

The morphology of the catalyst ink depends on how the sample was prepared. The dilution and drying process influence the final morphology and size of the agglomerates. However, it does not seem to influence the dispersion of the components, specially the 'viscous' film. Images in **Figure 4.16** show the morphology of the catalyst inks with the same chemical formula but fabricated in different days. The absence of the 'viscous' film in the ink shown in **Figure 4.16a** is indicative of a better dispersion if compared with the ink in **Figure 4.16b**.



Figure 4.16 Different distribution of the catalyst particles between (a) first and (b) second batch of catalyst ink with same chemical formula but prepared in different days. The first batch is more homogenous than the second, where 'viscous' features are visible (in white circles) and are probably PFSA ionomer/solvents/glycerol non-homogeneity.

4.3 Structural features of the cathode catalyst layer of a pristine commercial CCM sample (AFCC)

4.3.1 FIB section

Due to penetration of the embedding material in the microtomy section (Figure 2.1), structural features of the carbon support and/or PFSA ionomer are more accessible in the FIB section. The Pt nanoparticles interplanar distances can be determined using electron diffraction (Figure 4.17d), which correspond to metallic Pt. The rings seen demonstrate the nanoparticulate characteristic of the Pt and show the diffraction peaks of highest intensity. Interplanar distances of 4.4, 5.1, 7.1 and 8.3 1/nm correspond to hkl planes (111), (002), (022), (113) and (222) of cubic closed packed crystalline system. Therefore, with the brightfield and dark-field TEM images of the FIB section, shown in Figure 4.17a and b, certain characteristics can be determined: the carbon support size distribution is approximately 50 nm in size, porosity in nano and microscale can be visualized and Pt size distribution approximately 5 nm in size can be distinguished. However, due to the projection nature of these images, which result in the overlapping of the particles (seen as different levels of gray contrast in the carbon support particles on Figure 4.17c), the carbon support particle size distribution and porosity cannot be accurately determined.



Figure 4.17 (a) Bright-field and **(b)** dark-field images of the cathode in a CCM sample prepared with FIB milling. Only Pt nanoparticle distribution can be accurately assessed, as the projection nature of the images could give inaccurate information regarding the carbon support particle size distribution and porosity **(c)** Bright-field TEM image taken at 80 kV demonstrating the projection problem known to TEM images (different levels of gray in the carbon support area) **(d)** diffraction pattern demonstrating nanocrystalline Pt particles.

4.3.2 Electron tomography

To overcome the projection problem, electron tomography was used to determine the 3-D characteristics of the sample. The advantage of visualizing an orthoslice image of the reconstructed volume is that the information is not a
projection image; rather it is a digital slice of the 3-D reconstructed volume perpendicular to a viewing direction. Therefore, the image represents a slice through the structure rather than a projection of the structure. The former is more interpretable and quantifiable than the latter (FEI COMPANYTM, 2003). **Figure 4.18** shows an orthoslice view in the XY direction of the tomographic tilt series of the FIB section with the inset indicating the slice from the voxel image in a WBP reconstruction. The voxel projection is a summation of the 3D data set at a specific direction and, therefore, corresponds to the original projection images acquired in the tilt series. It is clearly visible from **Figure 4.18** that the Pt particles sit on the surface of the hollow graphitic carbon support, consistent with the work of Banham et al. (2011), which is not discernible in 2-D projection images (**Figure 4.17**). The knowledge of the position of the Pt particles on the carbon support can help predict the performance of the fuel cell, which is related to the surface area available for the ORR to take place (Gontard et al. 2008).



Figure 4.18 Orthoslice number 68 (of 141 slices) of FIB prepared CCM section. The tilt series was reconstructed with WBP, and the image shows that the Pt particles sit on the surface of the carbon support, which is identified by the presence of small Ga particles. The inset is a voxel representation showing the XY direction of the orthoslice.

Figure 4.19 shows a voxel projection image of a WBP reconstruction looking at the XY direction which corresponds to the 0° tilt angle from the original acquisition of the FIB section. Circled areas in both images correspond

to views of the same particles, but one is a projection view from the 3-D reconstructed volume and another is from the original tilt series. Images like these shows that the reconstruction algorithm chosen is adequate. An advantage of using voxel projections is the possibility of modifying their optical properties to enhance information (Midgley & Weyland 2011).



Figure 4.19 (a) Voxel projection image from a WBP reconstruction and **(b)** 0° tilt projection image from the original tilt series of the FIB section. The voxel image corresponds to the projection image as shown by the illustrated circles with the same colors in both images.

Even though the carbon support is not visible on the HAADF-STEM images (**Figure 4.20**), the Ga ions (contamination from the FIB milling) sit on the surface (or are embedded) of (in) the carbon support as well as the Pt nanoparticles. Therefore, the Ga ions help visualize the location of the carbon support and are small nanoparticles of approximately 1-2 nm in size. The determination of the resolution of a tilt series is not straightforward, but nanofeatures are clearly visible in the tomography data. The resolution of a reconstructed volume is approximately D/100 (Midgley & Weyland 2003). A rule of thumb is to consider the resolution 3*t/N, where t is the thickness of the sample and N is the number of images taken (Ziese et al. 2004). Although the diameter of the resolution of the acquired tilt series is ~1nm based on the smallest features visible in the tomograms.

Difficulties to visualize the carbon support and the Pt nanoparticles simultaneously in the same tilt series has been reported (Gontard et al. 2008). In order to visualize both structures, it was suggested that two tilt series should be acquired: first, a HAADF-STEM to determine the shapes of Pt particles and the second either ADF or BF-STEM to infer their position on the carbon support. Another alternative is to remove the Pt particles from the tilt series digitally with image processing techniques, interpolate the matrix on top of these missing particles, and then reconstruct the matrix. The group successfully used HAADF with a lower inner detector semi-angle and was able to determine the position of the Pt on the carbon support, even though the Pt saturated the images (Gontard et al. 2008). Since we used a FIB section and the Ga ions sit on the carbon support, this procedure was not necessary.

With careful analysis, it is possible to see movement of the particles during most of the tilt series acquisitions. **Figure 4.20 (a)** and **(b)** compares the original tilt series at 0° and 1° tilt angle, which correspond to the first and the 71st image taken from a total of 141 images, respectively. The circled regions clearly show the movement of the particles. Even though the movement was subtle, the alignment of the images is impossible as shown by the banana shaped features in the orthoslice view in the Z direction of the WBP reconstructed volume in **Figure 4.20 (c)**; the inset shows the voxel projection of the position of the orthoslice. The movement of the sample could be due to damage of the PFSA ionomer layer present in small proportions or to the porous nature of the sample (not a sustainable framework).

Another tilt series was acquired with the same FIB section, after further thinning in the FIB. **Figure 4.21** compares the -65° tilt projection image from the tilt series of the thicker and thinner section and shows that the thicker sample highly saturates the image at high tilt angles. This, in turn, will increase 'the missing wedge' causing elongation of the features in the Z direction because these images have to be removed for the reconstruction or they will be responsible for artefacts in the reconstructed volume (Midgley & Weyland 2003; Midgley & Weyland 2011).



Figure 4.20 (a) and (b) are projection images taken from the original tilt series of the FIB prepared CCM of the thicker sample at 0° and 1° , which correspond to the first and 71^{st} image taken. The circled area highlights the movement of the sample during the acquisition (c) Orthoslice number 68 (of 141 slices) in the Z direction reconstructed by WBP showing that the Pt particles are not well defined, indicating a misalignment of the images, in this case due to the movement of the sample. The voxel projection shows the Z direction of the slice.



Figure 4.21 Effect of sample thickness. HAADF-STEM projection images from the original tilt series at (a) -65° of thicker sample and (b) -64° of thinner FIB prepared CCM sample.

In order to avoid the movement of the particles, the focusing was done in an area approximately 0.5 μ m away from the area of interest. Even though this acquisition had a 2 degree increment, the quality of the reconstructed volume is far superior to that of the first (compare **Figure 4.22**, **Figure 4.20** and **Figure 4.18**). A comparison between the WBP and SIRT reconstructed volumes indicates that the quality of the SIRT reconstruction is superior than the WBP. The presence of artefacts, such as dotlike or floating objects present in **Figure 4.22** (a) was also observed in the WBP reconstruction of FePd nanoparticles, but were absent in the SIRT reconstruction (Sato et al. 2010).



Figure 4.22 Reconstructed volumes from two algorithms of thinned FIB-prepared CCM sample, (a) WBP and (b) SIRT with 25 iterations. It is clear that SIRT reconstruction has less noise and artifacts present than the WBP reconstruction as illustrated by the circled areas in both images.

4.3.3 Microtome section

Due to the heterogenous penetration of the PS in the cathode of the microtome section, as shown in **Figure 2.1**, we were able to visualize, with the TEM, regions on the side surface of the carbon support particles that appeared to be amorphous (arrow shown in **Figure 4.23**). This can be originating from three possible sources: the PFSA ionomer, PS or even amorphous carbon from the carbon support (**Figure 4.23**). These amorphous components are also seen at 80 kV (**Figure 4.23 c** and **d**), leading to better contrast for low-atomic number elements, and are seen on the outer layer of the carbon support particles, involving a Pt nanoparticle. The use of an embedding material in microtome sample preparation can complicate the interpretation of the images, as a new

material is introduced within the sample with similar contrast to other materials already present.

In **Figure 4.23(a)** and **(b)**, this feature is imaged and, within seconds of exposure to the electron beam, we observe that it is easily damaged as it clearly detaches and shrinks from its original morphology. Without spectroscopic analysis it is difficult to confirm whether this feature is due to the PFSA ionomer



Figure 4.23 Bright-field images of the cathode CCM of the microtomy section at **(a)** and **(b)** 200kV and **(c)** and **(d)** 80 kV. Could the amorphous components surrounding the carbon support particles be PFSA ionomer, PS or simply amorphous carbon support?

or simply residual carbon support material. Due to its sensitivity to the electron beam, the visible component is probably PFSA ionomer as the other components of the CCM (such as carbon black and Pt) would not damage this easily. The main challenge is to minimize the radiation damage so that analytical measurements can still be taken to confirm the elements present. The lack of successful electron tomography with the microtome section indicates that the embedding material is also sensitive to the electron beam, as the sample moved during the tilt series acquisition. The comparison of the features seen with both sections (microtome and FIB) confirms that the ion beam used for the FIB sample preparation causes extensive damage, as will be shown in section 4.4.

4.3.4 Cryo-Microtome

The embedding material used in microtomy is necessary to hold the sample together while sectioning. An alternative to avoid the polymeric embedding material is to use cryo-microtomy. The sample still has to be held together and a sucrose solution is commonly used. Maintaining the integrity of the cathode material proved to be harder than in ambient temperature microtomy, as shown in the optical micrographs in **Figure 4.24**. The sucrose solution was washed off with water after the sections were put onto the grid; this, however, can change the physical properties of the membrane and possibly the PFSA ionomer. The crystalline nature of the graphite sheets in the carbon support was maintained (**Figure 4.25c**) and a similar amorphous feature as was seen in the microtomy section is shown in **Figure 4.25b**. This feature is most likely residual carbon from the graphite sheets and not PFSA ionomer, as it was stable under the electron beam. EDX maps demonstrate that there is PFSA ionomer in this layer (**Figure 4.25c**).



Figure 4.24 Optical micrographs demonstrating that the integrity of the (a) cryomicrotomy section is not the same when the sectioning is done with an embedding material at room temperature, as shown in (b).



Figure 4.25 TEM analysis of the cryo-microtomy CCM commercial sample (a) TEM bright-field image indicating a similar amorphous feature as found in the microtomy section in Figure 4.23 (b) TEM bright-field images indicating the crystalline nature of the carbon support graphite sheets and (c) HAADF image with corresponding EDX maps of the squared region.

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4.4 Damage done by Focused Ion Beam (FIB)

4.4.1 Amorphization of carbon support and PFSA ionomer component

The cathode catalyst layer of the PEMFC consists of Pt nanoparticles on a graphitic carbon support (**Figure 4.26**). TEM bright-field images of this layer clearly indicate the crystallinity of the graphitic layers of the carbon support material and the Pt nanoparticles in a microtomed section (**Figure 4.26a**). The FIB section of the same sample, on the other hand, shows the support material is amorphized (**Figure 4.26b**). TEM clearly demonstrates the extensive damage the FIB preparation can causes to the crystalline nature of the carbon support particles. Amorphization is a common damage effect of FIB in other materials as well, such as Si (Mayer et al. 2007). The extensive damage can be particularly severe due to the porous nature of the material, facilitating the penetration of the ions and the internal surfaces that are normal to the incident beam.



Figure 4.26 TEM bright-field images of the cathode catalyst layer with Pt nanoparticles and carbon support (a) in the microtomed and (b) in FIB section. The crystalline nature of the carbon support particles is destroyed in the FIB section.

While at the fine scale damage is severe on the support, it is possible that the amorphization of the carbon support doesn't affect the porosity or pore-size distribution of the cathode catalyst layer, which can be assessed with FIB-SEM serial tomography. Although concerned with amorphization of the catalyst layer, Schulenburg et al. (2011) determined that there is no porosity difference in the cathode of a CCM milled with FIB-SEM at room temperature compared with cryo-conditions (at 30 kV). They concluded that the <u>high electron and heat conductivity of the catalyst layer prevented</u> a significant degradation of the porous structure of the catalyst structure. However, PFSA ionomer membranes (Vie & Kjelstrup 2004) and single PEMFCs (Burheim et al. 2010) actually have low thermal conductivities. Additionally, cryo-FIB of polymers with low thermal conductivity (polypropylene) delay but do not prevent local heating while milling (Schmied et al. 2012). Although the porous structure is maintained after FIB milling, the low thermal conductivity can lead to softening and reduction of rigidity during the final polishing steps (Bassim et al. 2012) as well as result in significant structural damage that should be acknowledged as it can influence other factors.

The amorphization of the carbon support can be easily assessed with TEM images. However, FIB milling not only causes damage to this carbon-containing component, as can be seen with STXM (Figure 4.27). The STXM C 1s edge of the cathode catalyst layer of the same CCM sample prepared with FIB and microtome is show in Figure 4.27. The overall spectrum of the cathode is shown for both sections in Figure 4.27a. Since the FIB section is only composed of the carbon support, Pt and PFSA ionomer (as well as Ga ions from the beam and W deposited to protect the sample for FIB sectioning shown in Figure 4.29), the PS signal from the embedding material used in the microtome sample was subtracted from the overall spectra for the microtome sample. The offset difference between spectra from both sections is probably due to the presence of the Ga and W in the FIB section. These heavy metals will also absorb photons but won't generate fine structural features at the C edge energy. The difference in the fine structure of the C edge for both sections is likely due to the FIB causing a loss of the C 1s fine structure and broadening of the C 1s continuum, induced by amorphization of both the graphitic carbon support and the PFSA ionomer.

Since the different components that contain carbon have different electronic fine structures, it is possible to map each component in the section. The approach consists of using reference spectra of the known components: PFSA ionomer and carbon support, to know if there are regions in the sampled area that contain high amounts of a particular component. The next step is to isolate the spectra from pure phase regions and therefore obtain internal reference spectra. The challenge starts with the FIB sample no longer having a pure carbon support or PFSA ionomer component and the PS penetrated into the cathode of the microtome sample. This means that we had to find alternative spectra for the damaged components for the FIB section.

For the C 1s stack fit of the FIB sample (**Figure 4.27b**), a distorted carbon support component was found isolated with the rest of the C containing component being amorphous carbon. The residual of the stack fit is a good indicator for a successful fit, and the absence of a pattern indicates that the FIB section is mostly made up of amorphous carbon, and not crystalline carbon support. The image with red brackets of the FIB region is the selected region for the carbon spectra shown in **Figure 4.27a**. Component maps for the carbon support, amorphous carbon and constant are shown with a quantitative thickness scale (in nm). The FIB sample is estimated to be around 100 nm thick, as indicated by the maximum thickness in the component map scale. A composite map with carbon support, amorphous carbon and constant is used to demonstrate that the section is mostly made up of amorphous carbon after FIB is used to mill the sample.

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Figure 4.27 C 1s edge spectra of **(a)** FIB and microtomed cathode section, **(b)** carbon support and amorphous carbon make up the FIB spectrum shown in (a) and component maps in nanometer scale of each in the FIB section, **(c)** graphitic carbon support, PFSA ionomer, PS, holey carbon make up the microtome spectrum shown in (a) and component maps in nanometer scale of the microtome section. The major difference between both sections is the amorphous carbon that makes up majority of the FIB sample instead of carbon support and PFSA ionomer that are majority in the microtome section. Master's Thesis - Lis G. A. Melo; McMaster University - Materials Science and Engineering

For the microtome section, all C containing components were isolated: PS, PFSA ionomer, carbon support, holey carbon and a constant. The C 1s internal reference spectra found for each component is shown in the graph in **Figure 4.27c**. These spectra were used for the stack fit, which generated the component maps shown in nanometer scale. PS and holey carbon are components that are not expected in the FIB sample, as they were not used to prepare that section. The difference in the C 1s edge spectra of the PFSA ionomer (Susac et al. 2011). The absence of signature peaks at the PFSA ionomer in the C 1s spectrum of the FIB section shows that the C 1s signal is not as useful (relative to the F 1s signal) to assess structural information about this component in the FIB section. Since the quantity of PFSA ionomer in the cathode is less than that present in the membrane, the membrane signal was masked and the PFSA ionomer is shown in the cathode of the microtome section (PSFA in cathode).

A comparison of C-edge spectra of FIB and microtome sections was done previously with a polyacrylamide (PAAm) sample. It was observed that the final polishing steps and the electron beam used for FIB milling were responsible for the structural changes observed (Bassim et al. 2012). Of the limited reports on evaluating FIB damage on soft materials, Bassim et.al. (2012) conducted an extensive study to minimize FIB induced damage on soft materials. The alterations of the chemical structure of two polymeric materials were analyzed with X-ray absorption in a STXM by varying the final polishing steps: low energy Ar⁺ ion milling and low energy FIB milling (at 500 ev to 2kV), and compared with a microtome prepared sample. It was found that the electron beam used for visualizing the sample during the FIB preparation was the major cause of chemical change, being responsible for hydrogen loss in both samples. Cryo-FIB was used in the final polishing for refractory lignite coal (aromatic bonds) and it was found to cause less structural chemical changes when used at 2 and 5 kV. Final polishing with 30 kV cryo FIB and 500 eV Ar⁺ cryo mill in absence of electron beam imaging caused an additional photoabsoption in the lignite coal sample. Ga⁺ ions also caused knock-on damage in the PAAm sample, causing more hydrogen loss, when the final polishing steps were varied.

Although using low currents may reduce damage caused by FIB (Schulenburg, 2012), our work shows that there is still significant degradation of the structure of the carbon support, as well as mass loss of the PFSA ionomer. The changes that we observed in our sample are beyond the damage that was observed in PAAm which was basically hydrogen loss. Although PAAm has a lower melting point than PFSA ionomers, whose thermal properties depend on the water content, a higher heating effect was calculated for FIB preparation in another polymer with higher melting point, lignite coal, than in PAAm (Bassim et al. 2012).

4.4.2 Gallium contamination

Figure 4.28 shows that Ga contamination can be seen as small particles of approximately 2 nm in size on 'top' of the carbon support particles, as was discussed in section 4.3.2. An HAADF image (Figure 4.28a) with atomic number contrast shows that the smaller particles are not Pt as the contrast is different from the 5-10 nm Pt nanoparticles present. These particles are also seen in a HRTEM image (Figure 4.28b), particularly at the edge of the carbon support particles. High-resolution images obtained at 80 kV also show that there is an amorphous layer at the edge of the carbon support particles embedded with Ga ions and Pt nanoparticles of approximately 5 nm (Figure 4.28c). This amorphous layer is a consequence of ion implantation, which results from knock-on damage by which Ga+ ions displace atoms in the target material (Giannuzzi et al. 2005). The implantation of some Ga ions occurs concurrently with the sputtering of the surface that is exposed if the energy of the incident ions is moderate. The sputtering generates a steady-state condition between the implantation of impurity atoms and removal of atoms from region of interest as well as the impurity atoms. The amount of impurity atoms implanted on the surface is inversely proportional to how rapidly the material is sputtered (Giannuzzi et al. 2005). Chemical alteration due to knock-on damage from the Ga ions is usually constrained to a thin surface layer of the FIB-prepared

sample, and a 'pristine' core should exist in the centre of the sample (Bassim et al. 2012). However, in porous materials, such as the catalyst layer in a PEMFC, it is possible that the penetration of the Ga ions is much deeper than in a rigid solid body due to the larger number of surfaces that will be normal to the incident beam and thus the ions travel deeper into the samples.





Figure 4.28 Ga contamination in the FIB section of the cathode catalyst layer CCM sample (a) HAADF image and (b) 200kV HRTEM image indicating the presence of small nanoparticles (~2nm in size) (c) 80 kV HRTEM (Titan2) showing Ga nanoparticles and an amorphous layer of 5 nm that surrounds the carbon support particle.

The contamination of Ga can be seen on the FIB section with EDX mapping (Figure 4.29). Figure 4.29a shows a HAADF image of the carbon support and Pt particles of FIB section and Figure 4.29b shows EDX maps of the region in (a). Ga can be seen everywhere, demonstrating that the smaller nanoparticles present on the carbon support are indeed Ga ions from the ion beam.



Figure 4.29 a) HAADF of cathode catalyst layer CCM sample b) EDX component maps demonstrating that Ga ions are not only on the carbon support particles, but also on Pt nanoparticles. Fluorine, Tungsten, Pt, Oxygen and Carbon have been detected as well.

Although different materials respond differently to the implantation of Ga, we can expect implantation of Ga on the surface of the carbon support particles. Lehrer *et.al.* (2000) analyzed the vertical and lateral gallium contamination in a single crystal silicon sample using different gallium ion doses (ranging from FIB inspection to sputter removal) by Secondary Ion Mass Spectroscopy (SIMS). Using a 30 kV with up to 7 nA current beam, it was observed that the measured gallium contamination increases with ion dose. Vertical and lateral contamination can reach some hundredths of nanometers into the sample.

It is important to minimize the dose, especially in the final polishing steps of the FIB milling. If the dose is high enough it is still sufficient to cause knockon damage in a PAAm sample, being responsible for hydrogen loss (Bassim et al. 2012). If the Ga contamination can be minimized, it is possible that the amorphization layer of carbon support and PFSA ionomer can be removed from the FIB section.

4.4.3 PFSA ionomer component mass loss

As was mentioned above, mapping the PFSA ionomer with the C-edge using STXM is a challenge in the FIB sample, as most of the sample becomes amorphous carbon following FIB milling. Although the radiation damage from the ion beam reduces the amount of fluorine present in the FIB-ed cathode, qualitative fluorine mapping can be done in the cathode of the catalyst layer with EDX linescan and mapping/STEM (**Figure 4.30**). The advantage of using EDX/STEM is the high spatial resolution possible with electron microscopes. However, low dose conditions used to prevent radiation damage to the PFSA ionomer are not compatible with the conditions needed for the analytical analysis.

An EDX linescan of the cathode region in the microtome section indicates that fluorine is detected, but due to the porous nature of the sample the variation of intensity of the signal can be related to the morphology of the sample (for example the thickness) and not necessarily the relative concentration (Figure 4.30 (b)). An advantage of doing elemental mapping is that the spatial distribution of each element is visible. EDX mapping of the cathode in both the microtome and FIB sections are shown in Figure 4.30 (a) and indicate that there may be fluorine loss in the FIB section. Although EDX is not a quantifiable technique for porous samples, Figure 4.30 (c) indicates that there is a variation in fluorine throughout the FIB section. Quantification with EDX is complex and depends on factors such as the fluorescence yield for the peak, the fraction of the peak measured, the ionization of the same peak, and also on factors related to the sample, such as thickness, weight fraction and atomic weight (Botton 2007). Each spectrum in Figure 4.30 (c) was generated from different regions within the sample, as shown in the corresponding image of the FIB section. This FIB section was analyzed by the STXM beforehand,

and the variation could also be due to radiation damage caused with the X-ray beam. EDX mapping to identify PFSA ionomer has been used in the SEM for a PEMFC anode catalyst layer (Scheiba et al. 2008). However, due to the large interaction volume of x-rays that result from the interaction of the (SEM) electron beam with sample, EDX mappings from cross-sections can be misleading as the information can be from deeper regions within the sample than what the surface sensitive (secondary) image show. Nevertheless, EDX is only a qualitative technique for measuring PFSA ionomer content.



Figure 4.30 (a) EDX maps of the FIB and microtome section indicating Ga contamination and a lower fluorine content in the FIB section, compared to the microtome section.



Figure 4.30 continued (b) region of EDX linescan of microtome section indicating presence of inhomogeneous fluorine content in the cathode region of the CCM. **(c)** indicated regions of FIB section where EDX spectra were derived indicating higher fluorine content closer to the bottom (indicated as B) of the sample, and closer to the membrane.

Another analytical technique widely available in TEMs is EELS. For light element analysis, EELS is more appropriate than EDX with the main challenge being the need for a thin sample. The probability of generation and excitation of X-rays (EDX) occur after the interaction of the electron beam with the sample and are secondary events. The excitation depends on the atomic number and the fluorescence yield of the elements present in the sample. Light elements emit less X-rays than heavier elements and these can be absorbed within the sample or the detector material (Botton 2007). On the other hand, the spectra generated in EELS are due to the primary scattering event that precedes the generation of X-rays: excitation of electronic states in the sample due to inelastic scattering of the electron beam. The intensity of the energy loss signals is strongly related with the thickness of the sample, and elements can be undetected when thick samples are analysed (Botton 2007).

The lowest thickness of a microtomy section that maintains the integrity of the cathode catalyst layer is approximately ~100 nm. The key to maintaining an uniform thickness has to do with the complexity of the CCM sample and considerations of the softness of both the membrane and embedding material, as well as of the carbon support/Pt catalyst. EELS spectrum imaging, linescan and spectra from regions were acquired for both FIB and microtome sections. However, the high thickness (~100 nm) and possibly non-homogenous distribution of the PFSA ionomer in nanometer scale or radiation damage prevented a reliable PFSA ionomer mapping by EELS in the microtome section (results not shown). Essentially, obtaining a thinner section is possible with the FIB, with the disadvantage of ion beam damage as already discussed. This means that EELS analysis is more favorable on thinner FIB sections (Figure **4.31**) than on thicker microtomy sections (results not shown), which explains why fluorine was more easily detected in the FIB section. Figure 4.31 demonstrates that EELS can be used to map PFSA ionomer in the cathode of a CCM (prepared by FIB sectioning), and shows a homogenous distribution of this component at the imaged scale. However, measuring the radiation damage done during this analysis is not straightforward and damage done with the FIB is severe.

This thickness dependence is less severe for STXM than for TEM-EELS and therefore thicker samples are allowed. Although the sample has to be transparent to X-rays, the optimum OD is in the range of 0.3-2, which corresponds to thicknesses of approximately 30-200 nm for C 1s and 200-500 nm for O 1s edges for unit density materials with carbon and oxygen as majority components. Thicker sections can be analysed for low density materials, such as porous membranes (Hitchcock et al. 2005). Therefore, reliable quantitative analysis of the fluorine content and spectroscopy was achieved with STXM for both sections, independent of the thickness (F maps are shown in **Figure 4.32**).

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Pt (215-272 eV) C (280-352 eV) O (520-600 eV) F (681-709 eV) Pt, F, C

Figure 4.31 Component maps of Pt, C, O and F from EELS spectrum imaging of the FIB section after STXM analysis. A RGB composite map is shown on the far right, indicating a somewhat homogenous distribution of fluorine in the cathode.

For the F 1s edge STXM maps in **Figure 4.32**, the constant is a value related to every other component present in the sample that does not contain fluorine. For the cathode, the constant is made up of Pt and carbon support. For the FIB section, there will also be Ga from the source and W from a protective layer used for FIB. For the microtome section, there are additional contributions from the holey carbon and PS (embedding material). The maps from both sections indicate that the PFSA ionomer is somewhat homogenously distributed in a micrometer scale, which is in agreement with EELS (Figure 4.31). The difference in colors for the composite map is that three components are needed, and the FIB only has two (while microtome has a membrane component). The more intense red in the right half side of cathode of the microtome section is related to the penetration of the PS. The difference in nanometer scale for the PFSA ionomer is an indicator that there is less PFSA ionomer in the FIB section compared to the microtome section.



Figure 4.32 STXM F1s edge stack fit indicating constant (everything in the sample that absorbs but does not contain F), the PFSA ionomer and membrane for the microtome section. Both are from cathode region from the same CCM sample.

The C 1s edge spectra and images from the FIB section were shown in **Figure 4.27.** Due to the damage done on this section, the characteristic C 1s spectral features of PFSA ionomer were not observed. The PFSA ionomer is actually better mapped with the F 1s edge, because it is the only component in the sample that contains fluorine (Susac et al. 2011). Therefore, the F 1s edge spectra is shown in **Figure 4.33** for the microtome and FIB section of the cathode catalyst layer of the same CCM sample and is related to the PFSA ionomer component only. There is a big difference between the offset of the F 1s edge spectra for the microtome and FIB sections (**Figure 4.33a**), which is probably due to the Ga contamination and the W that is used for protecting the sample while milling. However, if both F 1s edge spectra are rescaled, it is seen that the FIB section has a broader peak, indicating that there is some PFSA ionomer left, but with a different fine structure than in the microtome sample. This means that the chemical structure of the damaged product is different than

that of the original PFSA ionomer. The broader peak usually means that there is a range of F local chemistry environments and possibly loss of crystallinity, which could be associated with a disintegration of the Teflon backbone.

Quantitative analysis of the PFSA ionomer in the FIB section shows that there is significant mass loss compared with the microtome section (Figure **4.33b**). In order to make sure that this result is not due to inhomogenous distribution of the PFSA ionomer component and that the FIB section had less PFSA ionomer content, different regions in the microtome section were also analyzed, as well as a sample prepared with cryo-microtome (treated in section 4.3.4). Microtome sections 1 and 2 in (Figure 4.33b) indicate different regions of the cathode from the same specimen. It is seen that all microtome sections have a similar PFSA ionomer content of approximately 40, while the FIB section is nearly half of that amount. The fractional amount of PFSA ionomer was calculated by dividing the total amount of PFSA ionomer with the total sum of signal in the selected region. These signals come from the histograms generated from the maps that are shown in Figure 4.32. In this case, we don't know the reference of the non-fluoronated species and an arbitrary number was used to get the total sum. Although the final value is not absolute, it is quantitative and relevant. It is important to state that although STXM allows the determination of the thickness of each component, the damage caused by the ion beam in the FIB section is challenging to quantify as we do not know the electronic structure or elemental composition of the final damaged PFSA ionomer. The relative mass loss of fluorine is approximately 50% for the FIB sample preparation.

In another attempt to quantify fluorine in the FIB sample using different reference spectra (**Figure 4.34**), the fractional amount of PFSA ionomer is similar to the results shown in **Figure 4.33**. In this case, two reference spectra were used: PFSA ionomer and damaged PFSA ionomer. The PFSA ionomer reference spectra used was from the membrane in the microtome sample and the damaged PFSA ionomer spectra was taken from a region where there was a high amount of this component. For the quantification, the amounts of damaged and pristine PFSA ionomer together sum up to a similar amount as

shown in **Figure 4.33b** indicating that the quantitative amount of the component (damaged or pristine PFSA ionomer) is the same. A comparison of the mean value of the thickness of the component maps of damaged PFSA ionomer (5 ± 3 nm) and undamaged PFSA ionomer (0 ± 4 nm) shown in **Figure 4.34**a and b, respectively, indicate that the PFSA ionomer is mostly damaged.



Figure 4.33 F 1s edge spectra from stack images in the FIB and microtome sections of a cathode region in the same CCM sample showing (a) spectral shape and magnitude are dramatically different (b) consistency of PFSA ionomer content within the cathode (different regions (1 and 2) of microtome sample and cryo-microtome sample and quantitative analysis of fluorine indicating that there is a mass loss of approximately half of the PFSA ionomer in the FIB section.



Figure 4.34 Alternative F stack fit using 2 components for the FIB section: reference spectra from membrane of the microtome section and a damaged PFSA ionomer component taken from this section (a) damaged PFSA ionomer map (b) pristine PFSA ionomer map (c) constant map and (d) RGB composite map showing all components.

Why is the damage caused by the FIB sample preparation so high? The high mass of the Ga⁺ ion beam means that only a small energy is necessary to

displace atoms. The cross section of the interaction of the ion beam with matter and the amount of energy that is transferred is generally much higher than with electron beams (Banhart 1999). This means that ion irradiation causes more damage than electron irradiation since practically all of the kinetic energy of the ions is dissipated into the specimen. The local heating in a FIB prepared sample is confined to the region of interaction between incident ions and target atoms, which is in the order of a few tens of nanometers. This effect can be considered negligible for most materials (Giannuzzi et al. 2005).

The electronic structure of the sample strongly affects the damage mechanism. Since eV range electronic excitations in metals and graphite are not localized due to the presence of conduction electrons, knock-on atom displacements are more important. On the other hand, electronic excitations result in instabilities and rearrangements of the atomic bonds which may lead to bond-breaking in insulators (Krasheninnikov & Banhart 2007; Banhart 1999).

Since PFSA ionomers are insulators, bond breaking is most likely the primary mechanism of radiation damage. However, the majority of the damage could be done by secondary electrons used to image the sample while FIB milling. Therefore, it is possible that the presence of a thin layer of PFSA ionomer in the catalyst layer helps hinder the Pt/carbon support from dissipating the heat, which could then lead to a large increase of temperature damaging part of the PFSA ionomer layer in the cathode. The presence of Pt/C particles has been seen to affect the radiation damage (signal intensity as a function of beam dose) on fuel cell samples with varying amounts of PFSA ionomer (from pure Nafion® to 29% Nafion® in the catalyst layer): the sample with the lowest amount of PFSA ionomer was the most susceptible to radiation damage while a sample with pure PFSA ionomer was more resistant as these particles probably act as catalytic sites (He et al. 2013).

Ga⁺ implantation into the surface of the material results in knock-on damage, which occurs as these ions displace the atoms from the sample (Giannuzzi et al. 2005). This knock-on damage can remove functional groups, either side chains or long chains in polymers, resulting in surface chemistry alterations (Bassim et al. 2012). This could mean that when the Ga interacts

with the PFSA ionomer, instead of just sputtering its atoms, breaks down the side chains of the PFSA ionomer.

Chemical alteration due to knock-on damage from the Ga ions is usually constrained to a thin surface layer of the FIB-prepared sample, and a 'pristine' core should exist in the centre of the sample (Bassim *et.al.*, 2012). However, in porous materials, such as the catalyst layer in a PEMFC, it is possible that the penetration of the Ga ions is much deeper than in a rigid solid body.

In studies of the thermal behavior of PFSA ionomer membrane of different forms, such as in acidic form (Almeida & Kawano 1999) or in different gaseous environments (Samms et al. 1996), the mass loss is similar and is attributed to: water evaporation (up to ~250°C) followed by a desulfonation process, which is due to loss of SO₂ and side-chain decomposition and lastly PTFE backbone decomposition with a high mass loss at around 500°C. Basically, PFSA ionomer membranes are thermally stable up to approximately 300°C, where the sulfonic acid groups are first lost (Surowiec & Bogoczek 1988).

The effect of irradiation on materials is not always unwanted. Accompanied with heat treatment, beneficial effects have been observed on nanostructured materials, especially carbon nanosystems, such as highpressure transformations in the nanoscale. This means that the systems can be modified with almost atomic precision if using an electron beam, and this is important for technological applications. Therefore, it is possible to use energetic beams for functionalizing graphitic nanostructures, as the irradiationinduced defects increase the local chemical reactivity relative to that of the basal place of graphite, which is almost inert (Krasheninnikov & Banhart 2007).

Although using low ion currents may minimize damage caused by FIB (Schulenburg et al. 2012), our work shows that there is significant degradation to the structure of the carbon support done with FIB, as well as mass loss of the PFSA ionomer. In the quest to image PFSA ionomer in the catalyst layer the sample preparation is crucial to achieving nanoscale resolution. However, both sample preparation techniques used impose problems in the visualization of the PFSA ionomer: thickness for EELS with microtoming and damage with FIB. We believe that if the FIB damage is minimized, it is possible to image the PFSA

ionomer. This will require future work testing different low dose sample preparation and cryo-FIB procedures.

4.5 Damage done with Electron and X-ray radiation

Although PFSA ionomer is known to suffer radiation damage, the damage suffered by electron radiation could be more severe than originally thought. After our FIB sample was prepared, STXM was first used to assess the C and F 1s edge stack maps and stacks. After that, TEM analysis was done on the sample with the objective to image and map the PFSA ionomer in STEM/EDX and STEM/EELS mode. These results were shown in (**Figure 4.28**, **Figure 4.29**, **Figure 4.30**, and **Figure 4.31**. The sample was taken back to the STXM and a new F 1s edge stack analysis was done. Although the TEM dose wasn't quantified or controlled, comparison of the F map on the FIB sample before and after TEM analysis shows that the (already damaged) PFSA ionomer that was left after FIB sectioning (average thickness of 5.07 ± 2.36 nm) is entirely gone after electron microscopy analysis (average thickness of 1.32 ± 5.26 nm) (**Figure 4.35**). The area analyzed in **Figure 4.35** after TEM analysis is larger than the one before TEM analysis.



Figure 4.35 STXM F 1s edge maps of the FIB section before and after TEM analysis. The fractional amount of PFSA ionomer decreases from ~20% to nearly 0% after TEM analysis.

The analysis done with X-rays in STXM also causes damage to the PFSA ionomer component. We were able to assess the membrane mass loss suffered with the STXM analysis by analyzing a C 1s edge image in the microtome section. As shown in **Figure 4.27c**, the strongest C 1s peak of PFSA ionomer is at 292.6 eV. Therefore, an image taken in this energy shows primarily PFSA ionomer contrast as can be seen in **Figure 4.36**. The membrane region is the lightest intensity, indicating heavy concentration of PFSA ionomer. The darker region seen in the membrane is due to the radiation damage caused by STXM analysis (yellow circle indicated in **Figure 4.36**). A line profile taken from the optical density image at this energy indicated that there was approximately 35-40% mass loss, after several images and F 1s and C 1s stacks with dwell times of 50 and 55 ms at each pixel point, respectively, amounting to about 120 ms total exposure at each pixel.



Figure 4.36 Damage check after C 1s and F 1s stack-maps and stacks taken at 292.6 eV, peak of maximum intensity of PFSA ionomer. Line profile of the optical density image shows that the STXM analysis was responsible for 35-40% mass loss in the membrane.

The photon beam damage on the cryo-microtomy section is shown in **Figure 4.37**. The STXM analysis (which consisted of acquisition of preliminary imaging to find the region, two stack maps and two stacks at the C 1s and F 1 s edge) resulted in a mass loss of 20% for the C stack and 43% for the combination of the F 1s and C 1s stacks and both stack maps, as seen in the optical density image in **Figure 4.37a** taken at 292.6 eV. This energy corresponds to the first major peak of the membrane, as shown in **Figure 4.37b**. Stack map acquisition is much less damaging than the full stack acquisition (typically using only 2 ms/pixel instead of 50-60 ms/pixel), and thus the ionomer mapping from the F 1s stack map provides accurate quantitative analysis. **Figure 4.37b** compares C 1s edge spectra of the damaged by STXM (after stack maps and the F 1s and C 1s stack) (pink outlined area in **Figure 4.37a**) and the 'undamaged' membrane (only stack maps and C 1s stack was done in this region) (green outlined area). The comparison reveals that the damaged membrane has weaker σ^*_{C-F} signal and additional peaks at 285 eV

(formation of C=C bonds in the backbone) and 287 eV (probably from C-O bond formation).



Figure 4.37 Photon beam damage on membrane of a cryo-microtomed CCM sample. (a) A 292.6 eV image is shown, where the damage on the membrane is obvious (right side of the image). The pink square is membrane in the area where the F-stack was performed while the green area is from the C-stack outside the area where the F-stack was measured. (b) Spectrum from the pink and green regions shown in (a). These spectra were taken from the C-stack and indicate the C-edge spectra of the heavily damaged membrane, with distinct differences between the spectra.

Although the same technique (STXM) was used to assess the radiation damage (from electron and X-ray beam), here we show two ways of quantifying the mass loss of PFSA ionomer: using F 1s stack of the same region before and after TEM analysis and by using a line profile of the optical density of one image at 292.6 eV. Using one image is easier and faster to analyze the damage done and the stack images taken can induce further damage. However, for the FIB induced damage, using one image-method is not straightforward to quantify the electron/photon beam induced damage as the spectral features have been altered.

Figure 4.35 showed that the mass loss of PFSA ionomer in the cathode of the CCM was nearly 100% after TEM analysis, while **Figure 4.36** demonstrated only 35-40% mass loss in the membrane after STXM analysis. This difference is related to the different radiation doses used and difference in radiation damage suffered by the PFSA ionomer in the cathode compared to the membrane. It was seen that for PET, the same absorbed dose induced higher mass loss with

an electron beam in vacuum rather as compared with x-ray beam in He environment (Wang et al. 2009). We plan to further investigate this damage on both the membrane and PFSA ionomer component in the catalyst layers using both transmission electron and x-ray microscopies.

In work done by He et al. (2013), radiation damage caused by an electron beam was assessed in a catalyst layer of a CCM sample by low-loss EELS spectra with variation of controlled beam dose. Trying to understand the rate of mass loss by analyzing the signal intensity loss with variation of beam dose, they found that a pure PFSA ionomer sample is the first to suffer mass loss and suffers the least amount of mass loss in comparison to a catalyst layer with only 29% PFSA ionomer. The authors believe that the Pt nanoparticles act as radiation active sites, and therefore the more Pt, the higher mass loss PFSA ionomer suffers. This implies that the radiation damage PFSA ionomer suffers in the catalyst layer is different than in the membrane, which could also be related to its nanostructure. This can be further investigated by controlling the electron beam dose to both the cathode and membrane components of a CCM and comparing spectral feature differences using STXM analysis at the F 1s and C 1s edges.

Although we show that the PFSA ionomer suffers damage both from an electron beam (PFSA ionomer mass loss was quantified, but the electron dose wasn't controlled) and photon beam (membrane mass loss was quantified), the absence of electron microscopy papers imaging PFSA ionomer in the catalyst layer could be due to the way this material suffers radiation damage, which could also be related to its morphology.

The radiation damage caused by electron and X-ray beams is still not very well understood for all soft materials and the exact mechanism for PFSA ionomer damage is unknown. Yakovlev & Downing (2012) state that for imaging proton-exchange membranes, "the most serious problem caused by irradiation is electron beam-induced mass transfer and diffusion which could distort the appearance of the nanoscale structures." Electron beam radiation damage is known to cause a series of structural changes to polymers, such as ionization, chain scission, diffusion of the atoms, sputtering of the material (Yakovlev &

Downing 2012), bond breaking, mass loss, fading of crystallinity and charging (Michler 2008a). The mass decrease of a dry PFSA ionomer sample with cryo-TEM was "attributed to chain scission events followed by sublimation of the volatile polymer fragments" (Yakovlev & Libera 2006). Radiation damage is also responsible for the displacement of fluorine atoms in the PFSA ionomer and also mass loss in a catalyst layer sample (He et al. 2013). As shown in Figure **4.27c**, there is some PFSA ionomer in the embedding material in the microtome sample. Although this could be an artifact of imperfect stack fitting, it could also be leaching of PFSA from the membrane or catalyst layer during sample preparation. The effect of a controlled dose of X-rays (X-ray spectrometer operated at 40 kV) on PFSA ionomer membranes in the acid form has been studied with different spectroscopic techniques (UV, infrared and paramagnetic ressonance) (Almeida & Kawano 1998). After a certain dose (320 kGy), the membrane changed color and became brittle. The authors concluded that the degradation is mainly due to chain scission. The products of degraded PFSA ionomer with X-rays in vacuum are very similar to the degradation products of PTFE exposed to air, forming peroxy free radicals of -CF₂CF(OO.)CF₂- and -CF₂-CF₂OO. The spectroscopic techniques showed that there is formation of new bonds in irradiated membrane, related to C=O polar groups and C=C groups, scission of C-S and C-O-C bonds, and SO₂ production (Almeida & Kawano 1998).

As indicated by Paul *et.al.*, 2011, there may be a difference in the proton conductivity between bulk PFSA ionomer membrane and PFSA ionomer present in the catalyst layer, due to the nanostructural nature of the latter. It is possible that the morphology of the membrane influences its properties, in particular its conductivity (Peron *et.al.*, 2010). The presence of Pt/C particles can also act as catalytic sites (He et al. 2013) that facilitate the bond breaking that results in chain scission and mass loss of the PFSA ionomer. Therefore, the difficulty in imaging PFSA ionomer in the catalyst layer could be due to its nanostructural nature and differentiated properties, suffering extensive damage when imaged with TEM. This could explain the higher number of papers published that show the membrane morphology with TEM images and the fewer

amount of papers indicating PFSA ionomer morphology in the catalyst layer with the same technique.

We also believe that although staining may cause structural transformations to the PEM, it may be the only way to image this material. (Scheiba et al. 2008) believed staining the PFSA ionomer with Ba could prevent radiation damage, as they observed the formation of BaF2 crystals. On the other hand (Yakovlev & Downing 2012) believed that the nanoscale information can be imaged with high exposures such as required for high resolution imaging and elemental composition if there are atoms with lower mobility, such as sulfur. They demonstrated the stability of sulfur distribution of poly(styrene sulfonate)block-poly(methyl butylene) (PSS-PMB) block polymer to irradiation even when the chemical composition and structure of the material changed considerably. Thermal stability of ion-exchanged PFSA ionomer membrane with different cations demonstrated that Na⁺-PFSA ionomer is the most stable form of the material, with thermal analysis showing that it decomposes in one stage at approximately 500°C (Lage. et al. 2004). Na⁺-PFSA ionomer is also more resistant to X-ray degradation, as it becomes brittle with two times more dosage than H⁺-PFSA ionomer membrane (Almeida & Kawano 1998). Vibrational spectroscopy of H⁺ and Na⁺-PFSA ionomer indicated that there is higher concentration of unsaturated species in PFSA ionomer-H, which can explain its higher sensitivity to X-radiation (Almeida & Kawano 1998). Although ionexchange may change the structure at the molecular level, it may be sufficient to help prevent some of the radiation damage of the PFSA ionomer in the catalyst layer and make it possible to image this component in the catalyst layer.

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5 Summary

The present work has shown effects of different sample preparation methods of CCM samples with a focus on analyzing the cathode and especially the PFSA ionomer with electron and X-ray microscopy techniques. Microscopy techniques are the best available options to map the PFSA ionomer component in the cathode of PEMFC with nanoscale information. By varying the accelerating voltage and the sample holder, SEM allows the visualization of the original catalyst ink in different states. However, to confirm the presence of ionomer elemental analysis is necessary, which is only reliable in the thin film of the catalyst ink. To relate the performance of the fuel cell with the ionomer structure, the analysis has to be done in a CCM or MEA sample, prepared with ultramicrotomy or FIB. FIB causes extensive damage to the carbon support and ionomer structure, as well as mass loss of the ionomer. Microtomy is limited by the thickness of the section and the embedding material that is added to the sample. Not as easily available, STXM can be used to assess information about the PFSA ionomer component in both the FIB and microtome sections and also to assess damage on the sample from preparation techniques.

In order to effectively visualize the ionomer in the cathode at the nanoscale, other sample preparation techniques should be explored. It is possible that if the surface tension of the embedding material is taken into consideration, penetration of the epoxy can be minimized. The thickness of the section would still be a limiting factor, due to the different softness of the materials. It is possible that cryo-microtomy with other support materials could result in thinner sections. Cryo-FIB could be used to minimize the milling damage. However, cryo-conditions may also be responsible for structural changes of the ionomer or membrane material.

Although the sample preparation technique used is crucial for reliable microscopic analysis, the dose-damage relationship of the PFSA ionomer and membrane with electron, X-ray and ion beams will be extremely important for future microscopy work. It is possible that the nanostructure nature of the ionomer results in different properties compared with the membrane, and

different critical doses with radiation beams. Knowing the maximum dose these components can withstand will aide scientists to effectively map and visualize them in the PEMFC. If this information is related to the performance of the fuel cell, valuable insight into the optimization of the structure of the catalyst layer can minimize costs for the successful commercialization of this technology.

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6 References

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