Nanostructured TiOx as a catalyst support material for proton exchange membrane fuel cells

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NANOSTRUCTURED TIO$_X$ AS A CATALYST
SUPPORT MATERIAL FOR PROTON
EXCHANGE MEMBRANE FUEL CELLS

by

Richard S. Phillips

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Material for Proton Exchange Membrane Fuel Cells

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Richard S. Phillips

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I dedicate this to my wife, parents and 8 siblings for their encouragement and support over the years
Abstract

Recent interest in the development of new catalyst support materials for proton exchange membrane fuel cells (PEMFCs) has stimulated research into the viability of TiO$_2$-based support structures. Specifically, substoichiometric TiO$_2$ (TiO$_x$) has been reported to exhibit a combination of high conductivity, stability, and corrosion resistance. These properties make TiO$_x$-based support materials a promising prospect when considering the inferior corrosion resistance of traditional carbon-based supports. This document presents an investigation into the formation of conductive and stable TiO$_x$ thin films employing atomic layer deposition (ALD) and a post deposition oxygen reducing anneal (PDORA). Techniques for manufacturing TiO$_x$-based catalyst support nanostructures by means of ALD in conjunction with carbon black (CB), anodic aluminum oxide (AAO) and silicon nanowires (SiNWs) will also be presented.

The composition and thickness of resulting TiO$_x$ thin films was determined with the aid of Auger electron spectroscopy (AES), Rutherford backscattering spectrometry (RBS), X–ray photoelectron spectroscopy (XPS), energy-dispersive X–ray spectroscopy (EDS), and scanning electron microscopy (SEM). Film crystal structure was determined with X–ray diffraction (XRD) analysis. Film conductivity was calculated using four-point probe (4-PP) and film thickness measurement data. Resulting thin films show a significant decrease of oxygen in ALD TiO$_x$ films corresponding with a great increase in conductivity following the PDORA. The effectiveness of the PDORA was also found to be highly dependent on ALD process parameters.

TiO$_x$-based nanostructures were coated with platinum using one of three Pt
deposition techniques. First, liquid phase deposition (LPD), which was performed at room temperature, provided equal access to catalyst support material surfaces which were suspended in solution. Second, plasma enhanced atomic layer deposition (PEALD), which was performed at 450°C, provided good Pt particle dispersion and particle size controllability. Third, physical vapor deposition (PVD), which was also performed at room temperature, was used as a low temperature vapor-phase deposition technique for comparison with PEALD Pt coated materials. The temperature of the Pt deposition technique is an important parameter to consider due to the potential adverse effects of the strong metal support interaction (SMSI) which may take place at temperatures above 200°C. Platinum coated nanostructures were analyzed electrochemically using cyclic voltammetry (CV), rotating disk electrode (RDE) and accelerated stress tests (ASTs). CV and RDE results generally show that platinum activity values are initially not as high as those typically observed for platinum on carbon; however, AST results indicate that TiO$_x$-based materials are much more stable long-term and hence their level of activity is likely to overtake traditional platinum on carbon materials in a PEMFC system.
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List of Acronyms

2-D – Two dimensional
3-D – Three dimensional
4-PP – Four-point probe
AAO – Anodic aluminum oxide
AAM – Anodic aluminum oxide membrane
AES – Auger electron spectroscopy
ALD – Atomic layer deposition
AR – Aspect ratio
AST – Accelerated stress test
CB – Carbon black
CV – Cyclic voltammetry
CVD – Chemical vapor deposition
DLC – Diffusion limiting current
ECSA – Electrochemically active surface area
EDS – Energy-dispersive X–ray spectroscopy
IPA – Isopropyl alcohol
LPD – Liquid phase deposition
Nb,Ti,Oz – Niobium doped titanium oxide
ORR – Oxygen reduction reaction
PDORA – Post deposition oxygen reducing anneal
PEALD – Plasma enhanced atomic layer deposition
PECVD – Plasma enhanced chemical vapor deposition
PEMFC – Proton exchange membrane fuel cell
PVD – Physical vapor deposition
RBS – Rutherford backscattering spectrometry
RDE – Rotating disk electrode
SE – Secondary electron
SEM – Scanning electron microscope
SiNWs – Silicon nanowires
SMSI – Strong metal support interaction
TEM – Transmission electron spectroscopy
TiO$_x$ – Substoichiometric TiO$_2$
TiO$_x$/CB – TiO$_x$ coated carbon black
TiO$_x$/SiNWs – TiO$_x$ coated silicon nanowires
XPS – X-ray photoelectron spectroscopy
XRD – X-ray diffraction
Chapter 1. Introduction

1.1. Need for zero emission energy conversion

This section outlines the need for zero emission energy conversion including the positive impacts that it may have on air quality in highly populated urban areas and the possibilities for a renewable hydrogen fuel source in the future. It also highlights how the current hydrogen infrastructure is a current barrier to more widespread use of PEMFCs.

Although the future consequences of global warming are certainly in the minds of many, there are currently regions of the world that are negatively impacted by fossil fuel emissions. In particular, urban areas which are characterized by high density populations, combined with geographical barriers including mountains or mountain valleys, prevent the dissipation of fossil fuel emissions. It has been reported that between 50 and 90% of the emission/air pollutants that exist in urban areas are generated by automotive sources such as internal combustion engine (ICE) powered vehicles [1].

ICEs contain toxic compounds, such as volatile organic compounds (VOCs), which are not only hazardous to the environment but are toxic to humans. Following long term exposure VOCs such as polycyclic aromatic hydrocarbons (PAHs) have been linked to the development of cancer, allergy sensitization and asthma [2, 3]. These toxins currently impact the lives of millions of people in ways that are still not fully understood; this is especially a concern for individuals who mature in these regions which suffer from heavy concentrations of VOCs. Those who already suffer from respiratory problems are
at risk each and every time pollution concentrations exceed designated air quality tolerance levels throughout the year. Hence, these regions of the world have a real and current need for the development of zero emission energy conversion technology.

Moving from ICEs to a zero emission energy conversion technology, such as proton exchange membrane fuel cell (PEMFC) powered electric vehicles (EVs), which use the conversion of hydrogen and oxygen into water to generate electricity, would have a great impact on reducing poisonous gas emissions in high population areas. This is especially true in regions where geographical features, such as mountains and mountain valleys, prevent the dissipation of pollutants generated by vehicle emissions.

When moving toward PEMFC powered EVs, clean and renewable hydrogen fuel sources need to be considered. It is widely known that fossil fuel sources are a limited fuel source; when the fossil fuel is consumed it is converted from a useable form to an unusable form. This means that in the future the source will inevitably run out. On the other hand, a fuel source such as hydrogen can be produced using techniques including the electrolysis of H$_2$O [4, 5]. Since H$_2$O is an abundant resource, this makes it a very attractive source for hydrogen production.

There are some barriers which currently stand in the way of an appropriate hydrogen infrastructure. To start, sources of hydrogen are most commonly produced from fossil fuels such as natural gas [6]. Clean production of hydrogen requires further development of H$_2$O electrolysis and other clean technologies to help make them a more economically viable option than current hydrogen production techniques. Additionally, since technologies such as H$_2$O electrolysis require a power source to generate the
electricity necessary to drive the reaction which produces H₂, it is important that the power source also be zero emission.

Currently, 66% of power produced in the United States of America comes from the burning of fossil fuels such as coal and natural gas [7]. Thus, effectively, even “clean” hydrogen sources which require power to produce hydrogen will currently disqualify PEMFCs as a truly zero emission technology until zero emission power sources are more developed and implemented into the current power infrastructure. Other promising technologies which can cleanly produce hydrogen are currently under development [8 - 12].

In spite of the current limited availability of clean hydrogen sources, the increasing need for cleaner air in high density population areas makes PEMFC powered EVs a promising solution. Using current hydrogen sources may only serve to shift fossil fuel emissions from urban areas to outlying industrial areas, but the immediate improvement in human health would still be a step forward. Then when cleaner sources of hydrogen are made available, an already developed PEMFC technology will help in establishing a completely zero emission economy.

At the mention of zero emission transportation, some observers may only consider battery powered vehicles and the advancements made in this technology. However, it is important to point out that fuel cells have certain advantages over both fossil fuel and current battery technologies [13]. For starters, fuel cells have a higher efficiency than gas and diesel engines. Hydrogen, which is the fuel of a fuel cell, can be produced anywhere there is a source of water. Hence, there is the potential to reduce a nation’s dependence
on foreign fuel sources provided that the energy required to dissociate H₂O into H₂ and O₂ may be locally obtained. Fuel cell powered vehicles have the potential to allow for a farther travel range than battery powered vehicles since, just like a combustion engine, it is fuel source dependent (meaning that in order to double the range only the fuel is required to be doubled, not the fuel cell capacity).

Also, due to the fuel dependence of a fuel cell, the energy density can be much higher than for a battery. In other words, as the range of a fuel cell powered vehicle is increased the weight of the vehicle increases much less dramatically than it does for a battery powered vehicle [14]. Lastly, while the volume energy density of hydrogen is higher than for gasoline, it is still lower than that of a battery.

1.2. Current PEMFC Technology

A basic schematic of a PEM fuel cell is shown in Figure 1.1 [15]. It consists of two electrodes separated by a proton exchange membrane with two main flow channels for hydrogen at the anode and oxygen at the cathode [16]. The hydrogen is broken apart at the anode according to the reaction in Eq. 1, ideally yielding two electrons and two protons per hydrogen molecule.

\[ H_2 \rightarrow 2H^+ + 2e^- \]  

(1-1)

The electrons are conducted away from the anode through whatever system the PEMFC is powering and toward the cathode. The remaining protons are conducted through the proton exchange membrane toward the cathode. At the cathode a multi-step reaction takes place which involves a catalyst breaking apart oxygen and combining it with two protons and the necessary electrons to form H₂O according to the reaction in Eq.
2. Current fuel cells commonly use platinum (Pt) on colloidal carbon (represented in the lower right of Figure 1.1).

\[
\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O
\]  

It is important to note that in fuel cells designed for practical applications (like transportation) there is a gaseous water flowing in both channels to keep the proton exchange membrane humidified [17]. Also, to avoid needing two sources of fuel, the oxygen source will actually be air [18] (which contains mostly nitrogen, oxygen, argon, and carbon dioxide).

Figure 1.1: A basic schematic of the operation of a PEMFC is shown. The basic chemical reactions which take place at the anode (with H₂) and cathode (with O₂ and H⁺) are also shown. A close-up of the cathode is
shown in the lower right where the Pt on carbon electrode material is illustrated.

Since one of the main limiting factors in reducing cost of PEMFC manufacturing is the high cost of Pt (at around \( \approx \$1400 \) an ounce [20]), most research into Pt loading reduction takes place at the cathode of a PEMFC [21]. The anode requires much less Pt to break apart hydrogen and release two electrons than does the cathode to break apart oxygen and combine it with hydrogen [19]. Hence the cathode is the main limiting factor for reducing Pt requirements and seems the most logical direction to focus research, considering its potential for a higher rate of progress.

In addition to high manufacturing costs due to Pt, fuel cells tend to suffer from a short operational lifetime which translates into higher consumer costs. The short lifetime is due to certain failure modes common to PEMFCs which contribute to efficiency losses over time. Short lifetime is a significant barrier to PEMFC powered EVs becoming an economically viable alternative to ICE vehicles.

In an attempt to reduce Pt costs there are at least a couple of approaches that can be taken to decrease the amount of Pt required in electrode materials. First, the efficiency at which the Pt is used can be increased. Considering that only the surface atoms of a Pt structure actually participate in the catalyst reaction, the surface Pt atom to bulk Pt atom ratio can be increased [19]. Second, other less expensive metals could be coated with only a few atomic layers of Pt. And third, a mixed phase metal approach could be taken where Pt is mixed with other catalysts (such as Ni, Fe, and Co [22], [23]).
In order to increase the lifetime of a PEMFC, it is important to understand and overcome the different failure modes that lead to system degradation. Failures such as membrane breakdown, carbon corrosion (leading to Pt sintering), and electrode flooding (blocking of active catalyst sites) are commonly reported in the literature [24, 25]. Membrane breakdown may be due to chemical attacks, membrane drying, and thermal/mechanical stress. These are issues presently under investigation by others [26, 27]. The current research focuses on the issues of carbon corrosion and electrode flooding. Both of these failure modes are associated with the chemical and structural nature of the catalyst support material.

1.2.1. Carbon corrosion

The first setback to longer PEMFC lifetime addressed in this work is carbon corrosion [28, 29]. Carbon corrosion is a failure which occurs due to the harsh environment of a fuel cell. Conditions such as high acidity, strong electric fields, and high water concentrations combined with relatively high temperatures contribute to the oxidation of the carbon support according to Eq. 3. This corrosion results in the detachment and agglomeration/sintering of the Pt particles, reducing the electrochemically active surface available to perform the necessary chemical reactions (see Figure 1.2).

\[
C + H_2O \rightarrow CO_2 + 4H^+ + 4e^- \tag{1-3}
\]
The effect of carbon corrosion on traditional Pt on carbon electrodes is illustrated above. Following the reaction of carbon with water, the Pt will detach from the surface and begin to agglomerate, which in turn reduces the performance of the fuel cell.

1.2.2. Electrode flooding

The second setback is electrode flooding (a topic reviewed by Hui Li et al. [30]). Electrode flooding is a phenomenon which occurs at the cathode due to the tightly packed structure of colloidal carbon electrodes which limits the amount of gas transport pathways between carbon particles (see Figure 1.3). Since the byproduct of fuel cell cathode reactions is H₂O, it is necessary for there to be a way to transport it out of the system. However, if there are insufficient gas-transport pathways, the H₂O molecules can build up and consequently block active catalyst surfaces; hence, this can greatly reduce the efficiency of the fuel cell. In an attempt to avoid these critical failures, a support must be found which is designed to overcome them.
Figure 1.3: Shown above is an illustration of the effect the tightly packed structure of traditional Pt on C electrodes. When gas transport pathways are limited, the H$_2$O generated by the Pt catalyst may not be able to escape the electrode as quickly as it is being produced. This leads to a build-up of H$_2$O molecules which prevent further reactions from taking place, and reduces the overall performance of the PEMFC.

1.3. Suggested Answer to Current Issues (TiO$_2$)

In seeking a new support there are a few things that need to be considered. Firstly, the support should be conductive (i.e., at least several hundred Siemens per centimeter). It will also need to be stable in an acidic as well as an oxidizing environment and thus have surfaces which a catalyst will strongly adhere to. Additionally, the support should be structured to increase gas transport pathways which can reduce electrode flooding; high AR structures may prove useful in this regard.

Investigations into substoichiometric TiO$_2$ (hereafter referred to as TiO$_x$) have suggested that it may be a possible proton exchange membrane fuel cell (PEMFC)
catalyst support material replacement [28]. TiO₂, like many metal oxides, is known to be a chemically stable material. What makes TiO₂ of particular interest is its many substoichiometric/oxygen reduced forms. This is a desirable characteristic in that TiOₓ shows a large increase in conductivity with only slightly reduced stoichiometries. Perhaps the most interesting of these substoichiometric phases are referred to as Magneli phases which are represented by: TiₙO₂ₓ₋₁. Magneli phases exhibit high conductivity (≈ 1000 S/cm) which is stable and offers good corrosion resistance [28, 29, 31 - 37].

Looking at Figure 1.4, which shows how changes in the ratio of oxygen to titanium (O/Ti) effect both the conductivity and the etch rate (in acid) of the TiOₓ material [38], it can be seen that at an O/Ti ratio of 1.75 (i.e., Ti₄O₇) there is a sharp peak in conductivity. One of the targets of this research is to develop a method for manufacturing highly conductive TiOₓ films at temperatures ≤450°C by optimizing a combination of ALD deposition parameters and post deposition annealing to yield films with stoichiometries around 1.75.
Figure 1.4: Figure of conductivity and acid dissolution rate verses the oxygen to titanium ratio of TiO\textsubscript{x} materials (Reproduced from [38] with permission of The Royal Society of Chemistry).

The desirable properties of TiO\textsubscript{x} are due to the fact that in its pure stoichiometric form (TiO\textsubscript{2}) it is very chemically inert, but as the amount of oxygen decreases (even just a little) the conductivity greatly increases (to the semiconductor range). For example, in Ti\textsubscript{4}O\textsubscript{7} there are three layers of TiO\textsubscript{2} for every one layer of TiO [39]; that is to say that there are seven Ti-O bonds for every Ti-Ti bond (which arises from the oxygen vacancy). The seven Ti-O bonds help to maintain the chemical stability which is characteristic of TiO\textsubscript{2} while the Ti-Ti bond, which is organized with other Ti-Ti bonds to form a sheer plane, provides a conductive pathway for electrons. And though the Ti-Ti bonds are significantly fewer in number than Ti-O bonds, they still give rise to a dramatic increase
in conductivity. While the presence of these Ti-Ti bonds promotes the dissolution of TiO$_x$ materials in acid (also shown in Figure 1.4), their concentration is so much lower than the Ti-O bonds that Ti$_4$O$_7$ remains nearly as chemically stable as TiO$_2$[38].

1.3.1. The strong metal support interaction

In addition to being conductive and stable, Pt adhesion and activity has been reported to improve when deposited on TiO$_x$ due to the strong metal-support interaction (SMSI) [40 - 43]. The SMSI, as the name denotes, is essentially a strong attraction which takes place between a metal and a support material. In the case of TiO$_2$ based materials and Pt the attraction is quite strong. In fact, when the supporting TiO$_2$ material undergoes oxygen reduction, (causing oxygen vacancies at the surface), the interaction between the Pt and TiO$_x$ can change the chemical nature of the Pt [44].

The changes can be beneficial or detrimental depending on the Pt particle size, the level of oxygen reduction at the TiO$_x$ surface, and the temperature to which the Pt-TiO$_x$ material is exposed [45 - 47]. At low temperatures (below 200°C) the negative effects tend to be less prevalent, while at high temperatures (above 200°C) the effect can be very negative for small Pt particles (<5nm) [46], at least as far as PEM fuel cell applications are concerned. At lower temperatures, the Pt can strongly bind to the surface and will even exhibit higher levels of activity (both due to the SMSI). However, at higher temperatures, the SMSI can cause the Pt to become inactive; this occurs in a couple of ways (see Figure 1.5).

First, it has been reported that as the TiO$_2$ support material is oxygen reduced at temperatures greater than 200°C, the reduced TiO$_2$ will migrate onto the surface of the Pt
it is supporting which will begin to block the active Pt sites. The longer the reduction takes place the greater the impact of migrating TiO$_x$ [46].

The second way that TiO$_x$ can cause Pt to become inactive occurs for small Pt particles (<5nm) under the same conditions except that instead of migrating TiO$_x$, the Pt atoms themselves begin to migrate (or spread) across the surface [45, 47, 48]. This results in the Pt particle becoming flatter and has the effect of decreasing the ability of the Pt to adsorb hydrogen or oxygen, thus preventing it from performing its catalytic function.

Both of these adverse effects can be overcome either by working with the Pt on TiO$_x$ surfaces at lower temperatures or by using Pt particles which are larger than 5nm in diameter. When the SMSI is controlled sufficiently to utilize the positive effects between Pt and TiO$_x$, it may prove to give TiO$_x$-based materials a great advantage over carbon supports. These combined attributes of TiO$_x$ appear to make it a good candidate to replace traditional carbon catalyst supports. The question then is how can it be manufactured into a high AR nanostructure?
Figure 1.5: The two undesirable interaction mechanisms between TiO$_x$ and Pt caused by the SMSI where a) represents the migration of TiO$_x$ onto the active Pt sites and b) represents the spreading of Pt nuclei across the TiO$_x$ surface resulting in a reduction in the adsorption of H$_2$ or O$_2$.

1.4. TiO$_2$ Material Manufacturing Methods

There are several ways to manufacture TiO$_2$/TiO$_x$ support materials, including numerous wet chemistry methods, such as liquid phase deposition (LPD), sol-gel, titanium metal anodization, and hydrothermal, to name a few. There are also several vapor phase techniques which can be used to deposit TiO$_2$ on a surface including: chemical vapor deposition, plasma enhanced chemical vapor deposition, and physical vapor deposition, among others. Additionally, there are highly controlled, self-limiting growth techniques such as atomic layer deposition and plasma enhanced atomic layer deposition. The purpose of this section is to discuss several of these techniques along with each technique’s advantages, disadvantages and compatibility with high AR nanostructure formation.

1.4.1. Anodization of Ti metal

A popular wet chemistry technique for forming TiO$_x$ nanotubes is titanium metal
foil annodization. Foil anodization and nanotube formation occurs when a potential is applied to the Ti metal when it is immersed in an oxidizing electrolyte solution. Nanopores/Nanotubes will then naturally form in the metal foil as it oxidizes. The size and dimensions of these pores are dependent on the process parameters [49 - 52].

The method is as follows. The Ti Foil is attached to the anode in a two electrode cell with both electrodes suspended in an electrolyte solution. A cathode that is composed of the same material (or Pt) is common. The electrolyte solution is often temperature controlled. A chosen potential and/or current is applied for the desired duration, typically 1-24 h depending on the desired length of the pores and the thickness of the Ti foil.

The advantages of Ti foil anodization include having a certain degree of control over the pore/tube diameter, spacing, wall thickness and length. It is, again, simply a matter of controlling the process parameters.

Anodization of an entire Ti foil usually takes several hours to accomplish (≈ 10-24 h or more depending on the thickness of the foil). Since the purpose is to deposit Pt on the surfaces of the TiO₅ tubes it is important to be able to separate the TiO₅ tubes without destroying them. However, the tubes, following anodization are all still attached at a central base at the heart of where the Ti foil used to be. It can prove difficult to adequately separate/detach the tubes from the tube matrix to allow for complete catalyst coverage of the tube surfaces. Also, scaling of this technique requires the use of high voltage/high current power source systems which naturally lead to greater hazards and expense (at least in comparison with other solution based processing techniques).
1.4.2. **Hydrothermal method**

The hydrothermal method for manufacturing TiO$_x$ is a solution based approach which uses precursors, high pressures and high temperatures to cause the formation of TiO$_x$ structures [53, 54]. These reactions will typically take place in an autoclave.

There are various different Ti precursors in solution which could be used during the growth of TiO$_x$ structures that can be placed into an autoclave and raised to a constant high temperature and pressure. Controlling the parameters such as temperature, pressure precursor concentration, etc. provide a level of control over the resulting TiO$_2$ structure [55, 56].

There are a few advantages for using this technique to manufacture TiO$_x$ materials. Firstly, it has the potential to provide large yields of material from solution. Analogous to Ti foil anodization, the nanostructures can be formed and properties controlled simply by tailoring the process parameters. This method may also have the potential to be highly scalable for future mass production of materials [57].

There are, however, some disadvantages that are worth mentioning. First, the material processing times required can be fairly long, needing between 24-72 h. Second, nanostructures which are formed are typically unordered, tangled and difficult to separate which will pose a problem when attempting to conformally coat the surfaces with a catalyst. Last, it requires specialized equipment (i.e., an autoclave) to achieve the process parameter requirements, which is something usually avoided with liquid phase material processing.
1.4.3. Liquid phase deposition

The liquid phase deposition approach may utilize a metal precursor in solution with a template such as an anodized aluminum membrane (AAM) to perform the TiO$_x$ deposition [58, 59]. The AAM can be immersed in a solution containing a metal-fluoro complex (ammonium hexafluorotitanate in the case of TiO$_2$). The AAM is a nanoporous alumina material which is anodized to create nanopores in a similar fashion to the Ti foil anodization technique described in section 1.4.1 and is outlined in greater detail in section 2.3.1. With the AAM in solution a reaction takes place between the solution and the AAM surfaces where TiO$_2$ is deposited while the AAM surfaces are being slowly consumed.

Following the deposition, the template is removed from solution and annealed. The anneal helps to solidify the TiO$_2$ material that is deposited in the AAM pores and to react any unreacted chemicals within the matrix. Once annealed, the template containing the now solidified TiO$_2$ tube is dissolved in NaOH, leaving only the tubes behind.

The advantages of this technique are that the deposition only takes an hour and the tubes can be annealed and separated in roughly 3-4 h. There is also no specialized equipment required during TiO$_2$ tube deposition (i.e., outside of an annealing furnace which is commonly used and is often readily available in many labs). This technique for depositing TiO$_2$ is compatible with other material deposition processes which make it possible to combine TiO$_2$ with other materials [60].

Due to the consumption of the AAM template surfaces during the TiO$_2$ deposition, the tube faces end up being very close together when depositing thick TiO$_2$
layers, which is often necessary to increase mechanical stability in the final TiO$_2$ tubes. If the surfaces are too close together this can make it difficult to completely etch the AAM template which will result in greater NaOH etch times and may even make separation of the tubes impossible without causing structural damage. As has been indicated before, without adequate separation it can be difficult to conformally coat tube surfaces with a catalyst.

1.4.4. Sol-gel method

Sol-gel is a technique with many methods for forming nanostructured materials, but for the purposes of looking at the formation of high AR structures, the AAM template method is outlined here. This technique also involves using an AAM as a template for TiO$_2$ nanotube formation [54, 61 - 63].

This method is carried out by immersing the AAM template into the sol-gel solution for 10-24 h. The TiO$_2$ material is deposited on the aluminum oxide surfaces of the AAM template including within the pores according to [61, 64]. The deposited material is then removed from the sol-gel solution, cleaned and then placed into an oven which serves to solidify the TiO$_2$ material. The template is then removed using NaOH, as was described previously, leaving only the TiO$_2$ tubes. In some cases, surfactants are used in the literature to control tube morphology [65].

The sol-gel technique is advantageous in that it is a well-developed procedure for material growth which has a variety of chemistry approaches and is template compatible. This technique also provides some level of control over the structure of TiO$_2$, including control over the phase of the TiO$_2$ material deposited, by using different calcination
temperatures and additives [62]. Lastly, sol-gel is also a low cost manufacturing method which does not require specialized equipment beyond the use of an annealing furnace.

The sol-gel method’s disadvantages lie in the long processing times required as compared to the quantity yield of the desired material, and like other methods already described, it still faces the issue of agglomeration.

1.4.5. Discussion of wet chemistry techniques

In selecting an appropriate method for manufacturing TiO$_2$ nanostructures to serve as a catalyst support replacement for colloidal carbon materials, there needs to be a method that is compatible with high AR structure formation. All of the above techniques appear to have certain advantages and disadvantages as a manufacturing technique such as ease of structure formation, manufacturing time, controllability, scalability and cost. Generally speaking, all of the wet chemistry techniques discussed above are compatible with high AR structure formation and are fairly inexpensive to make owing to low equipment costs.

As far as scalability is concerned there are a few that stand out above the rest such as the hydrothermal and Ti foil anodization techniques. This is mostly due to the fact that there are fewer steps in the process of material formation which can reduce the complexity and hence reduce the amount of time required to manufacture the materials. Also, increasing yield is simply a function of increasing the amount of initial material at the beginning of the process; and secondary materials are not required, such as a removable template.
The main disadvantage of these techniques is the level of controllability there is over the final material’s properties. Controlling growth rate and total growth time are limited by the level of control over reaction initiation and reaction finalization for continuous growth techniques. Additionally, the level of synthesis repeatability is prone to be less than ideal with solution based chemistries due to: lower degrees of control over the environment of the reactions, the uniformity at which reactions take place in solution, where reaction take place, and eliminating sources of contamination.

1.4.6. Physical vapor deposition

The first vapor phase technique that will be summarized in this section is physical vapor deposition (PVD) which is a deposition technique which uses either a solid or liquid form of the material needed to be deposited as the source; this is opposed to using a precursor source which undergoes chemical reaction that can yield the material desired [66 - 68]. The source material is evaporated under high vacuum through various means such as ion sputtering, e-beam evaporation, thermal evaporation, molecular beam evaporation, etc. Any technique may work which can provide the source material with sufficient energy to transition between solid or liquid phases and the vapor phase. Once the material is in vapor phase it is then transported from the source to the substrate where it will condense on the surface. Various strategies have been developed for encouraging a high degree of uniformity and conformality over patterned structures [69, 70].

In addition to depositing a vaporized source material onto a surface, the source material (e.g., pure metal sources) can be combined with other gases (such as ammonia, oxygen, nitrogen, etc.) which can be reacted with the vaporized material to form a
compound (e.g., a metal oxide or a metal nitride). The new material is then deposited on the substrate as previously described. A diagram of an example PVD chamber is also shown in Figure 1.6. Depicted in Figure 1.6 is an ionized PVD chamber which uses a magnetron to generate the plasma used to sputter the source material target.

Figure 1.6: Shown above is a simple diagram of an example PVD reactor (IPVD in this case).

1.4.7. Chemical vapor deposition

Chemical vapor deposition (CVD) is a vapor phase deposition technique which utilizes a reactive precursor, often in conjunction with a reactant gas, that reacts with a heated surface to provide the energy necessary for reactions to take place [71, 72]. The surface reactions cause the precursor and reactant gases to produce both a gaseous and
solid byproduct. The solid byproduct remains on the surface following the reaction while
the gaseous byproduct flows out of the reactor with the inert carrier gas and any other
unreacted gases. Generally speaking, it is a steady state growth technique (i.e.,
temperature, pressure, precursor/reactant gas flow all remain constant for the duration of
the deposition). The growth rate in principle remains continuous as long as the
precursor/reactant gases are flowing evenly and consistently across the surface. With
CVD, critical parameters include controlling substrate temperature, chamber pressure,
and precursor flow rate. Precursor gas flow dynamics across the substrate surface are also
vitally important because the reaction and growth rate of the film are dependent on the
flux of precursor to the surface and hence the uniformity of the thin film will depend
greatly on this being carefully controlled.

Since gas phase (homogeneous) reactions are usually undesirable, it is important
to select reactant gases (and process conditions) which will be compatible with surface
(heterogeneous) only reactions [73, 74]. An example of a basic CVD reactor is shown in
Figure 1.7a.

Plasma enhanced chemical vapor deposition (PECVD) uses a plasma (e.g., DC or
RF generated plasma) containing the precursor or a combination of the precursor and a
reactant gas to provide some of the energy needed to cause the desired reactions to take
place which will result in a material being deposited continuously on a surface. PECVD
can facilitate surface reactions by using the potential energy of ions which exist in the
plasma to break chemical bonds at much lower system temperatures. A basic diagram of
a typical PECVD reactor is shown in Figure 1.7b.
Since some precursors used in CVD require high thermal energies (i.e., high temperatures) to enable the desired surface reactions to take place, this may have undesirable consequences on either the material being deposited (e.g., coalescence of CVD metals [75, 76]) or on the underlying layers, structures, or devices which the film is being deposited over [77]. Hence, plasma enhancement can allow for the desired surface reactions to take place at much lower temperature than would be otherwise achievable which can result in smooth, uniform films and less thermal damage to underlying materials, structures, or devices. Again, if the temperature window, plasma power and precursor/reactant gas chemistry are chosen appropriately, surface only reactions can be promoted and gas phase reactions can be minimized [78].
Figure 1.7: A comparison between CVD (a) and PECVD (b) processes chambers is shown. Reactors are structurally very similar except for the RF power source (13.56 MHz) which ionizes the gas between the showerhead and wafer chuck.
1.4.8. Atomic layer deposition

Atomic layer deposition (ALD) historically has been called atomic layer epitaxy (ALE) and atomic layer CVD (ALCVD) [79 - 82]. Early ALE was performed at appropriately high temperatures on cleaned crystalline surfaces [83 - 86]. Alternating pulsed half reactions were used to grow films epitaxially in an atomic layer by atomic layer (or molecular layer) fashion. Since this layer by layer technique was not limited to epitaxially growth ALCVD became a more appropriate title which eventually was simplified to just ALD.

ALD, like ALE, works on the principle of self-limiting half reactions of both precursor and reactant gases. The half reactions are separated into two steps by inert gas purge steps. The first step flows (or pulses) the precursor gas into the reactor where the substrate is supplied with the energy required for the incomplete reaction of the precursor molecule with the substrate (see Figure 1.8). The unreacted portion of the molecule (or ligand(s)) is required to act as a blocking agent to subsequent precursor molecules, which prevents them from chemisorbing to the substrate. The precursor molecules which were unable to react with the surface are then purged from the reactor with an inert gas (e.g., Ar) and then a reactant gas, which is reactive with the unreacted ligands of the precursor molecule, is pulsed into the reactor. Another purge step completes the ALD cycle and returns the reactor to the state which existed at the beginning of the ALD cycle. This sequence is repeated for each ALD cycle until the desired thickness is obtained.

The way to ensure the half reaction of precursor molecules is by carefully selecting a temperature window so that it will only provide enough energy for a partial
reaction to take place [87 - 88]. The temperature window is chemistry dependent, and will naturally fall between the temperature of no adsorption and the temperature where the complete reaction of the molecule takes place (e.g., parasitic CVD growth). ALD growth per cycle may still be affected by pulse time, pressure, and temperature within the self-limiting growth window but these changes in growth rate are much less significant; considering that, in these ranges, there is a maximum of single monolayer per cycle, the changes in growth rate which are observed are merely changes in how much of a monolayer is being deposited per cycle.

To give an example of ALD, Figure 1.9 has illustrated the basic process flow of typical ALD TiO$_2$ [81]. It starts with a hydroxyl group terminated surface left by a previous ALD cycle. Then the surface is exposed to titanium tetrachloride vapor which partially reacts with the surface. The unreacted Ti-Cl bonds serve as a shield against subsequent precursor molecules from reacting with the surface; thus only allowing a single layer to adsorb to the surface. Once coverage of the partially reacted precursor species is satisfactory, the system is purged of any unreacted TiCl$_4$ and then H$_2$O is pulsed into the reactor which reacts with the Ti-Cl bonds yielding, once again, a hydroxyl group terminated surface [81].
Figure 1.8: Shows the gas flow verses time of each step in an ALD cycle.

Adding the times for each step in the cycle gives the total cycle time.

Purges steps in between precursor and reactant gas pulses allow for self-limiting half reactions to take place.

Plasma enhanced ALD (PEALD) follows the same basic principles of thermally based ALD except that, like with PECVD, plasma is used to lower the temperature window at which the reactant species needs to react with the remaining ligands of the partially reacted precursor species. While the initial adsorption of the precursor may function in a similar fashion to thermal ALD, the reactant gas is not sufficiently reactive with the precursor ligands to complete the reaction (except at elevated temperatures). A way around this is to ionize the reactant gas, turning it into plasma. Ionization causes the reactant gas to become much more reactive with the remaining precursor ligands while maintaining a lower substrate temperature. In PEALD, this reactant plasma step replaces the regular reactant step of the ALD cycle as shown in Figure 1.10.
Figure 1.9: Two different growth mechanisms for TiO\textsubscript{2} using TiCl\textsubscript{4} and H\textsubscript{2}O are shown here. Each mechanism requires 4 ALD steps: 1) a TiCl\textsubscript{4} pulse which half reacts TiCl\textsubscript{4} with the surface, 2) a purge of the unreacted TiCl\textsubscript{4} from the process chamber, 3) a H\textsubscript{2}O pulse which completes the reaction and either terminates the surface with hydroxyl groups or leaves a strictly TiO\textsubscript{2} surface, and 4) finally the unreacted H\textsubscript{2}O is purged from the process chamber. These steps make one ALD cycle which can be repeated indefinitely until the desired thickness is reached [81].
1.4.9. Discussion of vapor phase techniques

As will be discussed in the next section, ALD is really the only vapor phase technique which shows great promise for the formation of high AR nanostructures due to the high degree of control it provides over film growth. It also brings to the table a high degree of control over material properties that is important to early stage research. Of course, this comes at the expense of higher equipment costs, though some of this cost should be able to be reduced with changes in system design which would be more optimized for this type of manufacturing [89]; currently, many ALD systems are not optimized for this.
1.5. Rationale for TiO$_2$ Support Structure Manufacturing Using ALD

As mentioned above, ALD shows great promise in the formation of high AR nanostructures. This section outlines some of the advantages and limitations of using ALD compared to PVD and CVD/PECVD. Figure 1.11 gives a representative coverage comparison between these three deposition techniques [90 - 92].

![Figure 1.11](image)

Figure 1.11: An illustration of the typical PVD, CVD and ALD coverage of a high AR structure is shown. It is clear the PVD and CVD have advantages for certain applications which do not involve these types of structures, (such as higher growth rate), but ALD is ideally suited for the high AR coverage needed to form high AR structures.

While improvements are being made all the time with PVD techniques, it is clear that conformal coverage of structures with aspect ratios greater than 10:1 is not easily
achievable with the current technology [69, 93]. The continuous growth nature of PVD, in combination with the directional flow of the vaporized source material, contributes to the technique’s incompatibility with high AR coverage [69]. The vaporized source material has much more direct access to surfaces which are perpendicular to the vapor flow and hence the growth rate on these surfaces is higher than on more parallel surfaces. Surfaces which are shielded from the directional vapor flow due to structural barriers will receive minimal coverage.

The level to which CVD can coat high AR surfaces is limited by its continuous growth nature. The less directional movement of the precursor molecules typically allows for better sidewall coverage than with PVD, but due to the geometries of high AR surfaces the impingement rate of precursor molecules is always higher near the top of these structures than near the bottom [94]; this means that unless the growth can be hindered in the upper regions of the high AR structures, (such as with the work of Yanguas-Gil et al. [95]), the growth of the CVD/PECVD film will tend to be more top heavy. However, even in the case where growth inhibitors were used to encourage more conformal growth on high AR structures, the depth of conformal coverage was less than AR = 20:1.

In principle, ALD is also affected by the gas flow dynamics of the precursor (at least initially). However, because each growth step is self-limiting in nature, the flow dynamics become less important since no more than one monolayer of atoms/molecules can be deposited during a cycle. This is really the key to the high AR coverage that is observed for the ALD films when compared to other vapor phase deposition techniques.
Structures with aspect ratios of thousands to one can be conformally coated using ALD [92]. It is mainly a question of time (i.e., how long can the deposition process reasonably take?)

Additionally, since ALD is a layer by layer growth technique it means that growth can be controlled down to less than a monolayer. To some extent this affords the ability to engineer the properties of the monolayer material that is being deposited as well. For example, during each precursor and reactant pulse of an ALD cycle there is a certain level of control over how much saturation the surface receives from either the precursor or reactant gases. In the case of TiO<sub>x</sub> deposited from TiCl<sub>4</sub> and H<sub>2</sub>O, the surface can be fully saturated with a TiCl<sub>4</sub>-n species (where n = 1-4), but deliberately fail to complete the reaction with the H<sub>2</sub>O pulse. While this does not necessarily provide direct control over the amount of oxygen in a TiO<sub>x</sub> film, (since an OH layer is required for subsequent TiCl<sub>4</sub>-n layers to form), it may help to encourage the formation of oxygen defects in the TiO<sub>x</sub> films following a post deposition oxygen reducing anneal (PDORA) which would lead to an increase in the film conductivity (as will be shown hereafter) [96, 97].

Again, owing to the layer by layer growth nature of ALD, sub-monomonolayer thickness control is possible. This translates into an ALD process potentially being able to control film thickness to within an angstrom. In practice, however, this tends not to be the case since a slight deviation in the process parameters, due to random system fluctuations, can lead to a slight change in the extent to which each pulse saturates the surface; even slight changes in the level of saturation per cycle between depositions can accumulate into a greater than angstrom uncertainty when depositing thick films (e.g.,
100s of ALD cycles). Nevertheless, for a well-controlled process, having thickness control to within less than 1% is common [98, 99].

Another important aspect of ALD thin film growth that should always be considered when depositing thick and thin films is that the growth rate for ultra-thin films may not always be the same as for thicker films. This is due to the diversity of surface interactions that the precursor may have with the substrate verses with the surface of a bulk film being deposited [100]. Hence, the initial growth rate for a film being deposited on a surface of a dissimilar material may be different than the growth rate of a film being deposited on the same material. In other words, it should be anticipated that the growth of at least the first few ALD cycle layers being deposited on a substrate of a different material will be different, (i.e., faster or slower and chemically different), than the growth will be after the influence of the substrate is blocked by a thick enough layer of the deposited material [101, 102]. This is important to consider when working with very thin films since the differences in growth rate will have a greater impact on the resulting thickness as well as other film properties. For thicker films, the initial growth interactions with the substrate will probably not lead to a very high degree of uncertainty due to the number of ALD cycle layers deposited without any influence from the substrate.

Lastly, if the deposition of a material down to less than a monolayer can be controlled, then it stands to reason that two materials can to be mixed with a similar degree of control. Owing to the layer by layer format of ALD it is possible to alternate the materials at each layer yielding a mixed phase material whose layers are indistinguishable [102 - 104] as illustrated in Figure 1.12. This is true provided that
certain requirements are met which allow for the two materials to be compatible with each other.

For obvious reasons it is important that both materials exhibit ALD growth within the same temperature window [102]. This is especially important since a major use for ALD is coating high AR structures. If one of the materials can’t be deposited in a self-limiting fashion, then the composition throughout a high AR coating will not be consistent.

In addition, the surface groups which remain following the ALD cycle of one material need to also be compatible with the precursor of the other material. For example, when combining two metal oxide materials in a layer by layer fashion at lower temperatures, the terminating surface groups, (e.g., hydroxyl groups), should be able to partially react with the precursor molecule for the other material. If both materials use the same type of oxidizer (e.g., H$_2$O), then combining materials may be more straightforward. In the current research TiCl$_4$ reacts with H$_2$O in an ALD cycle and leaves OH groups at the surface which are reactive with other metal precursors [105, 106].

Reactor pressure requirements for each ALD process are less of a concern since pressure control/change is easily controlled in a fairly rapid fashion by most ALD reactor systems through the use of a throttle valve.

Only slightly removed from the layer by layer method for mixing materials is a laminate method (see Figure 1.13). Instead of alternating single layers, (i.e., single ALD
cycles), when mixing two or more materials, there are deposited multiple layers of each material in an alternating fashion [107]. The process flow might follow something like 10 cycles of metal oxide “A” followed by 20 cycles of metal oxide “B” followed by 10 cycles of metal oxide “A” and so on. This method is useful when looking to obtain a particular concentration of each material. Also, in cases where a 50/50 mix of both materials is desired this method helps to achieve that in situations where ALD growth rates for each material are not the same.

![Diagram](image)

Figure 1.12: The effect of a Layer by layer ALD material mixing technique will typically yield a film which is thoroughly mixed. The individual layers will be indistinguishable from each other and effectively form a new material. Above is illustrated an example of an alternating layer by layer mix of Al₂O₃ and HfO₂.
Figure 1.13: The effect of a laminate ALD material mixing technique is that it will typically yield a film with distinguishable layers. These layers may also exhibit the properties of a thoroughly mixed film but may also exhibit the properties of the individual films. Above is illustrated an example of many layers of Al₂O₃ and HfO₂ being deposited in an alternating fashion.

1.6. Discussion—ALD Limitations

If an appropriately reactive surface can be heated and accessed by the various precursor, reactant, and purge gases, then, in principle, any surface can be conformally coated by an ALD process. However, conformality is still limited in practice because of time constraints. Especially when working with High AR surfaces, it may require very long pulse times to achieve surface saturation. And since the level of conformality of the final film is so dependent on the level of surface saturation, conformal coatings are not always practically obtained, (especially when attempting to manufacture large quantities of materials). In the case of very high AR structures the saturation step for a precursor
can be tens of seconds or more. And when combined with proportional purge and reactant gas pulse steps a single cycle can take on the order of a minute which, when considering that many ALD processes require 100s or thousands of cycles to achieve the desired film thickness, the process may become very impractical and costly.

Property changes are also important to consider when targeting high conformality over high AR structures. As will be shown later in Chapter 3, dramatically increasing pulse times can cause a considerable change in the TiO\(_2\) film conductivity.

### 1.7. Dissertation Overview—Chapter Descriptions

The following section provides a general overview of the content of each chapter contained in this work.

#### 1.7.1. Chapter 1: Introduction

This chapter provides an overview of the current state of PEMFC technology including the limitations which currently exist such as the instability of the traditional carbon catalyst supports caused by carbon corrosion and electrode flooding. Some of the main points of motivation behind the current research into catalyst support replacement are also provided. It is suggested that a possible solution to carbon corrosion and electrode flooding is to replace traditional carbon supports with nanostructured TiO\(_2\) supports. Various techniques for manufacturing TiO\(_2\) will be compared and the reasoning behind the use of ALD as a material deposition technique is also outlined.

Also, outlined are the different approaches that can be taken, using ALD, to manufacture mixed phase materials in a highly controlled fashion. Some of the
limitations of ALD are also discussed along with a brief description of the sources of these limitations.

1.7.2. Chapter 2: Experimental Details

This is an overview of the experimental details including the equipment used for manufacturing high AR TiO$_x$ materials. Outlined are the general details of equipment operation and the parameter limits of the equipment. The parameter ranges which were used during experiments are then summarized.

Then the various analysis tools which were used to analyze the properties of the resulting materials will be discussed. The basic theory behind each material analysis technique and the application of each technique to the current research is also provided.

1.7.3. Chapter 3: Support Material Development

This chapter summarized the development of the TiO$_x$ support material where the aim is to optimize the materials toward high stability and conductivity. The post deposition oxygen reducing anneal process which is used on all TiO$_x$ materials is described. The ALD TiO$_x$ film deposition parameters and their effects on film properties, such as conductivity and electrical stability, are discussed in detail.

The various techniques for manufacturing nanostructured TiO$_x$ materials are described as well as the optimized ALD TiO$_x$ process parameters which were used for each structuring technique. The mixed phase material, Nb$_x$Ti$_y$O$_z$, process development is outlined including the process development toward optimized composition and optimized template coverage. The optimized nanostructuring process that was used is also outlined
for Nb,Ti,O₂ type materials. Finally, the effects on conductivity of 2-D TiO₂ and Nb,Ti,O₂ films following their exposure to various chemicals used during manufacturing and analysis are also outlined.

1.7.4. Chapter 4: Electrochemical Performance

This chapter first describes the development of the inks used to create the electrode materials which were analyzed electrochemically. The electrochemical performance according to cyclic voltammetry and rotating disc electrode analysis for each material manufactured is then reported and discussed. Following this the results of the accelerated stress tests for these materials is then reported.

1.7.5. Chapter 5: Future Directions

Based on the current state of the research described in this work the limitations of the materials developed so far will be summarized as well as some suggested research, which could be performed in the future to further the development of TiO₂-based materials. Some rationale behind these suggestions will also be given.

1.8. References


[94] R. Phillips, P. Hansen and E. Eisenbraun, "Atomic layer deposition fabricated substoichiometric...


Chapter 2. Experimental Details

2.1. ALD Reactor System

The majority of thin film processing, including all of TiO$_x$ film processing, was carried out in a Genus/Aixtron 200–300mm wafer capable “bridge” ALD tool. This tool is equipped with two process modules—one for oxides and one for metals. The oxide process module contains a thermal ALD reactor and the metal module contains a plasma enhanced ALD reactor (the latter of which uses RF generated plasma during the reactant step of an ALD cycle). This setup provides the advantage of being able to process TiO$_x$ and catalyst without breaking vacuum. A diagram of this tool setup is shown in Figure 2.1.

The basic reactor design can be seen in Figure 2.2. It includes a showerhead, chuck, susceptor, pins, chuck shield, and evacuation line. The showerhead and chuck shield serve to encourage laminar flow of pulse and purge gases. The chuck provides resistive heat to the substrate. The susceptor and pins work with a robot transfer arm to consistently position the carrier wafer into the reactor.

The reactor wall temperature can be controlled in the range of 50–120 °C and is typically held at 100°C for all metal oxide depositions. This temperature was controlled by an M and W Systems Flowrite© heat exchanger which flows heated Galden® PFPE, a highly stable, inert fluorinated fluid, to and from the reactor. The chuck allows for a temperature range of 90–550°C.
Figure 2.1: Shown above is a diagram of the two main ALD process modules used in this work. Process module 4 (PM4) is where the TiO$_x$ films were grown using thermal ALD, and process module 2 (PM2) is where PEALD Pt was deposited.
Figure 2.2: An illustration of the ALD reactor used for the deposition of TiO$_x$-based films.

During processing, the pressure of the reactor is maintained using a pump stack which includes a roughing pump and Roots blower in connection with a throttle valve. When the reactor is not being utilized for ALD deposition processing, a turbo pump is used to maintain a $\approx 10^{-6}$ Torr base pressure. The highest measurable reactor pressure is 1000 mTorr.

On the metal oxide process module, there are 3 liquid source precursor cylinders (or bubblers) which connect to the reactor through $\frac{1}{4}$ inch stainless steel lines with VCR
metal gasket face seal fittings. The bubblers consist of inlet and outlet lines through which the carrier gas flows and are controlled by two pneumatic valves. Two of the three precursor bubblers are heated, having a storage volume of 250 ml. The other precursor bubbler is unheated with a storage volume of 500 ml.

There are two reactant gas sources on the metal oxide process module with one delivering H$_2$O and the other delivering O$_3$. The H$_2$O source is another liquid source bubbler contained within the process module and is set up in the same manner as the precursor source bubblers. The ozone is provided to the reactor via an MKS ASTeX AX8500 ozone generator which is connected to the reactor through similar VCR fittings and ¼ inch stainless steel lines. The generator supplies an ozone concentration of 248 g/Nm$^3$ to the system with a flow rate of 1000 sccm.

The Genus/Aixtron 610 system is designed to use pressure to control the flow of gas rather than a mass flow controller. This helps to provide consistent gas flow in a system that utilizes short pulse reaction steps. However, the flow rate can still be monitored under continuous flow by mass flow meters which enable the calibration of the line pressure to yield a desired flow rate during ALD processing. The precursor line pressure settings range from 0–100 Torr, (though in practice pressures less than 5–10 Torr are generally difficult to maintain and are less reliably measured).

2.1. Thin Film Processing

Titanium tetrachloride (TiCl$_4$, Strem Chemicals, Inc., 99.8+ %) and H$_2$O were respectively used as metal precursor and oxygen source for all TiO$_x$ films. These liquid sources were transported to the ALD reactor using argon as carrier gas. Delivery line
pressures of 100 and 60 Torr, for TiCl$_4$ and H$_2$O respectively, were used. TiCl$_4$ and H$_2$O remained unheated for TiO$_x$ processing though the system ambient temperature is \( \approx 30^\circ C \). The vapor pressure of TiCl$_4$ at this temperature is \( \approx 10 \) Torr.

An initial TiO$_2$ baseline ALD process was developed utilizing a 325°C substrate temperature, a 750 mTorr reactor pressure, and 2.0s/0.5s (TiCl$_4$/H$_2$O) precursor and reactant gas pulse times. Thermal anneals of this film in forming gas (5 % hydrogen in argon) at 600°C for 4 h did not result in a significant increase in conductivity.

In an attempt to more dramatically increase the conductivity of as deposited TiO$_x$ films, an in situ post deposition oxygen reducing anneal (PDORA) was developed. During the development, PDORAs were performed at temperatures ranging from 350°C to 450°C, using hydrogen as annealing gas, for 15 to 120 minutes. This approach proved more effective than thermal annealing and hence further research was done to optimize the ALD process to make the PDORA more effective. This was accomplished by depositing sequences of films while varying pulse times for TiCl$_4$/H$_2$O from 2s/0.5s to 16s/4s, varying temperatures from 125°C to 450°C, and varying thicknesses from 5 nm to 100 nm. System pressures were maintained at 750 mTorr (reactor), 60 Torr (H$_2$O line pressure), 100 Torr (TiCl$_4$ line pressure) and 40 Torr (Ar purge line pressure).

An “early level” stability test was designed to help evaluate the stability of 2D TiO$_x$ films. It involved heating up the films in an oxygen atmosphere (following the post deposition reducing anneal) and evaluating the changes in conductivity following timed exposures. While these tests are arguably not directly relatable to a fuel cell environment, they do provide a way to compare the stability of different TiO$_x$ films in a strongly
oxidizing environment. This way the most stably conductive ALD TiO$_x$ process can be identified and utilized for nanostructure fabrication.

Since the typical PEM fuel cell operates at $\approx 80^\circ$C, it naturally follows that any degradation of TiO$_x$ (due to oxygenation) that takes place at one temperature will happen more quickly at a higher temperature. In accordance with this, an O$_2$ anneal test was designed to evaluate the resistance of the TiO$_x$ films to oxygenation. This was evaluated by heating select films to 200$^\circ$C in a 625 Torr O$_2$ environment for 15, 30, 60 and 120 minutes. At each time interval 4–point probe measurements of the films were taken to investigate relative changes in conductivity with respect to O$_2$ anneal time.

2.3. Nanostructure Manufacturing Techniques

The following section outlines the various nanostructure manufacturing techniques used to create high aspect ratio TiO$_x$ structures using AAO templates and TiO$_x$ coated SiNWs (TiO$_x$/SiNWs). A technique is also outlined for manufacturing semispherical colloidal TiO$_x$ structures using carbon black.

2.3.1. Anodic aluminum oxide (AAO) template

Anodic Aluminum Oxide (AAO), as the name denotes, is created through the anodization of aluminum (Al). The anodization is carried out by immersing high purity Al into an oxidizing electrolyte solution and applying a potential to the Al (see Figure 2.3). The potential draws in the negatively charged oxygen species and causes them to react with the Al which in turn, through various electric attraction and repulsion as well as diffusion and mass transport effects, causes the formation of nanopores in the surface [1 - 8].
When the conditions of formation are carefully controlled, these pores can become highly ordered and parallel. To encourage parallel ordered growth Al will often undergo an inert gas anneal to increase crystal grain size [6, 9] and planarized through any number of electropolishing techniques [6, 9 - 11]. The length of the pores is simply controlled by the duration of the anodization process. The spacing, width, and wall thickness of the pores is controlled by the type of electrolyte, the current density, and the temperature of anodization process [2, 8]. Following the anodization, the pores are usually widened with a solution based etch until the thickness of the alumina side walls is minimized [4].

Figure 2.3: Illustrated here is a process flow outlining the manufacturing of AAO nanopores from high purity Al.
ALD TiO$_x$ is then deposited on the surface of the AAO. The self-limiting nature of the ALD process allows for the sidewalls of the AAO pores to be coated. The degree of conformality with which they are coated is dependent on the level of surface saturation that takes place during each ALD cycle [12, 13].

Once the AAO pore walls are coated with a sufficiently thick TiO$_x$ film, the TiO$_x$ coated AAO sample is placed into a solution of 5 M sodium hydroxide (NaOH) [14] for 30–60 minutes under sonication which etches the AAO template leaving behind the templated TiO$_x$ nanotubes (see Figure 2.4). The separated nanotubes are then separated using a centrifuge at 3000 rpm for 12 minutes. The nanotubes are cleaned with DI water 3–5 times, each with a separation time of 12 min at 3000 rpm in the centrifuge.

It is worthy to note that while the aim in manufacturing these high aspect ratio supports is to create a PEMFC cathode catalyst support material which is structurally optimized to prevent electrode flooding, these TiO$_x$ supports may also be suitable for other applications [15 - 19].

Premanufactured anodic aluminum oxide membranes (AAMs) produced by Whatman™ [20] were used for nanotube manufacturing in this work. The AAMs were 13 mm in diameter and 60 um thick with pores $\approx$ 200 nm in diameter. Pore sizes of at least 100 nm in diameter were desired to accommodate the required ALD TiO$_x$ film thickness. The pore size also allowed for easier cross sectional measurements which were used to optimize ALD coverage parameters.
Figure 2.4: A process flow showing that the AAO nanopore template was coated with ALD TiO$_x$ and then the template was removed via sonication in a 5.0 M solution of NaOH.

2.3.2. **Silicon nanowires**

Silicon nanowires (SiNWs) have been an interesting topic of research since the 1960s. The concept gained momentum following the work of Wagner and Ellis which explained the vapor–liquid–solid growth mechanism of SiNWs [21]. The basic mechanism [22] involves heating a small amount of a metallic solid (e.g., gold or Au) deposited on a crystalline Si surface. Small Au–Si alloy droplets will form from the deposited metal layer. The heated droplets are then exposed to a gaseous Si compound (e.g., SiH$_4$) which will break apart on the Au–Si droplet surface and the Silicon will
precipitate toward the droplet–Si interface. Under steady state conditions, the continuous exposure of the silicon compound will saturate the Au–Si droplets. This causes the continuous precipitation of Si at the Au–Si interface which shifts vertically away from the surrounding Si surface resulting in Si nanowire growth.

For the current work, SiNWs were grown using a chemical vapor deposition (CVD) growth technique following a vapor liquid solid (VLS) growth mechanism (see Figure 2.5). Plain Si <100> was sonicated in acetone, ethanol, isopropyl alcohol (IPA) for 3–3.5 min and then rinsed with DI water. The Si was then immersed in buffer HF for 1 min, and rinsed again with DI water. Physical vapor deposition (PVD) gold was deposited on a cleaned Si surface which was subsequently heated to 650°C in vacuum [23].

Once at temperature, the substrate was allowed to anneal in Ar for 15 minutes. Then a mixture of argon and silane were leaked into the reactor while maintaining a pressure of ≈ 100 Torr. This pressure and temperature were maintained for 90 minutes. The resulting SiNW were then coated with an ALD TiO<sub>x</sub> film deposited. Due to the more open nature, (i.e., there is generally greater spacing between the SiNW surfaces), precursor and reactant gas pulse times do not need to be as long as they need to be for AAO coatings to achieve 100% conformality. This is an important advantage over AAO structures when depositing PEALD Pt.
Figure 2.5: A basic process flow is shown for SiNW formation on a cleaned Si substrate. First, a thin layer of PVD gold is deposited on the surface and then heated to 650°C. Next, silane and argon are leaked into the reactor. The silane adsorbs onto the surface of the gold nanoparticles and breaks apart. The Si diffuses through the gold, and deposits at the gold–Si interface. This process will continue until the supply of silane ceases. The resulting nanowires are then coated with TiO$_x$.

2.3.3. Colloidal supports

In evaluating the performance of TiO$_x$ as a support material as well as a support structure, it is important to be able to compare colloidal carbon supports with colloidal TiO$_x$. Strictly speaking this is a challenge to accomplish with ALD since it requires a substrate on which to deposit a material. However, a core shell method was conceived in which colloidal carbon could be coated with TiO$_x$ to yield particles of comparable size to the traditional Vulcan XC–72 carbon black (or just CB). This technique involved mixing various concentrations of CB from 1mg/1ml (or a 1:1 ratio) in a solution of isopropyl alcohol (IPA) in water (20/80 volume ratio) to 5:1 ratio of CB to the same solution. These
solutions were then dispersed onto 3x3cm cleaved SiO₂ (100 nm) on crystalline Si substrates. The cleaved substrate was used because it provides a clean, smooth surface with sharp edges. The sharp edges are important to the dispersion process since they create a barrier for the ink solution. The edges also enable the dispersion of a determined quantity of ink (typically 1ml) sufficient to completely fill the 3x3cm SiO₂ surface without spilling over the edges.

The aim of dispersing various concentrations of CB inks onto these surfaces is to obtain as thin a layer as possible which is also continuous across the surface. This is desired in order to allow for optimal ALD TiOₓ coatings of the CB particle surfaces. It is important that the ink solution be thoroughly and uniformly mixed in order to be able to obtain consistent dispersion (i.e., layer thickness) from sample to sample. Hence, all materials were thoroughly sonicated for at least 60 min prior to dispersion.

Room temperature (RT) dispersions and drying, or RT dispersions followed by heated drying, generally did not result in good layer coverage of SiO₂ substrates. Consequently, various drying temperatures (150 –170°C) were used in an effort to obtain a more uniform dispersion. This approach was formulated to help evaporate the IPA in the ink solution more rapidly. IPA is a necessary part of the solution due to how it assists the solution in dispersion across the surface. However, it has the adverse consequence of creating turbulence within the solution after the initial dispersion. This turbulence leads to agglomeration of the CB within the solution over time. It was anticipated that rapid drying of the solution would minimize the time the solution experienced this turbulence and allow for much more uniform dispersion.
Cleaved SiO\textsubscript{2} substrates were weighed before and after the CB layers were dispersed to evaluate the repeatability of the dispersion, (i.e., repeatability of the CB layer mass). Then ALD TiO\textsubscript{x} films were deposited over the CB layers (see Figure 2.6) and weighed once more to evaluate the mass increase due to the films for the calculation of the TiO\textsubscript{x}/CB layer mass ratio.

Following the development of TiO\textsubscript{x} coated CB (TiO\textsubscript{x}/CB) materials, both LPD and PEALD Pt were deposited. LPD Pt was deposited after the material layer was mechanically removed from the SiO\textsubscript{2} substrate. While this removal is necessary, it also means that there is a potential for Pt to be deposited on exposed carbon surfaces resulting from the breakup of the TiO\textsubscript{x}/CB layer.

PEALD Pt was directly deposited on the TiO\textsubscript{x}/CB following the PDORA. This provides the PEALD Pt process with an advantage over the LPD Pt as the TiO\textsubscript{x} layers are completely unbroken before they are removed from the SiO\textsubscript{2} substrate so that the Pt deposited via PEALD will only be able to deposit on TiO\textsubscript{x} surfaces.

2.4. Mixed Phase Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} Process Development

There have been many efforts made elsewhere to further increase the conductivity of TiO\textsubscript{x}. Among these, there have been reports which found that incorporating another metal into a TiO\textsubscript{2} matrix enhanced conductivity and stability [24 - 26]. One promising metal among those reported is niobium (Nb) [25 - 27]. It has been reported that the conductivity of Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} materials is maximized when the ratio of Nb/(Ti + Nb) is between 0.09 and 0.15 [28]. Outlined below are the steps which were taken to develop and optimize Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} films for composition and for nanostructure manufacturing.
Figure 2.6: An illustration of TiO$_x$/CB from the dispersion of CB onto a 2-D substrate to the ALD TiO$_x$ coating of the CB surfaces.

2.4.1. NbO$_x$ processing

Nb is supplied by the metal organic compound niobium (V) ethoxide or Nb$_2$(OEt)$_{10}$ (supplied by Strem Chemicals, Inc. 99.9+ %). The process parameters which were used are outlined in Table 2-1. The NbO$_x$ film optimization involved evaluating both the growth rate of the film (in order to appropriately engineer composition of Nb$_x$Ti$_y$O$_z$), as well as optimizing the films conformality over AAO templates.

Table 2-1: Nb$_2$O$_5$ process parameters including: the precursor source temperature ($T_{\text{source}}$), the precursor carrier gas pressure ($P_{\text{source}}$), the substrate temperature ($T_{\text{substrate}}$), the ALD pulse time ratio of Nb$_2$(OEt)$_{10}$ to H$_2$O, and the number of ALD cycles used during each process.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{source}}$ (°C)</th>
<th>$P_{\text{source}}$ (Torr)</th>
<th>$T_{\text{substrate}}$ (°C)</th>
<th>Nb$<em>2$(OEt)$</em>{10}$/H$_2$O Pulse (sec)</th>
<th>ALD Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$_2$O$_5$ _1</td>
<td>100</td>
<td>50</td>
<td>300</td>
<td>5/4</td>
<td>200</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ _2</td>
<td>110</td>
<td>50</td>
<td>300</td>
<td>5/4</td>
<td>200</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ _3</td>
<td>110</td>
<td>50</td>
<td>300</td>
<td>5/4*</td>
<td>100</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ _4</td>
<td>110</td>
<td>100</td>
<td>300</td>
<td>5/4</td>
<td>200</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ _5</td>
<td>110</td>
<td>100</td>
<td>300</td>
<td>10/4</td>
<td>200</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ _6</td>
<td>110</td>
<td>100</td>
<td>300</td>
<td>10/4</td>
<td>800</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ _7</td>
<td>120</td>
<td>100</td>
<td>300</td>
<td>10/4</td>
<td>800</td>
</tr>
</tbody>
</table>

*Ar purge times were doubled from 5 seconds to 10 seconds

In order to ensure that the composition of the Nb$_x$Ti$_y$O$_z$ material is consistent throughout the templated nanostructure, it is important to first make sure that the NbO$_x$ film coverage is the same as the TiO$_x$ film. Ideally this would be done by obtaining 100% conformality for each film before combining them. However, since the TiO$_x$ film loses conductivity with increasing pulse time, (as will be demonstrated in the next chapter), the conformality had to be less than 100% to maintain the highest conductivity possible that would also yield a high AR structure. This makes the matching of the ALD NbO$_x$ film a little more difficult but still achievable, as will be seen in the next chapter.

### 2.4.2. Nb$_x$Ti$_y$O$_z$ processing

Since the desired composition is the ratio Nb/(Ti + Nb)= 9–15%, film deposition parameters were designed based on respective TiO$_x$ and NbO$_x$ growth rates and are outlined in Table 2-2. It was determined that ALD cycles could not be 1:1 between TiO$_x$ and NbO$_x$ in order to obtain the desired composition range. Also, the individual ALD layers of the mixed film will not necessarily have the same growth rates as the ALD
layers of the non-mixed films. Consequently, TiO\textsubscript{x}:NbO\textsubscript{x} ALD cycle ratios were varied between 1:1 and 8:1. Substrate temperatures were varied between 200 and 300°C. Based on the results of the depositions outlined in Table 2-2, the optimized Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} process was selected for deposition on AAM templates.

Table 2-2: Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} ALD process parameters including: the substrate temperature (T\textsubscript{substrate}), the precursor source temperature (T\textsubscript{source}), the ALD pulse time ratio of TiCl\textsubscript{4} to H\textsubscript{2}O, the ALD pulse time ratio of Nb\textsubscript{2}(OEt)\textsubscript{10} to H\textsubscript{2}O, the ratio of TiO\textsubscript{x} ALD cycles to NbO\textsubscript{x} cycles and the number of cycles (composed of the repeating TiO\textsubscript{x}/NbO\textsubscript{x} cycle ratio sequence) used during each process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T\textsubscript{substrate}</th>
<th>T\textsubscript{source}</th>
<th>TiCl\textsubscript{4}/H\textsubscript{2}O Pulse Ratio (s)</th>
<th>Nb\textsubscript{2}(OC\textsubscript{2}H\textsubscript{5})\textsubscript{10}/H\textsubscript{2}O Pulse Ratio (s)</th>
<th>TiO\textsubscript{x}/NbO\textsubscript{x} Cycle Ratio</th>
<th>Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-1}</td>
<td>200</td>
<td>100</td>
<td>4/1</td>
<td>5/1</td>
<td>1:1</td>
<td>100</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-2}</td>
<td>300</td>
<td>110</td>
<td>4/4</td>
<td>5/4</td>
<td>1:1</td>
<td>100</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-3}</td>
<td>300</td>
<td>120</td>
<td>4/4</td>
<td>10/4</td>
<td>1:1</td>
<td>100</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-4}</td>
<td>300</td>
<td>120</td>
<td>4/4</td>
<td>10/4</td>
<td>1:1</td>
<td>200</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-5}</td>
<td>300</td>
<td>120</td>
<td>8/2</td>
<td>10/4</td>
<td>8:1</td>
<td>45</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-6}</td>
<td>300</td>
<td>120</td>
<td>8/4</td>
<td>10/4</td>
<td>7:2</td>
<td>45</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-7}</td>
<td>300</td>
<td>120</td>
<td>4/4</td>
<td>10/4</td>
<td>7:2</td>
<td>45</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-8}</td>
<td>300</td>
<td>120</td>
<td>4/4</td>
<td>10/4</td>
<td>4:4</td>
<td>45</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-9}</td>
<td>200</td>
<td>120</td>
<td>4/4</td>
<td>10/4</td>
<td>4:4</td>
<td>45</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-10}</td>
<td>200</td>
<td>120</td>
<td>4/4</td>
<td>10/4</td>
<td>7:2</td>
<td>45</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-11}</td>
<td>200</td>
<td>120</td>
<td>4/4</td>
<td>10/4</td>
<td>7:1</td>
<td>45</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}\textsubscript{-12}</td>
<td>200</td>
<td>120</td>
<td>4/4</td>
<td>10/4</td>
<td>8:1</td>
<td>70</td>
</tr>
</tbody>
</table>
2.5. Chemical Stability Tests for 2–D TiO\textsubscript{x} Films

Since TiO\textsubscript{x}-based materials are exposed to various chemicals during template separation, cleaning and electrochemical analysis, it is important to know how exposure to these chemicals is likely to affect the conductivity of the materials before CV and RDE analyses take place. As it is anticipated that there will be some level of degradation to the film while it is under a potential in an electrolyte solution, it is important to be able to eliminate all other factors from the data which are also degrading the film. Also, considering that it is uncertain how the composition of Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} affects the stability of the material, it was necessary to test films with various compositions of Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}.

Films were first exposed to 0.1 M HClO\textsubscript{4} (the CV and RDE analysis electrolyte) for 0 to 240 minutes to simulate exposure during analysis. The conductivity of each film was then measured using 4–point probe after 0, 15, 60, and 240 minutes. Following this test, select films were exposed to 5.0 M NaOH for 25 min and conductivity measured. All films were then exposed to water and heated to 80°C for 90 minutes and again measured for changes in conductivity.

2.6. Catalyst Deposition Techniques

Two methods for depositing Pt were utilized in the current work due to their individual strengths for depositing on either SiNW or TiO\textsubscript{x} nanotube surfaces. PEALD Pt is more limited in its ability to penetrate and deposit between structures which are more closely packed than open in nature. Using the ALD tool described above roughly 20:1 aspect ratio coverage was achieved; and although this is good for a metal deposition technique, it is not quite ideal for depositing Pt on all surfaces of TiO\textsubscript{x} nanotubes since
the nanotubes tend to agglomerate upon separation from the AAO template. On the other hand, SiNWs provide adequate spacing between TiO\textsubscript{x} surfaces to accommodate the 20:1 aspect ratio limit of the Pt depositions making SiNWs more ideally suited for PEALD Pt processing.

LPD Pt was used for TiO\textsubscript{x} nanotubes because it is a very common technique used for Pt on carbon materials [29 - 34], and the aqueous environment the deposition technique provides give the deposited Pt access to all of the nanotube surfaces. However, LPD also provides less control over nucleation size and particle distribution; hence LPD Pt does not maximize Pt surface to volume ratio as well as PEALD Pt nor does it maximize Pt utilization on nanostructured TiO\textsubscript{x} as will be shown later.

2.6.1. LPD Pt processing details

The LPD Pt deposition processes were used to coat the various nanostructured materials that are reported in this work. A 20 wt. % LPD Pt target loading was deposited on TiO\textsubscript{x} coated Vulcan XC–72 by taking 15.5 mg of chloroplatinic acid hexahydrate (H\textsubscript{2}PtCl\textsubscript{6} \cdot 6H\textsubscript{2}O) and 27 mg of TiO\textsubscript{x} coated Vulcan XC–72 which were dispersed in 50 mL of ethylene glycol, sonicated and stirred for >12 h. A solution mixture of 2.0 g of sodium borohydride and 50 mL of ethylene glycol was added slowly to the catalyst support and precursor solution under vigorous stirring. The solution was stirred for 2 h to ensure complete reaction. The resulting materials were centrifuged and washed several times with DI water. Once the material was clean and separated it was allowed to dry at 80°C.

Similarly a 20 wt. % LPD Pt target loading was deposited on TiO\textsubscript{x} nanotubes by
taking 6.9 mg of chloroplatinic acid hexahydrate (H$_2$PtCl$_6$ · 6H$_2$O) and 9.5 mg of TiO$_x$ nanotubes which were dispersed in 20 mL of a 50:50 solution ethylene glycol and water. The support material and Pt precursor solution were sonicated and stirred for >12 h. A solution mixture of 0.676 mg of sodium borohydride and 10 mL of ethylene glycol was added slowly to the catalyst support and precursor solution under vigorous stirring. The solution was stirred for 2 h to ensure complete reaction. Then 15 ml of 0.1 M HCl was added to the mixture and allowed to react. The resulting materials were centrifuged and washed several times with DI water. Once the material was clean and separated it was allowed to dry at 65°C.

2.6.2. PEALD Pt

The fundamentals of the PEALD process were explained previously in chapter 1. The parameters which were used for the Pt depositions are described here. PEALD Pt depositions were performed using the plasma capable reactor on the same Genus/Aixtron Stratagem$^{300}$ 300–mm wafer capable ALD cluster tool mentioned previously. A metal–organic Pt precursor (Me$_3$(MeCp)Pt) [35 - 38] was used in conjunction with a 500 W ammonia (NH$_3$) RF plasma (13.56 MHz). The substrate temperature was held at 450°C. ALD pulse times for both the precursor and reactant gas (and associated RF plasma) were 8 seconds. Reactor pressure was held at 500 mTorr [23].

It should be noted that in the case of TiO$_x$/CB materials, both LPD and PEALD Pt were deposited. LPD Pt was deposited after the material layer was mechanically removed from the SiO$_2$ substrate while PEALD Pt was directly deposited on the TiO$_x$/CB following the PDORA. This distinction is important to note since the removal of the TiO$_x$
material prior to the Pt deposition means that there is a potential for Pt to be deposited on exposed carbon surfaces which result from the breakup of the TiO$_x$/CB layer. Since PEALD Pt doesn’t require the material to be broken up, this manufacturing approach provides PEALD Pt with an advantage of being able to ensure that only the TiO$_x$ surfaces will be coated with Pt.

2.7. Analysis Techniques

Various analysis techniques were used to measure changes in film stoichiometry, structure, conductivity, AAO pore coverage, growth rate, and stability as well as the functionality of nanostructured TiO$_x$ as a catalyst support material. The basic principles of each of these analysis techniques are described in the sections below.

2.7.1. Auger electron spectroscopy

The basic principle behind Auger electron spectroscopy (AES) [39, 40] is that when a core shell electron is removed from an atom, (usually with a high energy electron beam, though a high energy photon may also be used), this removal of an electron leaves behind a hole in the electron cloud causing the atom to be in an unstable state. This instability can be corrected by an outer shell electron moving to the lower energy state of the unstable hole. In order to do this, an amount of energy equal to the difference between the two orbital energies must be transferred. Often this electron transition can be coupled with another outer shell electron which will absorb the energy released from the transition causing it to be emitted from the atom (see Figure 2.7). This will happen provided the energy difference between the core shell electron and the transitioning outer shell electron is greater than the binding energy of the second outer shell electron. The
emitted electron is called an Auger electron. The kinetic energy of the Auger electron is:

\[ E_{kin} = E_{CS} - E_{OS1} - E_{OS2} \]  

where \( E_{kin} \) is the kinetic energy of the Auger electron, \( E_{CS} \) is the energy of the core shell electron state, \( E_{OS1} \) is the energy of the outer shell electron state, and \( E_{OS2} \) is the energy of the Auger electron’s outer shell electron energy state prior to emission.

Figure 2.7: The mechanism for Auger electron emission begins with the collision of a high energy electron with a ground state electron in a sample atom (a). The ejected ground state atom leaves a hole and an outer shell electron transitions to the ground state. Auger electron emission occurs when this energy the energy equal to the difference between the two states is transferred to another outer shell electron (b). An illustration of the relative energy levels associated with these transitions is also shown (c).
Since this is happening to many atoms of the same element all at once, each ejecting an electron with the same characteristic energy, these electrons can be detected and their energies measured. These energies are characteristic of the element under analysis and with the appropriate sensitivity factor (i.e., a probability factor which establishes the rate at which an incident electron is likely to generate an Auger electron of a particular energy for a particular element). Combining the Auger electron energy measurements with the known sensitivity factors for each element enables the quantitative calculation of elemental ratios in an atomic percent fashion.

Figure 2.8 illustrates the interaction volume of a high energy electron beam with the various regions where different types of analysis can be performed. The low energy electrons used in AES analysis make it a very surface sensitive chemical analysis technique [41]. The mean escape depth (MED) of auger electrons which are emitted below the surface of a material is generally only a few nanometers. This is a very useful property for analyzing thin film materials.

The AES analysis was performed on a PHI 660 scanning auger electron spectrometer [42]. Analysis was performed with a 10keV electron beam. Sputtering depth profiles were also taken of select films which utilized a high energy ionized argon beam to remove material layers from the sample surface. AES was used in the research primarily as an elemental identification and composition confirmation technique.
Figure 2.8: The interaction volume of an electron beam is illustrated above. At the surface and within the bulk of a material the high energy primary beam generates backscattered, secondary and Auger electrons as well as characteristic X–rays.

2.7.2. Rutherford back–scattering spectrometry

Rutherford backscattering spectrometry (RBS) [43 - 45], as applied to thin film analysis, is a technique where probing ions (helium in the present research) are accelerated through a very high potential (on the order of MV) and directed toward the surface to be analyzed. The basic principle follows an elastic scattering ball model where collisions take place between two particles of different masses. The energy and angle
with which the probing ion (or projectile) is scattered gives an indication of the mass of the atom off which it scattered. The energy of the scattered projectile as a function of the projectiles initial energy is

\[ E_{BS} = k \cdot E_0 \]  

where \( E_0 \) is the initial energy of the projectile, \( E_{BS} \) is the energy of the back scattered projectile and \( k \) is the kinematic factor. The kinematic factor incorporates the masses of the incident ion (\( m_1 \)) and the scattering atom (\( m_2 \)) as well as the scattering angle as seen in Eqn. 2-3.

\[ k = \left( \frac{m_1 \cos \theta_1 + \sqrt{m_2^2 - m_1^2 (\sin \theta_1)^2}}{m_1 + m_2} \right)^2 \]  

(2-3)

The probing ion must be lighter than the atoms in the material being analyzed in order for backscattering to take place. A percentage of the ions will scatter back toward the incident beam with an energy characteristic of the mass of the element it collided with. To understand the probability of a scattering event taking place for a particular element requires the differential cross–section:

\[ \frac{d\omega}{d\Omega} = \left( \frac{Z_1 Z_2 e^2}{4 E_0} \right)^2 \frac{1}{(\sin \theta / 2)^4} \]  

(2-4)

where \( Z_1 \) and \( Z_2 \) are the atomic numbers of the projectile and target atoms respectively, and \( \theta \) is the scattering angle.

Since ions will collide and scatter off the target atoms not only at the surface but also in the bulk of the film, there will be interactions between the scattered projectile and
the other target atoms closer to the surface as it travels toward the detector. These interactions result in energy losses in the scattered projectile which varies continuously with the depth of the scattering event within the bulk of a film. This manifests itself as peak broadening in RBS data. Knowing how the energy losses increase with depth, due to interactions with the bulk of a material (i.e., a materials stopping power), allows film thickness information to be extracted.

RBS experiments were conducted on an IBA Dynamitron linear accelerator [46] with a 2 MeV He$^4$ ion beam (single positive charge). After the collection of the RBS spectrum, the Rutherford Universal Manipulation Program (RUMP) software package [47] was used to model the spectrum data. RBS data served in this research primarily as a confirmation of thin film composition and thickness.

2.7.3. X–ray photoelectron spectroscopy

X–ray photoelectron spectroscopy [48, 49] is a chemical analysis technique which utilizes low energy X–rays to supply energy to the core shell electrons in the near surface atoms of a sample (see Figure 2.9). These electrons can be emitted from the surface provided the energy is sufficient to overcome the binding energy of the core electron state. The kinetic energy ($E_k$) can then be measured by a spectrometer (with work function $\phi$), and the binding energy ($E_b$) of a core electron can then be calculated from:

$$E_b = h\nu - (E_{kin} + \phi) \quad (2-5)$$

where $h$ is Planck’s constant and $\nu$ is the frequency of the photon.

Since binding energies of different core electron states are characteristic to each
element, elemental identification becomes possible. In order to evaluate the relative atomic density of a compound, the differential cross–section needs to be determined

\[
\frac{\partial \sigma}{\partial \Omega} = \frac{\sigma_{tot} L_{x}(\gamma)}{4 \pi}
\]  

(2-6)

where \(\frac{\partial \sigma}{\partial \Omega}\) is the differential cross–section, \(\sigma_{tot}\) is the total cross–section (the integrated differential cross–section over all solid angles), and \(L_{x}(\gamma)\) is called the asymmetry factor.

This factor given by:

\[
L_{x}(\gamma) = 1 + \frac{1}{2} \beta \left( \frac{3}{2} \sin^2 \gamma - 1 \right)
\]

(2-7)

where \(\beta\) is the asymmetry parameter which is dependent on the X–ray radiation, the electron level and the atomic number. Values for \(\beta\) have been theoretically determined for MgK\(_x\) and AlK\(_x\) X–ray sources [49].

In practice, compositional values can be determined from empirical data, and often with greater accuracy. The fractional atomic concentration of an element A may be determined from:

\[
C_{A} = \frac{I_{A}/S_{A}}{\sum_{n}(I_{n}/S_{n})}
\]

(2-8)

where \(I_{A}\) is the measured peak intensity for element A and \(S_{A}\) is the empirically determined atomic sensitivity factor (ASF) for the measured peak [48]. \(I_{n}\) and \(S_{n}\) are the peak intensity and ASF for element(s) n which includes all detectable elements contained in the material being analyzed. ASFs used in this work were experimentally derived by Wagner et al [50].
Figure 2.9: An illustration of the basic mechanism behind X-ray photoelectron spectroscopy which involves transferring the energy of a high energy photon (X-ray) to a ground state electron in the sample atom. Provided the energy is sufficient, the electron will be emitted from the sample atom with a characteristic energy equal to the energy of the photon minus the binding energy of the ground state electron and the work function of the detector.

Film stoichiometry data employing XPS sputter depth profiles were performed using a Thermo VG Scientific Theta Probe XPS system. An aluminum Kα X-ray source (1486.6 eV) was used in conjunction with a monochrometer operating at 100 W. The spot size for the X-rays that impinge on the to-be-analyzed surface was 400µm. Sputtering of the surface material was accomplished using the system equipped argon ion gun which operated at 2.5keV. A low energy electron flood gun was also used to provide surface charge neutralization in order to reduce undesirable elemental peak shifts caused by
charge buildup.

The O to Ti ratios reported in this work represents the average measured values according to the sputter profile data. Also, to ensure measured atomic concentration values represented the bulk TiO$_x$ film, only data points immediately following a 10 to 90 second sputter of the TiO$_x$ surface were taken.

2.7.4. **Energy–dispersive X-ray spectroscopy**

As mentioned before, X–rays can be generated from a high energy electron beam when the primary electrons excite core–shell electrons in an atom. As with AES, this vacancy (or hole) which is created will be filled with an electron from a higher energy level in the electron cloud of the atom. In AES, the energy generated during this transition is transferred to another electron in the electron cloud. But there is also a probability that instead of transferring the electron–transition energy to an electron it will be transferred in the form of an X–ray with an energy which is characteristic of the electron transition (thus, making elemental identification possible). This technique for analyzing these emitted X–rays is called energy–dispersive X–ray spectroscopy (EDS or EDX) [51, 52].

The advantage that EDS has over its electron emission chemical analysis counterparts is that it is much less surface sensitive. This is useful when the bulk composition of a material is desired. In XPS or AES the addition of ion sputtering is required to analyze atoms within the bulk due to the shallow escape depth limiting the emitted electrons; however, EDS analyzes X–rays which typically transmit more easily through solids, allowing X–rays generated far below the surface to be detected for
chemical analysis. The EDS analysis in this research was carried out using a Thermo Noran Voyager EDS detector attached to a Zeiss LEO 1550 field emission SEM.

2.7.5. Scanning electron microscopy

Scanning electron microscopy (SEM) is a surface imaging technique which provides a high magnification view of materials and structures which cannot be seen in the visible spectrum. A basic SEM system is composed of an electron emitter whose electrons are accelerated by an electric field through a series of apertures, magnetic lenses (e.g., condenser and objective lenses), and deflection coils toward a sample surface. The apertures and magnetic lenses serve to focus and shape the electron beam while the deflection coils raster the beam across the sample surface (see Figure 2.10).

When the electron beam impinges upon the surface (refer back to Figure 2.8), there are a few things that can happen: the incident electron can backscatter, cause secondary electrons (SEs) to be emitted from the atoms on the surface, or stimulate the emission of photons (such as X-rays). Each of these events can be detected and the information used to analyze the properties of the sample. Backscatter electrons may provide so-called “Z contrast” which allows for contrast between atoms with higher or lower mass to be observed due to the difference in rate at which primary electrons will elastically scatter off of them. SE emission collection is the most common method for SEM surface imaging since the SEs signal is very strong.

The SEM image is created by simultaneously rastering (or scanning) the electron beam across a surface and collecting either primary or secondary electrons through their respective detectors. The electron signal intensity at each point on the surface can be
plotted according to the raster of the beam, and can then be converted to an image of the scanned surface. Image contrast from an SE signal results mainly from changes in the shape of the surface and the interaction volume of the electron beam (see Figure 2.11).

The interaction volume is the volume beneath the sample surface that the primary electron beam interacts with. SEs are generated throughout this volume, but due to their low energy and the stopping power of the sample material, only SEs generated near the surface are detected; this is one of the principles that gives rise to the high resolution capabilities of SEM.

Naturally, it is expected that as the surface changes shape in directions parallel to the beam there should be a change in signal intensity at the detector (i.e., surfaces which are elevated will be brighter than surfaces which are recessed). Also, when the primary electron beam approaches an edge more of the secondary electrons which are generated below the surface become detectable which manifests itself as an increase in the SE signal; hence, edges may appear brighter in SEM images than surfaces perpendicular to the electron beam.

The high resolution, high contrasting properties of SEM make it very suitable for analyzing nanostructured materials. In this research a Hitachi s–4800 field emission SEM was used which has a maximum resolution of $\approx 1$ nm and an acceleration voltage range of 0.5 to 30 kV. TiO$_x$ film thickness measurements were performed looking at cross sectioned samples. The in–lens secondary electron (SE) detector was used to detect secondary electrons induced by an electron beam with acceleration voltages of 1–5kV. Typical sample working distances were between 3 and 5 mm.
Figure 2.10: A simple illustration of the functionality of a scanning electron microscope system which is composed of an electron gun that accelerates electrons (using a strong electric field) through a series of apertures, magnetic lenses and deflection coils toward a sample surface.

2.7.6. Transmission electron microscopy

Transmission electron microscopy (TEM) is an analysis technique that employs
electrons to generate a sample image with much higher resolution than a light microscope or even an SEM can achieve. TEM accelerates electrons using high potentials (typically in the 100s of kV) toward a sample surface. The electrons are transmitted through the sample and focused onto a phosphorescent screen using condenser, objective, intermediate and projector lenses and a series of apertures (see Figure 2.12). Since the stopping power of most materials on an electron is quite high even high energy electrons will only transmit through samples which are less than a couple hundred nanometers thick. This can make sample preparation fairly difficult when looking at large materials but in the current work the nanostructures which are formed are often small enough that sample preparation is minimal. The basic principle that gives rise to the high resolution capability has to do with the wave and particle properties of electrons (as theorized by Lois–Victor de Broglie). Since an electron can often be treated as a wave its properties can be thought of in a way that is analogous to light. The maximum resolution obtained from a light microscope is dependent on the wavelength of light with which an object is being viewed according to
Figure 2.11: The interaction of an electron beam is shown on different surface geometries. Depending on the angle and shape of the sample surface, the area through which secondary electrons can be emitted changes.
\[ d = \frac{\lambda}{2n \sin \theta} \approx \frac{\lambda}{2NA} \]  \hspace{1cm} (2-9)

where \( d \) is the maximum resolution, \( \lambda \) is the wavelength, \( n \) is the index of refraction, \( \theta \) is the angle of incidence and \( NA \) is the numerical aperture [53].

Figure 2.12: A simplified illustration of a transmission electron microscope system which is composed of an electron source, condenser lenses and apertures which focus the electron beam prior to its interaction with the sample. Electrons which are transmitted through the sample pass through an objective lens, objective and selected area apertures,
intermediate lenses and focused on a phosphorescent screen after passing through the projector lens.

A similar argument applies to wave–particles such as electrons where the electron wavelength is approximately given by:

\[
\lambda_e \approx \frac{h}{\sqrt{2m_oE \left(1 + \frac{E}{2m_o c^2}\right)}}
\]  \hspace{1cm} (2-10)

where \( \lambda_e \) is the de Broglie wavelength (modified to relativistic effects of a high energy electron), \( h \) is Planck’s constant, \( m_o \) is the rest mass of an electron, \( E \) is the electron energy, and \( c \) is the speed of light.

The theoretical resolution of a TEM is:

\[
r_{th} = 1.22 \frac{\lambda_e}{\beta}
\]  \hspace{1cm} (2-11)

where \( r_{th} \) is the theoretical resolution (the radius of the Airy disk) and \( \beta \) is the maximum angle of collection of the objective lens aperture [54]. This implies that by increasing the size of the lens aperture (or removing it all together) the resolution can be improved. However, in practice, magnetic lenses (like optical lenses) cause various types of aberrations (spherical, chromatic, etc.) in the transmitted electron image which need to be considered when determining the maximum resolution of TEM systems.

A more conventional approach in determining the practical resolution limit requires spherical aberration to be considered which results in a minimum Airy disk radius, \( r_{min} \), of:
where $C_s$ is the spherical aberration coefficient [54]. For TEM systems which use aberration correction (i.e., small $C_s$ values), can yield a resolution of $r_{\text{min}} \approx 70$ pm [55]. Without correction, a typical maximum resolution of $r_{\text{min}} \approx 250$–300 pm is observed [56]. However, for samples much thicker than 35 – 50 nm chromatic aberrations can be introduced which will typically increase $r_{\text{min}}$ by a factor of 10 [54]. The TEM system used in this work was a JEOL 2010–F field emission TEM which operates with a 200 kV electron gun and has a 0.19 nm point–to–point maximum spatial resolution.

### 2.7.7. X–ray diffraction

X–ray diffraction is a crystal structure analysis technique which provides a way to not only determine the crystal structure [57 - 59] but also the grain size [60, 61] and preferred orientation of the crystal. It begins with the X–ray source which scans across the surface of a sample at a number of angles. At particular angles parallel X–ray photons, which are scattering off the atoms within different crystal lattice planes, will experience constructive interference (CI) while at all other angles they will experience destructive interference. In XRD reflection mode the geometry follows Bragg’s law:

$$2d \sin \theta = n\lambda$$

(2-13)

where $d$ is the spacing between the scattering (or diffracting) crystal planes, $\theta$ is the angle of incidence, $n$ is any integer, and $\lambda$ is the wavelength of the X–ray beam (see Figure 2.13). By measuring the angle at which these constructive interference events (CIEs) occur we can calculate the $d$ spacing of the crystal planes. Since each crystal structure is going to have different $d$ spacings for its various planes the angles at which CI occurs...
will be unique to that structure.

When investigating poly crystalline materials, looking at the relative intensity of these CIEs will indicate the preferred crystal orientation [62]. Grain/particle size can fundamentally be determined from the Scherrer equation [60, 61]:

$$ t = \frac{C \lambda}{B \cos \theta} $$  \hspace{1cm} (2-14)

where C is the crystal shape factor and B is the full width at half maximum (FWHM) of the CIE intensity profile. In this work XRD analysis was performed on a Bruker D8 XRD tool with a CuKα X–ray source.

Figure 2.13: The basic mechanism behind X–ray diffraction which involves parallel X–ray photons scattering off the atoms within the sample. Atoms located within different crystal lattice planes will experience constructive interference (CI) while at all other angles they will experience destructive interference according to Bragg’s law.
2.7.8. 4–point probe

Four–point probe (4–PP) is a multi–probe electrical analysis technique which enables the determination of thin film sheet resistance [63]. A basic schematic of the 4–PP setup is shown in Figure 2.14, in that figure $d$ and $a$ represent the dimensions of the two dimensional (2–D) thin film and $s_p$ represents the probe spacing. Assuming an infinite thin film plane whose thickness is less than one half $s_p$ the sheet resistance may be calculated from the current, $I$ (measured between probes 1 and 4), and the potential, $V$ (which is measured between probes 2 and 3) according to:

$$R_s = \frac{\pi}{\ln(2)} \left(\frac{V}{I}\right) = 4.53 \left(\frac{V}{I}\right)$$

(2-15)

where the number 4.53 is a geometric factor representative of an infinite plane.

Since, in practice, an infinite plane measurement is not possible, a good approximation to three significant figures is obtained when the smallest dimension ($d$, assuming $a/d > 1$) of the 2–D film being measured is 40 times the spacing of the probes ($40s_p$) [64]. Films whose smallest dimension is only $10s_p$ have geometric factors $\approx 93\%$ that of the infinite approximation. Hence, as a rule of thumb only films which are more than $10s_p$ should use the infinite approximation to minimize error [64].

The resistivity ($\rho$) and conductivity ($\sigma = 1/\rho$) can be calculated when the thickness of the film is known according to:

$$\rho = 4.53t \left(\frac{V}{I}\right) = R_s t$$

(2-16)

where $t$ is the thickness of the film. It is important that when measuring thin films that the
underlying substrate be insulating to avoid incorporating the substrate into the resistance measurement. In this work, 4–PP measurements were carried out on a Signatone sheet resistance probe. Conductivity values were calculated with 4–PP currents in the μA to mA range, potentials in the mV to V range and thicknesses between 5 and 100 nm.

![Figure 2.14: A basic schematic of the four–point probe analysis where d and a represent the dimensions of the two dimensional (2–D) thin film and s_p represents the probe spacing. The sheet resistance is calculated from the current, I (measured between probes 1 and 4), and the potential, V (which is measured between probes 2 and 3).](image)

2.7.9. Electrochemical characterization

In order to electrochemically characterize these Pt coated TiO_x structures two analysis techniques were used: cyclic voltammetry (or CV) and rotating disk electrode (or
RDE) [65, 66]. The motivation behind using CV and RDE analysis techniques in this work is to provide a relatively faster and much less expensive method for comparing the performance of catalyst materials since they don’t require a membrane electrode assembly (or MEA) to be manufactured to analyze each material.

2.7.9.1. Cyclic voltammetry

Cyclic voltammetry is a potential–sweeping three–electrode measurement technique which includes a reference electrode, a working electrode, and a counter electrode connected to a potentiostat (see Figure 2.15). The reference electrode is a stable electrode with a known potential that is used as a zero reference point for CV measurements. The working electrode (i.e., the electrode containing the sample material) is embedded in an insulating shaft with the to–be–analyzed electrode surface at the bottom of the shaft that is submersed in the electrolyte solution. The counter electrode, or current carrying electrode, is used in conjunction with the working electrode to measure the current resulting from the various reactions that take place at the working electrode surface between the catalyst material and the electrolyte. This analysis should take place in an inert gas purge environment. This technique is discussed in detail by Richard Nicholson [67]; and by others [68 - 70] as pertaining to the current research.

A saturated calomel electrode (SCE) was used as the reference electrode which is +0.241V vs. the standard hydrogen electrode (SHE). A 0.1M concentration of perchloric acid (HClO₄) was used as electrolyte. In the current work, potential sweeps between 0–1.5 V vs. SHE were typical.

The region of most interest in this work is known as the hydrogen adsorption
region \((H_{ads})\) which can be seen in Figure 2.16. The area of this region \((Q_{Hads})\), which is below the double layer region, is used to calculate the electrochemically active surface area \((ECSA)\) of the Pt according to:

\[
ECSA_{Pt} \left( \frac{m^2}{g_{Pt}} \right) = \left( \frac{Q_{Hads} (\mu C)}{210(\mu C/cm^2)_L_{Pt}(mg_{Pt}/cm^2)A_{geo}(cm^2)} \right) 10^{-1}
\]  \hspace{1cm} (2-17)

where \(L_{Pt}\) is the platinum loading per area and \(A_{geo}\) is the geometric area of the working electrode. The measured \(Q_{Hads}\) value is normalized by the \(210\mu C/cm^2_{Pt}\) term which represents the \(Q_{Hads}\) per area for a 2–D Pt electrode.

![Figure 2.15: An illustration of a typical cyclic voltammetry measurement system.](image-url)
2.7.9.2. Rotating disk electrode

Rotating Disk electrode analysis requires the same setup as CV but instead of using a stationary working electrode the electrode is rotated at a determined rate (see Figure 2.17). The centripetal effects of the rotation cause the used electrolyte to move away from the electrode which in turn draws up fresh electrolyte. This allows for the measurement of the diffusion limiting current (among other things) of the oxygen reduction reaction (or ORR). RDE as an analysis technique is reviewed in greater detail by Compton et al [71].

In the current work, potential sweeps between 0–1 V vs. SHE were typical. The rotation rates of analysis for each material were 100, 400, 900, and 1600 rpm. The system was also purged with pure O₂ to maximize the ORR reaction. Figure 2.18 shows an
example set of ORR polarization curves obtained through RDE analysis. These curves represent the electrochemical behavior of the same material analyzed above for CV analysis (i.e., 20 wt. % Pt on carbon).

2.7.9.3. **Accelerated stress testing**

Accelerated stress tests (ASTs) were performed on catalyst materials to evaluate the long term electrochemical stability of the materials. Sulfuric acid (H₂SO₄) was used as the electrolyte in these tests for better comparison with stability tests performed in the literature [72, 73]. A 0.5M solution of H₂SO₄ was used as opposed to 0.05 M that would typically be used during regular CV analysis to increase the rate of breakdown. Changes in the electrochemically active surface area were monitored over 2000 cycles (in 500 cycle increments) between 0 and 1.2V at a sweep rate of 100 mV/s.

![Figure 2.17: An illustration of the electrode used in RDE analysis.](image)
Figure 2.18: An example of a typical ORR polarization curve for a 20 wt.
% Pt on carbon catalyst material obtained through RDE analysis. The
diffusion limiting current (DLC) values at various working electrode
rotation rates are used in the calculation of activity values.

2.7.10. Adhesion testing

Since some manufactured structures involve more than a single layer of material
(e.g., TiO$_x$/SiNWs and TiO$_x$/CB) and structures need to be separated and dispersed as a
layer on the working electrode, it is desirable to understand the level to which these
materials will adhere to each other. Hence, a common qualitative adhesion test, the
“scotch tape” test [74 - 76], was performed on TiO$_x$ films coating 2-D Si, SiO$_2$ and glassy
carbon substrates as well as on PEALD Pt coatings on 2-D TiO$_x$ films.

2.8. Summary

In this chapter, the design aspects of the atomic layer deposition (ALD) reactor
used for the development of TiO$_x$-based materials were discussed including the
deposition parameter ranges. Nanostructure manufacturing techniques that were used to form high aspect ratio TiO$_x$ structures were summarized including the use of AAO as a template for TiO$_x$ nanotube formation, SiNWs as a core shell approach to making TiO$_x$ nanorods, and TiO$_x$ coatings dispersed colloidal carbon layers. The mixed phase Nb$_x$Ti$_y$O$_z$ material development parameters were outlined as well as a series of chemical stability tests used to evaluate the stability of both TiO$_x$ and Nb$_x$Ti$_y$O$_z$ materials. Two different catalyst deposition techniques were mentioned (PEALD Pt and LPD Pt) which were used to coat nanostructured materials in preparation for electrochemical analysis.

Background into the different material characterization techniques was presented including: AES, RBS, XPS, EDS, SEM, TEM, XRD, 4-point probe, CV, and RDE. Accelerated stress testing was also outlined as a method for evaluating the long term performance of newly manufactured materials.

2.9. References


Chapter 3: Support Material Development

This chapter provides an overview of the ALD TiO$_x$ deposition optimization which was performed in this work. The optimization includes: the initial TiO$_x$ film development, the development of a post deposition oxygen reducing anneal, optimizing deposition parameters to increase the effectiveness of the post deposition oxygen reducing anneal, optimizing film coverage over high AR structures, mixed phase Nb$_x$Ti$_y$O$_z$ development and preliminary electrical stability testing of conductive films.

3.1. Initial ALD TiO$_x$ Development

Early baseline TiO$_x$ films were deposited at 325°C with 2.0s/0.5s (TiCl$_4$/H$_2$O) pulse times. As shown in Figure 3.1, a thermal anneal of these films in forming gas (5% hydrogen in argon) at 600°C for 4 h only yielded films with minimal conductivity ($\approx$1 S/cm). In order to increase conductivity more dramatically, either much higher temperatures would be required for a thermal anneal in forming gas or an alternative method for reducing oxygen would need to be developed. In response to this dilemma, a post deposition oxygen reducing anneal (PDORA) was developed in house which utilized pure hydrogen as the oxygen reducing gas. Initial TiO$_x$ films annealed using this process exhibited a more dramatic increase in conductivity (changing from 1.9 to 72 S/cm) while only needing to be heated to 450°C for 60 minutes (see Figure 3.1).
Figure 3.1: A comparison is shown above between the effectiveness of a thermal anneal in forming gas (@ 600°C for 4 h) and the PDORA in pure H₂ (@ 450°C for 60 min) at increasing the conductivity of ALD TiOₓ films.

XPS sputter depth profiles of the TiOₓ film exposed to the PDORA showed only a 4% reduction in oxygen concentration (with respect to Ti) which easily falls within the 6% calculated error (see Figure 3.2). While it is assumed that oxygen reduction is occurring in the TiOₓ film resulting in the increased conductivity of the film, XPS analysis is not sensitive enough to observe this change; however, more conductive films shown in future sections do measure statistically significant reductions in oxygen which give credence to this assumption.
Figure 3.2: The effects of a thermal anneal in forming gas (@ 600°C for 4 h) and the PDORA in pure H\textsubscript{2} (@ 450°C for 60 min) on the ratio of oxygen to titanium in ALD TiO\textsubscript{x} films.

### 3.2. PDORA Development

As part of a study to optimize the effectiveness of a PDORA on TiO\textsubscript{x} conductivity, several films were deposited at 325°C with pulse times of 2.0s/0.5s (TiCl\textsubscript{4}/H\textsubscript{2}O). These samples were annealed in H\textsubscript{2} according to the parameters shown in Table 3-1. It was observed that the anneal served to significantly increase the conductivity of the TiO\textsubscript{x} films after just 15 minutes; while films annealed for much longer times (i.e., up to 120 minutes) only showed marginal improvement as presented in Figure 3.3a. The conductivity of these films ranged from 39 to 44 siemens per centimeter (S/cm). As indicated in Figure 3.3b, increasing anneal temperature from 350°C to 450°C did not appear to have a significant effect on conductivity. As a result of these findings, all subsequent PDORA processes performed on TiO\textsubscript{x} films and TiO\textsubscript{x}-based materials
discussed in this work will consist of 30 minutes in H\textsubscript{2} at 450°C.

Conductivity values exhibited by reduced TiO\textsubscript{x} materials have been reported elsewhere at several hundred S/cm [1], yet the results mentioned above indicate that optimization of the PDORA process alone yields TiO\textsubscript{x} thin films that are less than 100 S/cm. Hence, the next section describes a modified approach for improving TiO\textsubscript{x} thin film conductivity.

Table 3-1: Parameters of H\textsubscript{2} PDORAs and resulting conductivity of TiO\textsubscript{x} films where T\textsubscript{A} is the anneal temperature, P\textsubscript{chamber} is the chamber pressure, P\textsubscript{H2} is the pressure of the H\textsubscript{2} in the delivery lines, t\textsubscript{ox} is the thickness of the TiO\textsubscript{x} film, R\textsubscript{s} is the sheet resistance, and \(\sigma\) is the conductivity of the TiO\textsubscript{x} film.

<table>
<thead>
<tr>
<th>Film</th>
<th>T\textsubscript{A} (°C)</th>
<th>Time (min)</th>
<th>P\textsubscript{chamber} (mtorr)</th>
<th>P\textsubscript{H2} (torr)</th>
<th>t\textsubscript{ox} (nm)</th>
<th>R\textsubscript{s} (Ω/□)</th>
<th>(\sigma) (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>450</td>
<td>30</td>
<td>500</td>
<td>50</td>
<td>34</td>
<td>8.0 x10\textsuperscript{3}</td>
<td>37</td>
</tr>
<tr>
<td>A2</td>
<td>450</td>
<td>90</td>
<td>500</td>
<td>50</td>
<td>34</td>
<td>8.5 x10\textsuperscript{3}</td>
<td>36</td>
</tr>
<tr>
<td>A3</td>
<td>350</td>
<td>30</td>
<td>500</td>
<td>50</td>
<td>33</td>
<td>10 x10\textsuperscript{5}</td>
<td>27</td>
</tr>
<tr>
<td>A4</td>
<td>350</td>
<td>30</td>
<td>500</td>
<td>50</td>
<td>37</td>
<td>8.5 x10\textsuperscript{3}</td>
<td>33</td>
</tr>
<tr>
<td>A5</td>
<td>450</td>
<td>15</td>
<td>500</td>
<td>50</td>
<td>33</td>
<td>7.7 x10\textsuperscript{5}</td>
<td>39</td>
</tr>
<tr>
<td>A6</td>
<td>450</td>
<td>30</td>
<td>500</td>
<td>50</td>
<td>32</td>
<td>7.5 x10\textsuperscript{3}</td>
<td>42</td>
</tr>
<tr>
<td>A7</td>
<td>450</td>
<td>60</td>
<td>500</td>
<td>50</td>
<td>34</td>
<td>6.7 x10\textsuperscript{5}</td>
<td>43</td>
</tr>
<tr>
<td>A8</td>
<td>450</td>
<td>120</td>
<td>500</td>
<td>50</td>
<td>33</td>
<td>6.7 x10\textsuperscript{3}</td>
<td>44</td>
</tr>
</tbody>
</table>
It can be seen that when the PDORA time was longer than 15 minutes and the temperature was within the range of 350 – 450°C there was no significant change in conductivity.

3.3. Optimization of TiO$_x$ in Conjunction with the PDORA

The following section aims to improve the effectiveness of the PDORA by examining post anneal conductivity changes in response to ALD process parameters. Temperature, thickness, and pulse times (TiCl$_4$/H$_2$O) were varied to evaluate changes in conductivity. A preliminary stability test was performed to evaluate changes in conductivity of films following an exposure to a heated O$_2$ environment.

3.3.1. Temperature effects

As part of the initial evaluation of the effects of temperature on the properties of TiO$_x$ films, top-down film structural analysis was performed in SEM. Shown in Figure 3.4 are two sequences of top-down SEM micrographs. The first row represents films which were deposited in a temperature range of 125 to 450°C. The second row represents...
those same films following a PDORA. The growth morphology for thin film TiO\textsubscript{x} using TiCl\textsubscript{4} and H\textsubscript{2}O in an ALD reactor has been studied elsewhere for temperatures between 100 and 400°C [2, 3]. TiO\textsubscript{x} films typically start as an amorphous coating but as the film thickness increases, small crystals of anatase TiO\textsubscript{2} begin to form within the film and grow as the film thickness continues to increase [4].

The PDORA was most effective on films which were deposited between 175 and 225°C (as calculated from 4-point probe and cross-sectional SEM thickness measurements). The range in conductivity of films following the PDORA was 2.9-200 S/cm (see Figure 3.5). The highest conductivity was measured for films deposited at 200°C.

X-ray photoelectron spectroscopy was used to evaluate changes in composition when increasing deposition temperature. Individual measurements of composition were taken along the depth profile of the TiO\textsubscript{x} films, and the compositional data was averaged to yield the reported composition; these values are plotted in Figure 3.6. This data reveals that as deposition temperature was increased, the measured oxygen concentration also increased. The horizontal dotted line intersecting with the “O/Ti trend” line in Figure 3.6 represents the ratio at which the maximum conductivity occurred (i.e., O/Ti = 1.75). The solid horizontal line represents the O/Ti ratio measured for a single crystal rutile TiO\textsubscript{2} (001) standard obtained from MTI Corp. (i.e., O/Ti = 2.75).
Figure 3.4: Top down SEM of ALD TiO$_x$ surfaces deposited at temperatures from 125 to 450°C. The top row shows as deposited films and the bottom row shows the films following the PDORA. Scale bars
Figure 3.5: This graph depicts oxygen reduced TiO$_x$ film conductivity vs. ALD deposition temperature.

Figure 3.6: The oxygen to titanium ratios are plotted for TiO$_x$ films deposited at temperatures ranging from 125°C to 450°C (circles). Compositional values were obtained from XPS sputter depth profiles. A trend appears, indicating that as temperature increases, oxygen increases as well (dotted line). The highest conductivity was observed at the ratio
O/Ti = 1.75 (dotted horizontal line). The O/Ti ratio of rutile TiO₂ (001) is also presented (solid horizontal line).

To evaluate the stability of oxygen reduced TiOₓ films, an “early level” stability test (as mentioned in chapter 2) was designed. The test involved heating up the films in an oxygen atmosphere (200°C) and evaluating the changes in TiOₓ film conductivity following timed exposures (30 and 60 min). Figure 3.7 plots the conductivities of the same films presented in Figure 3.5 before and after oxygen exposures. The TiOₓ film deposited at 200°C exhibited a nearly 20% decrease in conductivity after the first 30 min exposure and only an additional few percent decrease following a second 30 min exposure. Hence, it appears that the most conductive film (deposited at 200°C) was among the most stable.

Figure 3.7: Conductivity measurements vs. ALD deposition temperature are shown for the as deposited TiOₓ film and for the same film annealed for 30 min and 60 min in O₂ at 200°C (indicated by σ in the legend). The
percent change in conductivity following the 30 min and 60 min O\textsubscript{2} exposures is also shown (indicated by \(\Delta\sigma\) in the legend) where the percent change represents the total change in conductivity from pre O\textsubscript{2} exposure to post O\textsubscript{2} exposure.

3.3.2. Thickness effects

It was necessary to find an optimal thickness for TiO\textsubscript{x} films (or at least an optimal thickness range) prior to the exploration of nanostructure manufacturing. Films were deposited between 5 and 100 nm thick (or 80-1600 ALD cycles). Top-down and cross-sectional SEM micrographs of the 15-100 nm TiO\textsubscript{x} films are presented in Figure 3.8 and Figure 3.9, respectively. These micrographs appear to confirm the typical growth which has been reported for TiO\textsubscript{x} films elsewhere [2 - 4]. Due to SEM analysis limitations, the 5 nm TiO\textsubscript{x} film is not shown.

At 15 nm, a TiO\textsubscript{x} film is observed with small nuclei beginning to form (see Figures 3.8 and 3.9). As the film thickness increases the nuclei sizes also increase to become a larger and larger portion of the overall film. Between 50 and 100 nm the nuclei appear to coalesce.

The conductivity vs. TiO\textsubscript{x} film thickness is plotted in Figure 3.10. The low conductivity of films < 25 nm thick suggests that nanostructured materials should be manufactured with TiO\textsubscript{x} films whose thickness are \(\geq\) 25 nm.
Figure 3.8: Top down SEM micrographs of 15 nm (a, e), 25 nm (b, f), 50 nm (c, g), and 100 nm (d, h) blanket TiO$_x$ films are shown. The micrographs show side by side comparisons of as deposited (a-d) and PDORA (e-h) films [4]. While as deposited films show no conductivity, films ≥25 nm show a significant increase in conductivity following the PDORA. Scale bars in each micrograph represent 500 nm.
Figure 3.9: SEM cross-sections of 15 nm (a), 25 nm (b), 50 nm, and 100 nm (d) TiO$_x$ films deposited at 200°C are displayed. Scale bars represent 200 nm.

Figure 3.10: Conductivity measurements vs. TiO$_x$ film thickness are shown.
The 5 – 100 nm films were also tested for stability in a heated O$_2$ environment. It was found that films thicker than 25 nm were much more conductive and stable than thinner films. Conductivity changes were evaluated by thickness following exposure of the films to a heated oxygen atmosphere for 30, 60, and 120 minutes. Figure 3.11, like Figure 3.7, show both the conductivity of each film following each heated exposure as well as the percent change in conductivity. The 50 nm film exhibits the highest conductivity and stability after 120 min in a 200°C O$_2$ atmosphere. The film exhibited only a 13% decrease after 30 minutes, an additional 4% after 60 minutes, and only another 3% after a total of 120 minutes of exposure time.

Figure 3.11: Conductivity measurements vs. TiO$_x$ film thickness are shown (indicated by σ in the legend) for the oxygen reduced TiO$_x$ film and for the same film annealed for 30 min, 60 min and 120 min in O$_2$ at 200°C. The percent change in conductivity following the 30 min, 60 min, and 120 min O$_2$ exposures is also shown (indicated by Δσ in the legend),
where the percent change represents the total change in conductivity from pre O\textsubscript{2} exposure.

XPS depth profiles were taken of the 5-100 nm TiO\textsubscript{x} films before and after the PDORA (see Figure 3.12). Figure 3.13 shows a plot of XPS measured O/Ti ratios for the 5 – 100 nm films before and after the PDORA as measured by XPS sputter depth profiles. The O to Ti ratios of these films (including the rutile TiO\textsubscript{2} standard) indicates that oxygen decreases when film thickness is increased. This is actually an artifact of preferential sputtering, where oxygen is more easily sputtered than titanium from TiO\textsubscript{x} films (i.e., the longer the sputter, the lower the ratio of O to Ti) [5]. It should be noted that the films generally decrease in oxygen following the PDORA. For the 25 and 50 nm films, a 20 to 30\% reduction in the O to Ti ratio was observed. This corresponds with the increased conductivity seen in Figure 3.10 and Figure 3.11. However, the 100 nm film shows almost no change in the O to Ti ratio following the PDORA. It is believed that this is due to a sputter rate transition between oxygen and titanium. When the TiO\textsubscript{x} surface becomes too oxygen deficient it becomes less energetically favorable to remove oxygen as rapidly and an equilibrium point is reached [5, 6]. It appears that in the case of the 100 nm film (with 120 s sputter times between analysis points), a limiting O to Ti ratio is reached, where XPS measures essentially the same composition before and after the PDORA.
Figure 3.12: Shown are example XPS depth profiles of a 25 nm TiO\textsubscript{x} film deposited by ALD before (a) and after (b) the PDORA.
3.3.3. Film coverage

In carrying out the coating of anodic aluminum oxide membrane (AAM) templates, some process optimization needed to occur to ensure maximum coverage of AAM pores while still maintaining the needed high conductivity of the TiO$_x$ films. The SEM and 4-point probe results indicate that film coverage and film conductivity are not independent of each other and hence both need to be considered when engineering the ALD process to form nanostructures. Table 3-2 shows the tabulated TiO$_x$ film deposition parameters and resulting film thickness, sheet resistance, and calculated conductivity for each film.
Table 3-2: Temperatures and precursor gas pulse times (TiCl$_4$ and H$_2$O) for select TiO$_x$ films with their resulting thickness ($t_{ox}$), sheet resistance ($R_s$) and conductivity ($\sigma$) are tabulated below.

<table>
<thead>
<tr>
<th>Film</th>
<th>Temp (°C)</th>
<th>TiCl$_4$/H$_2$O Pulse Time</th>
<th>$t_{ox}$ (nm)</th>
<th>$R_s$ (Ω/□)</th>
<th>$\sigma$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A6</td>
<td>325</td>
<td>2.0s/0.5s</td>
<td>34</td>
<td>7.5 x10$^3$</td>
<td>42</td>
</tr>
<tr>
<td>C1</td>
<td>450</td>
<td>8.0s/2.0s</td>
<td>29</td>
<td>11 x10$^3$</td>
<td>31</td>
</tr>
<tr>
<td>C2</td>
<td>325</td>
<td>8.0s/2.0s</td>
<td>33</td>
<td>14 x10$^3$</td>
<td>21</td>
</tr>
<tr>
<td>C3</td>
<td>275</td>
<td>8.0s/2.0s</td>
<td>30</td>
<td>7.7 x10$^3$</td>
<td>41</td>
</tr>
<tr>
<td>C4</td>
<td>175</td>
<td>8.0s/2.0s</td>
<td>25</td>
<td>1.7 x10$^3$</td>
<td>240</td>
</tr>
<tr>
<td>C5</td>
<td>125</td>
<td>8.0s/2.0s</td>
<td>33</td>
<td>48 x10$^3$</td>
<td>6.3</td>
</tr>
<tr>
<td>D1</td>
<td>175</td>
<td>16.0s/4.0s</td>
<td>26</td>
<td>10 x10$^3$</td>
<td>38</td>
</tr>
</tbody>
</table>

Shown in Figure 3.14 are SEM cross-sections of a sample TiO$_x$ deposition on AAM pores at various pore depth fractions. Pore depth fraction is the normalized distance from the pore opening at the AAM surface to the pore depth representing a 100:1 aspect ratio (i.e., L:d where L is the pore depth and d is the pore diameter). The values are normalized this way in order to be able to compare the pore coverage for AAM pores of different diameters. Displayed in Figure 3.15 are a number of conformality measurements for TiO$_x$ films which were deposited at various temperatures and with different pulse times. It was observed that temperature had no statistically significant effect on the conformality of TiO$_x$. This observation is based on the fact that the conformality data appears to display only random variations for films deposited with 8 and 2 second pulse times (for TiCl$_4$ and H$_2$O, respectively).

However, the pulse times do have a noticeable effect, as expected. When going
from 2 and 0.5 seconds (for TiCl$_4$ and H$_2$O, respectively) to 16 and 4 seconds, there is a \(~2.5\times\) increase in conformality. Upon observing this, the question that naturally arises is: why not continue increasing the pulse times? The answer is twofold. First, to deposit a film with a 30+ second precursor pulse equals about 22 h of deposition time. While for purely research purposes this is not an issue, for future large-scale manufacturing purposes it certainly is. Second, and more importantly, as ALD pulse times were increased the conductivity of the films decreased. Figure 3.16 plots the conductivity vs pulse time of films deposited at three different temperatures (175, 200, and 325°C). It can be observed that the conductivity universally decreases when pulse time is increased.

In trying to strike a balance between AAM pore coverage and film conductivity, it was determined that 8 and 2 second pulse times would provide an optimal combination of the two. However, the level of conductivity seen in films using 4s/1s pulse times does naturally stimulate the question of whether there is another type of structure more compatible with shorter pulses. Section 3.4.2 below will discuss how silicon nanowires (SiNWs) are a suitable surface for the 4s/1s pulse time TiO$_x$ process.
Figure 3.14: Cross-sectional SEM micrographs of TiO$_x$ coated AAM pores are shown. Film thickness measurements were taken at different pore depth fractions to calculate the level of conformality at each depth. In the micrographs there are three general regions observed: the AAM pores (the darkest regions), the AAM template (the lighter regions separating the dark regions), and the TiO$_x$ film (the narrow intermediate tone regions lining the AAM).
Figure 3.15: Shown above is a plot of the calculated conformality (based on SEM measurements) as a function of fractional pore depth. This revealed that increasing pulse times from 2.0s/0.5s to 8.0s/2.0s (film A6 to C2) and from 8.0s/2.0s to 16.0s/4.0s (film C4 to D1) showed noticeable increases in conformality. Films C1 thru C5 represent films deposited with 8.0s/2.0s pulse times and at temperatures ranging from 450°C to 125°C [4].
Figure 3.16: Effects of pulse time on conductivity (a) and percent conductivity change (b) of 2-D TiO$_x$ films at three different temperatures are shown.

3.4. Nanostructure Manufacturing

The next section presents the results of the manufacturing processes described in section 2.3 of chapter 2, where AAM template, SiNW core-shell, and carbon black core-shell techniques were described.

3.4.1. TiO$_x$ nanotube fabrication using AAM templates

As mentioned previously, the optimized TiO$_x$ film chosen for AAM coverage was deposited at 200°C with 8s/10s/2s/10s (TiCl$_4$/Ar/H$_2$O/Ar) pulse times. The reactor pressure was 750mtorr and gas line pressures were held at 100 Torr, 60 Torr, and 40 Torr for the TiCl$_4$, H$_2$O and the Ar purge, respectively (see Figure 2.2 of chapter 2). Following the separation of the TiO$_x$ nanotubes (NTs) from the AAM support, LPD Pt was deposited on the NTs as described in section 2.6.1. Pt particles are roughly 6-8 nm and
sporadically dispersed across the TiO$_x$ NT surface. SEM micrographs representing each step in the TiO$_x$ NT manufacturing process are shown in Figure 3.17. There were regions without any visible LPD Pt deposition (not shown) as well as regions with very high LPD Pt deposition (in the form of Pt particle clustering).

Figure 3.17: A process flow showing that the AAM nanopore template was coated with ALD TiO$_x$ (a) and then the template was removed via sonication in a 5.0 M solution of NaOH (b). A LPD Pt process was then used to coat the resulting TiO$_x$ NTs (c). The Pt particle dispersion appears to access all surfaces but does not coat all surfaces consistently (d).

Since average O/Ti values of TiO$_x$ films which utilized the PDORA had been shown to exhibit significant oxygen reduction, it was pertinent to also know whether a crystal phase change had occurred within reduced TiO$_x$ materials. Hence, X–ray
diffraction (XRD) analysis was performed to investigate the phases present in an oxygen reduced TiO$_x$ NT powder. However, the XRD spectra only indicated the presence of anatase TiO$_2$ [7, 8]; no peaks were observed which were representative of oxygen reduced crystalline phases of TiO$_2$ (see Figure 3.18) [9 - 11]. Hence, the significant increase in conductivity observed in TiO$_x$ is here attributed to oxygen defects [12, 13].

![XRD data](image)

Figure 3.18: XRD data of a TiO$_x$ film following a PDORA. Only anatase TiO$_2$ crystal peaks are visible in the 2θ spectrum.

### 3.4.2. Silicon nanowires

The VLS grown silicon nanowires (SiNWs) were coated with an ALD TiO$_x$ film deposited using the same recipe that was used to coat AAMs but with TiCl$_4$/H$_2$O pulse times of 4s/1s rather than 8s/2s (see Figure 3.19). The 4s/1s recipe was previously shown to yield 2-D films with much higher conductivity than the 8s/2s recipe. And due to the relatively sporadic growth nature of the as grown SiNW structures, the shorter TiCl$_4$/H$_2$O
pulse times become much more permissible when contrasted with AAM surfaces. TiO$_x$ coatings over SiNWs measured nearly 100% conformality. It is important to note that the sporadic growth of SiNW structures also provides an advantage over AAM templated NTs during the deposition of PEALD Pt.

![SEM of the TiO$_x$/SiNWs following the PDORA. The scale bar indicates 1µm [8].](image)

Figure 3.19: SEM of the TiO$_x$/SiNWs following the PDORA. The scale bar indicates 1µm [8].

SEM micrographs of each step of this process are shown in Figure 3.20. The process begins with as grown SiNWs, which are then coated with TiO$_x$ followed by PEALD Pt. For this particular process, the Pt particles are fairly small, and consequently, high resolution TEM was performed. Figure 3.21 shows TEM micrographs representing the manufacturing steps for TiO$_x$/SiNWs (including the PEALD Pt step), where Pt particle size was determined to be $\approx$ 3-4 nm.
Figure 3.20: Shows top down SEM of as grown SiNWs (a), TiOₓ/SiNWs (b), Pt on TiOₓ/SiNWs (c) and a close up of the Pt coating (d). The ALD TiOₓ film easily coats SiNW surfaces and the PEALD Pt shows nice coverage across the TiOₓ surface.
Figure 3.21: TEM micrographs show the steps of Pt on TiO$_x$ coated SiNW manufacturing starting with as grown SiNWs (a) followed by the ALD TiO$_x$ coating (b) and then the PEALD Pt coating of the TiO$_x$ surfaces (c). The Pt particle size is $\approx$ 3-4 nm for 100 PEALD cycles.

A TiO$_x$ on SiO$_2$ substrate was used to perform XPS analysis of the deposited PEALD Pt. The XPS surface scan of typical Pt 4f peaks is shown in Figure 3.22, where strong Pt 4f$^{5/2}$ and 4f$^{1/2}$ peaks can be observed at 71.2 and 74.5 eV, respectively. These peaks are indicative of mostly metallic Pt.
Figure 3.22: An XPS spectrum is shown of Pt 4f peaks with Pt 4f\(^{7/2}\) and 4f\(^{5/2}\) peaks, (observed at 71.2 and 74.5 eV, respectively), suggestive of mostly metallic Pt.

AES data was also taken of the witness TiO\(_x\) substrate to confirm the presence of Pt. This technique provides a high degree of surface sensitivity that is useful for ultra-thin coatings of Pt. However, with Pt particles on the order of 5 nm it is likely that some of the Auger electron signal from the underlying TiO\(_x\) film will also be detected. This will result in the Pt signal becoming somewhat less than what would be representative of the actual Pt coverage. Figure 3.23 shows an AES surface survey of 200 PEALD cycles of Pt on a 2-D TiO\(_x\) film. Approximately 50 atomic % Pt is observed; though, as just mentioned, the actual surface coverage is likely higher. EDS measurements (see Table 3-3 in section 3.4.4) indicate a Pt loading of 5.6 wt. %.
Figure 3.23: AES spectrum of PEALD Pt on 2-D TiO$_x$ shows $\approx$ 50 at. % Pt coating the TiO$_x$ surface.

In addition to the 100 cycle PEALD Pt coated TiO$_x$/SiNW material reported above, two other vapor phase Pt coated TiO$_x$/SiNW materials were prepared in this work for electrochemical characterization (see section 4.1.3 of chapter 4). The first was coated with PEALD Pt (600 cycles) yielding a $21 \pm 7$ wt. % Pt loading (see Figure 3.24a) and the second was coated with PVD Pt with a $2.9 \pm 1.1$ wt. % Pt loading (see Figure 3.24b).
3.4.3. Colloidal materials

In order to obtain conformal coverage of 2-D 3x3 cm SiO₂ substrates, the CB dispersion technique described in Chapter 2 was used. A minimum of 1 mg to 1 ml (mass to volume ratio) of CB in a solution of 1 part IPA to 4 parts H₂O was required to make a continuous CB layer.

Two quantities of CB were chosen for ALD TiOₓ coating. First, a 2.5 mg CB to 1 ml solution (or just 2.5:1) was dispersed and coated with TiOₓ using the same 8s/2s (TiCl₄/H₂O) pulse time recipe used on AAM templates. Second, a 1:1 CB to solution ratio was dispersed and coated with the same 4s/1s (TiCl₄/H₂O) pulse time recipe used on SiNWs. Both ALD recipes were used in an attempt to provide a colloidal TiOₓ baseline for both TiOₓ NT and TiOₓ/SiNW materials. The before and after SEM micrographs of the TiOₓ deposition on a CB layer are shown in Figure 3.25a-b.
Figure 3.25: The steps of synthesizing the TiO$_x$/CB materials are shown above. The process begins with dispersing CB onto a 2-D surface (a), followed by ALD TiO$_x$ (b), and coating with PEALD Pt (c) or LPD Pt (d).

Pt was deposited on both of the TiO$_x$ coated CB (TiO$_x$/CB) materials, each according to the material for which it attempts to provide a colloidal baseline (i.e., LPD Pt for the TiO$_x$ coated 2.5:1 CB layer and PEALD Pt for the TiO$_x$ coated 1:1 CB layer). The PEALD Pt process consisted of 600 cycles of the recipe described in chapter 2. The results of these two deposition methods may be observed in Figure 3.25. The LPD Pt exhibited the same Pt particle size (6-8 nm) and dispersion (sporadic) that was observed for TiO$_x$ NTs. The PEALD Pt, however, showed consistent particle distribution over the upper surface but limited dispersion below the upper surface of the TiO$_x$/CB layer due to the coverage limits of PEALD Pt. The particle size, according to top-down SEM, is $\approx 10$
nm on average.

### 3.4.4. Catalyst deposition summary

A summary is shown in Table 3-3 of the resulting Pt loadings ($L_{Pt}$) following LPD, PEALD and PVD Pt depositions on the various fabricated support materials. $L_{Pt}$ values were calculated from multiple EDS measurements of dispersed samples utilizing both LPD and PEALD Pt. EDS is used to measure Pt loadings as it is less surface sensitive in nature. The use of X-rays rather than electrons emitted from the analyte provides elemental information from both the surface and bulk atoms of a multilayered structure. Hence, the overall elemental ratio of multilayer 3-D structures can be obtained more easily with EDS than with either XPS or AES. An example EDS spectrum of PEALD Pt on TiO$_x$/CB is shown in Figure 3.26.

Table 3-3: The platinum loading ($L_{Pt}$) of the various catalyst materials are listed here. Materials are separated into two groups: LPD Pt coated and vapor phase Pt coated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$L_{Pt}$ (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_x$/CB (LPD Pt)</td>
<td>4.1 ± 0.6</td>
</tr>
<tr>
<td>TiO$_x$ NTs (LPD Pt)</td>
<td>16 ± 4</td>
</tr>
<tr>
<td>Nb$<em>{y}$Ti$</em>{1-y}$O$_z$ NTs (LPD Pt)</td>
<td>19 ± 3</td>
</tr>
<tr>
<td>TiO$_x$/CB (PEALD Pt)</td>
<td>2.2 ± 0.3</td>
</tr>
<tr>
<td>TiO$_x$/SiNWs (PEALD Pt) 1</td>
<td>5.6 ± 0.4</td>
</tr>
<tr>
<td>TiO$_x$/SiNWs (PEALD Pt) 2*</td>
<td>21 ± 7</td>
</tr>
<tr>
<td>TiO$_x$/SiNWs (PVD Pt)*</td>
<td>2.9 ± 1.1</td>
</tr>
</tbody>
</table>

*Calculated values (see Figure 3.27 and Table 3-4)
A model was created for calculating Pt loadings on TiO$_x$/SiNW materials to potentially enable the calculation of future ultra-low Pt loadings which may not be detectable using EDS. The basic model utilized measurements of: the average diameter of silicon nanowires, TiO$_x$ film thickness, Pt particle size and Pt particle distribution (i.e., area density) as illustrated in Figure 3.27a. Since Pt particles are often not circular, a half ellipsoid approximation was used based on measurements of three axes (2a, 2b, and c) as shown in Figure 3.27b. Densities used for TiO$_x$, Pt, and Si were 4.23, 2.65, and 21.45 g/cm$^3$, respectively. The percent coverage of Pt particles on TiO$_x$/SiNW surfaces is modeled to be 100% for PEALD Pt and 50% for PVD Pt. The estimations are made based on the observed limits of both deposition techniques but are likely higher than is representative of the actual material. Consequently, it is expected that calculated Pt loadings will be slightly higher than the measured loading.
Figure 3.27: An illustration representing a Pt coated TiO$_x$/SiNW is shown above. Measurements of the SiNW diameter ($d_{Si}$), TiO$_x$ film thickness ($t_{TiO_x}$), and Pt particle volume ($V$, calculated from $2a$, $2b$, and $c$ axis measurements), were used in the calculation of the Pt loading.

Table 3-4 shows the results of this model applied to three different TiO$_x$/SiNW materials. The calculated uncertainty representing the combined uncertainties of multiple measured variables is fairly high (between 30 – 40%). The first material listed, “TiO$_x$/SiNWs (PEALD Pt) 1,” representing 100 PEALD Pt cycles on TiO$_x$/SiNWs, was also measured using EDS. The average Pt loading was measured to be $5.6 \pm 0.4$ wt. %, while the loading calculated from the model previously described is $7.1 \pm 2.5$ wt. %. It is clear that even though the model predicts a higher Pt loading than the loading measured
by EDS, the EDS value does fall within the calculated uncertainty of the model.

Table 3-4: The key parameters used in the calculation of Pt loading for three different materials are shown here. They include SiNW diameter \((d_{Si})\), TiO\(_x\) film thickness \((t_{TiOx})\), average Pt particle volume \((V_{ave})\), the number of Pt particle per area \((P_{dens})\), and the maximum percent coverage \((C_{\%})\) of the TiO\(_x\)/SiNW structures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d_{Si}) (nm)</th>
<th>(t_{TiOx}) (nm)</th>
<th>(V_{ave}) ((\text{nm}^3))</th>
<th>(P_{dens}) ((\text{cm}^{-2}))</th>
<th>(C_{%})</th>
<th>(L_{Pt}) ((\text{wt. %}))</th>
<th>EDS ((\text{wt. %}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_x)/SiNWs (PEALD Pt) 1</td>
<td>37</td>
<td>25</td>
<td>15</td>
<td>2.1E+12</td>
<td>100</td>
<td>7.1 ± 2.5</td>
<td>5.6 ± 0.4</td>
</tr>
<tr>
<td>TiO(_x)/SiNWs (PEALD Pt) 2</td>
<td>57</td>
<td>32</td>
<td>230</td>
<td>7.9E+11</td>
<td>100</td>
<td>21 ± 7</td>
<td>-</td>
</tr>
<tr>
<td>TiO(_x)/SiNWs (PVD Pt)</td>
<td>67</td>
<td>25</td>
<td>14</td>
<td>2.2E+12</td>
<td>50</td>
<td>2.9 ± 1.1</td>
<td>-</td>
</tr>
</tbody>
</table>

3.5. Adhesion Test Results

The adhesion test ("scotch tape" test) results are tabulated in Table 3-5 where adhesion tests were performed on ALD TiO\(_x\) coated Si, SiO\(_2\), and glassy carbon substrates (all 2-D). PEALD Pt, deposited on a 2-D TiO\(_x\) coated SiO\(_2\) substrate, was also tested. The results fell into two categories: "pass," representing films which remained adhered to the substrate (with no observable delamination), and "fail," representing films which were almost completely removed from the substrate. Of all the coatings tested, only TiO\(_x\) deposited on glassy carbon failed the adhesion test. These results are promising since they at least qualitatively indicate that the PEALD Pt coated TiO\(_x\)/SiNWs will remain fairly robust during ink preparation (which occurs prior to electrochemical testing). This is important since Si is known to have potentially adverse effects on the activity of Pt [14] and the good adhesion of the TiO\(_x\) to the SiNW surfaces should help
protect the Pt surfaces. Also, while the TiO\textsubscript{x} coated glassy carbon failed the adhesion test, Pt deposited on TiO\textsubscript{x} surfaces is not expected to be adversely affected by carbon exposure.

Table 3-5: The results of the adhesion test of TiO\textsubscript{x} and Pt coatings of 2-D substrates. Test results fall into two categories: pass and fail.

<table>
<thead>
<tr>
<th>Film</th>
<th>Substrate</th>
<th>Adhesion Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{x}</td>
<td>Si</td>
<td>Pass</td>
</tr>
<tr>
<td>TiO\textsubscript{x}</td>
<td>SiO\textsubscript{2}</td>
<td>Pass</td>
</tr>
<tr>
<td>TiO\textsubscript{x}</td>
<td>Glassy Carbon</td>
<td>Fail</td>
</tr>
<tr>
<td>PEALD Pt</td>
<td>TiO\textsubscript{x} on SiO\textsubscript{2}</td>
<td>Pass</td>
</tr>
</tbody>
</table>

### 3.6. Mixed Phase Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} Process Development

This section discusses the results of the development of a mixed phase Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} material. Before a mixed phase film could be developed, a baseline Nb\textsubscript{2}O\textsubscript{5} (or just NbO\textsubscript{x}) process needed to be established. This involved establishing a film with a reasonable growth rate and adequate AAM template coverage properties to allow for nanostructure manufacturing.

#### 3.6.1. Nb\textsubscript{2}O\textsubscript{5} process development

The deposition parameters which were used to initially develop the ALD NbO\textsubscript{x} process are shown in Table 3-6 along with the measured thickness and conductivity of each film following the PDORA. The maximum growth rate was 0.4 Å/cycle. The conductivity for all Nb\textsubscript{2}O\textsubscript{5} films was very low, much lower than optimized TiO\textsubscript{x} films (less than 1 S/cm vs. 100s of S/cm for TiO\textsubscript{x}).
Since Nb$_2$O$_5$ 6 (110°C precursor source temperature) and Nb$_2$O$_5$ 7 (120°C precursor source temperature) exhibited very similar growth rates, it was evident that the surface saturation was being achieved during the ALD process. But it was important to also evaluate the coverage of these processes on AAM templates to evaluate the comparative coverage of the films on high aspect ratio surfaces.

Table 3-6: Shown are Nb$_2$O$_5$ process parameters including: the precursor source temperature ($T_{\text{source}}$), the precursor carrier gas pressure ($P_{\text{source}}$), the substrate temperature ($T_{\text{substrate}}$), the ALD pulse time ratio of Nb$_2$(OEt)$_{10}$ to H$_2$O, the number of ALD cycles used during each process and the resulting thickness and conductivity for each film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{source}}$ (°C)</th>
<th>$P_{\text{source}}$ (Torr)</th>
<th>$T_{\text{substrate}}$ (°C)</th>
<th>Nb/H$_2$O Pulse (Seconds)</th>
<th>ALD Cycles</th>
<th>Thickness (nm)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$_2$O$_5$ 1</td>
<td>100</td>
<td>50</td>
<td>300</td>
<td>5/4</td>
<td>200</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ 2</td>
<td>110</td>
<td>50</td>
<td>300</td>
<td>5/4</td>
<td>200</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ 3</td>
<td>110</td>
<td>50</td>
<td>300</td>
<td>5/4*</td>
<td>100</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ 4</td>
<td>110</td>
<td>100</td>
<td>300</td>
<td>5/4</td>
<td>200</td>
<td>5.4 ± 1.1</td>
<td>0.50 ± 0.10</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ 5</td>
<td>110</td>
<td>100</td>
<td>300</td>
<td>10/4</td>
<td>200</td>
<td>6.7 ± 1.3</td>
<td>0.65 ± 0.15</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ 6</td>
<td>110</td>
<td>100</td>
<td>300</td>
<td>10/4</td>
<td>800</td>
<td>32.5 ± 0.5</td>
<td>0.52 ± 0.08</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ 7</td>
<td>120</td>
<td>100</td>
<td>300</td>
<td>10/4</td>
<td>800</td>
<td>30.8 ± 0.5</td>
<td>0.25 ± 0.01</td>
</tr>
</tbody>
</table>

*Purge times were doubled from 5 seconds to 10 seconds

In order to ensure that the composition of a Nb$_x$Ti$_y$O$_z$ material is consistent throughout the nanostructure, the NbO$_x$ film coverage must be the same as the TiO$_x$ film. Ideally, this would be done by obtaining 100% conformality for each film before combining them; however, due to TiO$_x$ film conductivity losses described in section 3.3.3, the conformality had to be less than 100%. Fortunately, the percent conformality...
observed for Nb$_2$O$_5$ at various pore depth fractions was a fairly close match to the conformality observed for a 4s/1s ALD TiO$_x$ film (see Figure 3.28).

XPS analysis of the Nb$_2$O$_5$ film confirms the existence of stoichiometric Nb$_2$O$_5$ at the surface of the film. Figure 3.29 shows the Nb3d binding energy peaks characteristic of Nb$_2$O$_5$ where 3d$^{5/2}$ and 3d$^{3/2}$ are observed at 207 and 210 eV, respectively.

Figure 3.28: A comparison of NbO$_x$ and TiO$_x$ conformality over AAM pores is shown. The film NbO$_x$ 7 appears to have similar coverage characteristics to the TiO$_x$ process.
Figure 3.29: The surface Nb 3d peak is shown, which is representative of Nb$_2$O$_5$ with characteristic 3d$^{5/2}$ and 3d$^{3/2}$ peaks at 207 and 210 eV, respectively.

### 3.6.2. Nb$_x$Ti$_y$O$_z$ processing

As a reminder of what was stated in the previous chapter, the desired composition for Nb$_x$Ti$_y$O$_z$ films follows the ratio Nb/(Ti + Nb) = 10-15% (based on the work of A. O’Toole [15]). Due to the lower growth rate of plain Nb$_2$O$_5$ (0.4 Å/cycle vs. 0.6 Å/cycle for TiO$_x$), the calculated cycling ratio was between 8:1 and 8:2 (e.g., 8:1, 7:1, 8:2, etc.) in order to obtain the desired Nb ratio. However, the materials did not grow as expected at 300 °C; instead, the film growth rate greatly increased above that which was anticipated based on the individual NbO$_x$ and TiO$_x$ film growth rates. Since the TiO$_x$ film was optimized at a 200°C deposition temperature, it was decided to decrease the Nb$_x$Ti$_y$O$_z$ deposition temperature to 200°C.

Individual measurements of composition were taken along the depth profile of the


Nb$_x$Ti$_y$O$_z$ films, and the compositional data was averaged to yield the reported composition. From these values resulting ratios of Nb/(Ti + Nb) were calculated and are tabulated in Table 3-7. The XPS compositional data indicates that the growth of TiO$_x$ was promoted when cycle ratios of TiO$_x$:NbO$_x$ were much greater than 1:1 at 300°C. But when the temperature was lowered to 200°C, the growth rate was more representative of a combined NbO$_x$ and TiO$_x$ process. At 200°C, an ALD cycle ratio of 7:1 (TiO$_x$:NbO$_x$) or 8:1 resulted in Nb$_x$Ti$_y$O$_z$ films with compositions in the target range.

Each film was also measured with 4-point probe following the PDORA to evaluate changes in conductivity. Contrary to what has been reported elsewhere, the incorporation of Nb into the TiO$_x$ films appears to only have a negative effect on the films conductivity. The relationship between conductivity and Nb concentration in TiO$_x$ films can be observed in Figure 3.30; the conductivity appears to decrease dramatically as concentration of Nb increases beyond Nb/(Ti + Nb) = 10%. There are some insights in the literature as to why this may be occurring in the Nb$_x$Ti$_y$O$_z$ film as it is engineered in this work. Gao et al. [16] have reported that when Nb becomes integrated into the structure of a TiO$_2$ material it behaves as a stabilizer against both oxidation and oxygen reduction (i.e., the addition and subtraction of oxygen). Hence, the effects of the PDORA should not be as significant with a Nb$_x$Ti$_y$O$_z$ film as they were with a pure TiO$_x$ film; in other words, a Nb$_x$Ti$_y$O$_z$ film will be resistant against the oxygen reduction which is responsible for TiO$_x$ film conductivity. While Nb could bring chemical stability to TiO$_x$ films, preventing oxygen reduction is incompatible with the optimized ALD TiO$_x$ and PDORA processes. It appears that to make a Nb$_x$Ti$_y$O$_z$ film conductive requires that
either the as deposited film be conductive or that the as deposited film not rely on oxygen reduction to become conductive. Hence, either the deposition or the post deposition processes need to be modified (perhaps significantly).

Also, Ruiz et al. [17] have suggested that the conductivity of Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} films arises from Nb incorporation into materials with Ti vacancies rather than O vacancies. This is also in conflict with the current ALD TiO\textsubscript{x} material processing since it is clearly engineered for O vacancies.

Table 3-7: Data is shown for Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} including the substrate temperature (\(T_{\text{substrate}}\)), the NbO\textsubscript{x}:TiO\textsubscript{x} ALD cycle ratio, Nb composition, film thickness (t) and conductivity (\(\sigma\)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_{\text{substrate}}) (°C)</th>
<th>TiO\textsubscript{x}:NbO\textsubscript{x} Cycle Ratio</th>
<th>Nb/(Ti + Nb) (%)</th>
<th>t (nm)</th>
<th>(\sigma) (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 1</td>
<td>200</td>
<td>1:1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 2</td>
<td>300</td>
<td>1:1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 3</td>
<td>300</td>
<td>1:1</td>
<td>7</td>
<td>14.8</td>
<td>6.9</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 4</td>
<td>300</td>
<td>1:1</td>
<td>50</td>
<td>39.5</td>
<td>0.58</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 5</td>
<td>300</td>
<td>8:1</td>
<td>7</td>
<td>150</td>
<td>148</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 6</td>
<td>300</td>
<td>7:2</td>
<td>10</td>
<td>134</td>
<td>90</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 7</td>
<td>300</td>
<td>7:2</td>
<td>10</td>
<td>103</td>
<td>194</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 8</td>
<td>300</td>
<td>4:4</td>
<td>44</td>
<td>38.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 9</td>
<td>200</td>
<td>4:4</td>
<td>51</td>
<td>38</td>
<td>0.49</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 10</td>
<td>200</td>
<td>7:2</td>
<td>19</td>
<td>41.2</td>
<td>2.7</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 11</td>
<td>200</td>
<td>7:1</td>
<td>12</td>
<td>40.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Nb\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4} 12</td>
<td>200</td>
<td>8:1</td>
<td>11</td>
<td>70.5</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Figure 3.30: Conductivity vs. Nb/(Ti + Nb) ratio in Nb$_x$Ti$_y$O$_z$ films is shown above. Conductivity appears to drop rapidly above 10 % Nb.

### 3.6.3. Nb$_x$Ti$_y$O$_z$ support manufacturing

Nb$_x$Ti$_y$O$_z$ 12 was chosen as the recipe for manufacturing Nb$_x$Ti$_y$O$_z$ nanotubes (the process parameters are more fully tabulated in Table 2-2 of chapter 2). Nanotubes (NTs) were separated from the AAM templates using a solution of 5 M NaOH and cleaned as outlined in section 2.3.1 of Chapter 2. The separated NTs can be seen in Figure 3.31. LPD Pt was subsequently deposited on the Nb$_x$Ti$_y$O$_z$ NTs according to the LPD recipe outlined for plain TiO$_x$ NTs in section 2.6.1 of chapter 2.
Figure 3.31: SEM micrographs of Nb$_x$Ti$_y$O$_z$ NTs following separation from AAM template are shown. Scale bars represent 5µm.

EDS was performed on the LPD Pt coated Nb$_x$Ti$_y$O$_z$ NTs and used to calculate a rough estimate of the Pt loading. Due to the low concentration of Nb in the support material, the Nb peak was not measurable so Nb/Ti values were assumed from XPS data. This yielded an average value of 19 ± 3 wt. % Pt (see Table 3-3 above).

Figure 3.32: A sample EDS spectrum is shown for LPD Pt on Nb$_x$Ti$_y$O$_z$ NTs. Nb Peak is not visible in the EDS spectrum.
3.7. Chemical Stability Tests for 2-D TiO\textsubscript{x} Films

TiO\textsubscript{x} based film chemical stability tests were performed as outlined in section 2.5 of chapter 2. The changes in conductivity associated with the exposures of TiO\textsubscript{x} and Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} films to perchloric acid (HClO\textsubscript{4}), sodium hydroxide (NaOH), and water (H\textsubscript{2}O) are shown in Table 3-8; results are separated into groups according to film label (in bold). The chemical exposure tests are described below each film label according to chemical name. The exposure times and resulting conductivities are listed along with the percent change in conductivity (from the original unexposed film) following each exposure.

Table 3-8: Chemical stability test results for 2-D films are shown below. Each section lists the film label (in bold) followed by the solutions the film was exposed to. The duration of exposure to each solution is denoted by t (min). The thickness, T (nm), and thickness error, ΔT (nm), are also listed for each film following the PDORA. Conductivity, σ (S/cm), and conductivity error, Δσ (S/cm), were calculated from 4-PP measurements.

<table>
<thead>
<tr>
<th>Film/Test</th>
<th>t (min)</th>
<th>T (nm)</th>
<th>ΔT (nm)</th>
<th>σ (S/cm)</th>
<th>Δσ (S/cm)</th>
<th>Change</th>
<th>Error</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{x}</td>
<td>0</td>
<td>43.6</td>
<td>0.7</td>
<td>154</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.1 M HClO\textsubscript{4}</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>159</td>
<td>4</td>
<td>3%</td>
<td>4%</td>
<td>0-60 HClO\textsubscript{4}</td>
</tr>
<tr>
<td>0.1 M HClO\textsubscript{4}</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>159</td>
<td>4</td>
<td>3%</td>
<td>4%</td>
<td>0-240 HClO\textsubscript{4}</td>
</tr>
<tr>
<td>5.0 M NaOH</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>153</td>
<td>4</td>
<td>-3%</td>
<td>4%</td>
<td>0-25 NaOH</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>155</td>
<td>4</td>
<td>1%</td>
<td>4%</td>
<td>0-90 H\textsubscript{2}O</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} 5</td>
<td>0</td>
<td>150</td>
<td>5</td>
<td>148</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HClO\textsubscript{4}</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>138</td>
<td>5</td>
<td>-7%</td>
<td>5%</td>
<td>0-60 HClO\textsubscript{4}</td>
</tr>
<tr>
<td>HClO\textsubscript{4}</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>130</td>
<td>5</td>
<td>-12%</td>
<td>5%</td>
<td>0-240 HClO\textsubscript{4}</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>109</td>
<td>5</td>
<td>-16%</td>
<td>5%</td>
<td>0-90 H\textsubscript{2}O</td>
</tr>
<tr>
<td>Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} 6</td>
<td>0</td>
<td>134</td>
<td>5</td>
<td>90</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HClO\textsubscript{4}</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>4</td>
<td>11%</td>
<td>11%</td>
<td>0-60 HClO\textsubscript{4}</td>
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<tr>
<td>HClO\textsubscript{4}</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>97</td>
<td>4</td>
<td>8%</td>
<td>10%</td>
<td>0-240 HClO\textsubscript{4}</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>97</td>
<td>4</td>
<td>0%</td>
<td>6%</td>
<td>0-90 H\textsubscript{2}O</td>
</tr>
<tr>
<td>Nb&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;y&lt;/sub&gt;O&lt;sub&gt;z&lt;/sub&gt; 7</td>
<td>0</td>
<td>103</td>
<td>2</td>
<td>194</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>----</td>
<td>-----</td>
<td>---</td>
<td>-----</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>195</td>
<td>5</td>
<td>0%</td>
<td>4%</td>
<td></td>
</tr>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>196</td>
<td>4</td>
<td>1%</td>
<td>4%</td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>201</td>
<td>9</td>
<td>3%</td>
<td>5%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nb&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;y&lt;/sub&gt;O&lt;sub&gt;z&lt;/sub&gt; 8</th>
<th>0</th>
<th>38.9</th>
<th>0.6</th>
<th>2.0</th>
<th>0.1</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
<td>0.1</td>
<td>-8%</td>
<td>8%</td>
</tr>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>1.69</td>
<td>0.04</td>
<td>-14%</td>
<td>6%</td>
</tr>
<tr>
<td>NaOH</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>2.03</td>
<td>0.06</td>
<td>20%</td>
<td>4%</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>1.9</td>
<td>0.1</td>
<td>-5%</td>
<td>7%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nb&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;y&lt;/sub&gt;O&lt;sub&gt;z&lt;/sub&gt; 9</th>
<th>0</th>
<th>38.0</th>
<th>0.4</th>
<th>0.49</th>
<th>0.01</th>
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<th>-</th>
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<tbody>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>0.50</td>
<td>0.02</td>
<td>3%</td>
<td>4%</td>
</tr>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>0.47</td>
<td>0.01</td>
<td>-3%</td>
<td>2%</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>0.47</td>
<td>0.01</td>
<td>0%</td>
<td>3%</td>
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</table>

<table>
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<th>Nb&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;y&lt;/sub&gt;O&lt;sub&gt;z&lt;/sub&gt; 10</th>
<th>0</th>
<th>41.2</th>
<th>0.4</th>
<th>2.68</th>
<th>0.03</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>3.2</td>
<td>0.30</td>
<td>19%</td>
<td>11%</td>
</tr>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>2.64</td>
<td>0.05</td>
<td>-1%</td>
<td>2%</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>2.53</td>
<td>0.04</td>
<td>-4%</td>
<td>2%</td>
</tr>
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</table>

<table>
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<th>Nb&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;y&lt;/sub&gt;O&lt;sub&gt;z&lt;/sub&gt; 11</th>
<th>0</th>
<th>40.7</th>
<th>0.4</th>
<th>7.7</th>
<th>0.2</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>8.7</td>
<td>0.5</td>
<td>13%</td>
<td>7%</td>
</tr>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>7.4</td>
<td>0.1</td>
<td>-4%</td>
<td>4%</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>7.2</td>
<td>0.2</td>
<td>-3%</td>
<td>3%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nb&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;y&lt;/sub&gt;O&lt;sub&gt;z&lt;/sub&gt; 12</th>
<th>0</th>
<th>70.5</th>
<th>0.7</th>
<th>6.4</th>
<th>0.4</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>7.8</td>
<td>0.3</td>
<td>21%</td>
<td>8%</td>
</tr>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>7.4</td>
<td>0.3</td>
<td>16%</td>
<td>8%</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>7.7</td>
<td>0.4</td>
<td>3%</td>
<td>7%</td>
</tr>
</tbody>
</table>

Figure 3.33 shows the changes in conductivity with respect to HClO<sub>4</sub> exposure time. For the most part, observed changes in conductivity were small. The percent changes in Nb<sub>x</sub>Ti<sub>y</sub>O<sub>z</sub> films 5, 8, and 12 are outside of their respective error values; however, in Figure 3.34 it becomes apparent that these changes do not follow a clear pattern with either film thickness or Nb concentration.
Figure 3.33: Conductivity vs. HClO₄ exposure time for films with high (a) and low (b) conductivity is shown.
Figure 3.34: Conductivity change vs. thickness (a) and conductivity vs. Nb concentration (b) are shown.
Small changes in conductivity following extended exposure to HClO₄ are a good sign. These results indicate that any losses in conductivity during the electrochemical analysis of TiOₓ-based materials are not due simply to electrolyte exposure.

Selected films, TiOₓ and NbTiOₓ 8 (labeled NbₓTiₓO₂ 8 in Table 3-7), were exposed to NaOH for 25 min (see Figure 3.35). These films were chosen because they represented the extremes in Nb concentration and were of comparable thickness. A noticeable improvement in conductivity was initially observed for NbTiOₓ 8; however, when considering the conductivity loss which resulted from this film’s exposure to HClO₄, the overall change was not significant.

![Conductivity change vs. Nb concentration](image)

Figure 3.35: Conductivity change vs. Nb concentration is shown. While it appears that following the exposure of NbTiOₓ 8 to NaOH improved the conductivity of the film, it is actually not significant when considering the change in the conductivity of the film overall.
All manufactured support materials undergo a drying process following separation from the AAM template (or Si substrate in the case of SiNWs) and subsequent cleaning in H₂O. Separated and cleaned materials are dried in an oven at 80°C. Consequently, to complete these tests, all films were exposed to water and heated to 80°C for 90 minutes and again measured for changes in conductivity. The results are plotted in Figure 3.36, which shows changes in conductivity vs. Nb concentration, and conductivity vs. film thickness. The NbₓTiᵧOₘₙ was the only film which measured a significant change in conductivity (decreasing 16 ± 5%).

Considering the overall changes in conductivity, as shown in Figure 3.37, it is apparent that most films did not change more than 10% (positive or negative) from their original conductivity values following all of the above exposures. The exceptions are NbₓTiᵧOₘₙ (which decreased ≈ 25%) and NbₓTiᵧOₘₙ 12 (which increased ≈ 20%). Even so, the results of these chemical stability tests indicate that both TiOₓ- and NbₓTiᵧOₘₙ-based materials should generally remain conductive during ink preparation.
Figure 3.36: Conductivity change vs. Nb concentration (a) and conductivity vs. film thickness (b) are shown.
Figure 3.37: Overall changes in Conductivity vs. Nb concentration (a) and conductivity vs. film thickness (b) are shown.
3.8. Summary and Discussion of Results

ALD TiO\textsubscript{x} films, which are optimized to be used in conjunction with a PDORA, are fairly conductive. However, the conductivity needed for the current TiO\textsubscript{x} material to be comparable to CB is still higher than currently obtained [18]. It is expected that some modification will need to take place before TiO\textsubscript{x} will be a suitable stand-alone replacement material for traditional carbon based supports. But, as will be presented in Chapter 4, there are great advantages to TiO\textsubscript{x}-based materials, as they now are, when electrochemical stability is considered.

TiO\textsubscript{x} films mixed with Nb did not yield the desired increase in conductivity. This may be due to the method by which conductive TiO\textsubscript{x} films are processed in this work. Hence, future investigations into ALD Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} films may still be worthwhile if they are focused on forming Ti defects rather than O defects.

Both TiO\textsubscript{x} and Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z} films generally did not experience adverse effects from exposure to HClO\textsubscript{4}, NaOH, or heated H\textsubscript{2}O. This implies that any conductivity losses observed in the support materials during CV and RDE analysis are likely independent of the electrode ink formation process.

3.9. References


Chapter 4: Electrochemical Performance

In preparation for electrochemical analysis, solutions of H₂O, isopropyl alcohol (IPA), and Nafion (5 wt. % polymer in solution) were used to make electrode inks from the Pt coated support materials investigated in this work. The ratios of IPA:H₂O:Nafion were between 59.6% - 79.6% v/v (H₂O), between 20 - 40% v/v (IPA), and 0.4% v/v (Nafion). Materials were combined in either a 1:1 or a 2:1 mass to volume ratio of catalyst material to IPA:H₂O:Nafion solution, respectively. The solution and material (i.e., the electrode ink) were then sonicated for ≈ 60 min or until materials remained suspended in solution. The solution ratios were determined based on the quality of resulting electrode layers which were formed by drying between 10 – 200 µl of the different inks (see Table 4-1 and Table 4-2) in an oven at 65°C. Electrode layers were formed on a glassy carbon working electrode (see section 2.7.9.1 of chapter 2) with a geometric surface area of 0.196 cm².

4.1. Cyclic Voltammetry and Rotating Disk Electrode Analysis

Cyclic voltammetry (CV) and rotating disk electrode (RDE) analyses were performed on the Pt coated materials: Vulcan XC-72 carbon black (CB), TiOₓ coated CB (TiOₓ/CB), TiOₓ-based nanotubes (including NbₓTiₓO₂ nanotubes) templated from AAO, and TiOₓ coated SiNWs (TiOₓ/SiNWs).

As indicated in sections 2.6 and 3.4 of chapters 2 and 3, respectively, either liquid phase deposition (LPD) or plasma enhanced atomic layer deposition (PEALD) of Pt were employed to coat nanostructure materials. Physical vapor deposition (PVD) of Pt was
also used on TiO$_x$/SiNWs to provide a room temperature vapor phase deposition process to contrast with the much higher temperature (i.e., 450°C) PEALD process. This was necessary in order to evaluate the effects of the strong metal support interaction (SMSI) between PEALD Pt and the TiO$_x$/SiNW supports (see section 1.3.1 of chapter 1 for explanation of SMSI).

4.1.1. Pt on carbon standard

For all materials utilizing Pt obtained through liquid phase deposition (LPD), a 20 wt. % Pt on Vulcan CB (Pt on CB) standard was used for comparison. In the CV curve (see Figure 4.1a), peaks representing the various bond formations which take place within the potential range during forward and reverse sweeps are seen (individual peak labels can be found in Figure 2.16 of chapter 2). The region of interest in this work is the hydrogen adsorption (H$_{ads}$) region of the CV curve, which is important when comparing the stability of one catalyst material with another and is used when calculating the electrochemically active surface area (ECSA) [1, 2].

Figure 4.1b displays a set of oxygen reduction reaction (ORR) polarization curves representative of RDE data for 20 wt. % Pt on CB. These curves are obtained by rotating the working electrode at various rotation rates (e.g., 100, 400, 900, 1600 rpm, etc.), in an O$_2$ rich environment (i.e., O$_2$ is flowed continuously into the system to purge out other gases). This reveals the diffusion limiting current (DLC) values of the ORR reactions at each rotation rate as indicated previously in Figure 2.18 of chapter 2. These values are needed to understand the relative ORR performance of each material in comparison to Pt on CB [1, 2]. And while the CV and RDE performance level of Pt on CB is what the
materials developed in this research desire to achieve (or surpass), stability is the key strength of TiO$_x$-based catalyst supports, as will be shown in section 4.2.

Figure 4.1: CV (a) and ORR polarization curves (b) (obtained from RDE analysis) for 20 wt. % Pt on Vulcan CB are shown. This material is used as a standard for comparison with the materials fabricated in this work which utilize LPD Pt.

4.1.2. Materials with LPD Pt

Key results of CV and RDE analysis are shown in Table 4-1 for all LPD Pt catalyst materials. The table shows the platinum loading ($L_{Pt}$), the mass of the electrode material analyzed, the calculated mass of Pt ($M_{Pt}$), the calculated ECSA, and the diffusion limiting current (DLC) of each electrode layer. The individual results for these materials are discussed below.
Table 4-1: Summary of CV and RDE results including: Pt loading ($L_{Pt}$), mass of the electrode layer ($M_{electrode}$), the mass of the Pt in the electrode layer ($M_{Pt}$), electrochemically active surface area (ECSA), and diffusion limiting current (DLC @ 1600 rpm) values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$L_{Pt}$ (wt. %)</th>
<th>$M_{electrode}$ (µg)</th>
<th>$M_{Pt}$ (µg)</th>
<th>ECSA (m²/g$_{Pt}$)</th>
<th>DLC$_{1600}$ (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt on CB Standard</td>
<td>20</td>
<td>20</td>
<td>4.0</td>
<td>81</td>
<td>-5.0</td>
</tr>
<tr>
<td>TiO$_x$/CB (LPD Pt) 1</td>
<td>4.1</td>
<td>20</td>
<td>0.8</td>
<td>66</td>
<td>-5.1</td>
</tr>
<tr>
<td>TiO$_x$/CB (LPD Pt) 2</td>
<td>4.1</td>
<td>40</td>
<td>1.6</td>
<td>70</td>
<td>-5.1</td>
</tr>
<tr>
<td>TiO$_x$/CB (LPD Pt) 3</td>
<td>4.1</td>
<td>60</td>
<td>2.4</td>
<td>69</td>
<td>-5.1</td>
</tr>
<tr>
<td>TiO$_x$ Nanotubes</td>
<td>16</td>
<td>60</td>
<td>9.6</td>
<td>0.67</td>
<td>-2.6</td>
</tr>
<tr>
<td>TiO$_x$ Nanotubes with CB</td>
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<td>60</td>
<td>9.6</td>
<td>19</td>
<td>-5.0</td>
</tr>
<tr>
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<td>19</td>
<td>20</td>
<td>3.8</td>
<td>0.41</td>
<td>-2.8</td>
</tr>
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<td>5.7</td>
<td>0.46</td>
<td>-2.9</td>
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<td>Nb$_x$Ti$_y$O$_z$ Nanotubes 3</td>
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<td>40</td>
<td>7.6</td>
<td>0.44</td>
<td>-3.2</td>
</tr>
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<td>50</td>
<td>9.5</td>
<td>0.26</td>
<td>-2.3</td>
</tr>
<tr>
<td>Nb$_x$Ti$_y$O$_z$ Nanotubes 5</td>
<td>19</td>
<td>80</td>
<td>15</td>
<td>0.34</td>
<td>-2.9</td>
</tr>
</tbody>
</table>

4.1.2.1. TiO$_x$ coated CB

Initially, TiO$_x$/CB was a material developed to provide a TiO$_x$-based support material which would be similar in size and shape to traditional colloidal CB (as mentioned in section 2.3.3 of Chapter 2). When compared with Pt on CB standard, the TiO$_x$/CB shows reasonably high currents in CV and RDE analysis (see Figure 4.2). The ECSA was calculated to be about 70 m²/g$_{Pt}$, which is very near the 81 m²/g$_{Pt}$ calculated for Pt on CB. Additionally, Table 4-1 shows that the ECSA values of LPD Pt on TiO$_x$/CB supports are much higher than high aspect ratio (AR) supports such as TiO$_x$ or Nb$_x$Ti$_y$O$_z$ nanotubes (NTs).
Figure 4.2: CV (a) and ORR polarization curves (b) for LPD Pt on TiO$_x$/CB are shown.

4.1.2.2. TiO$_x$ NTs from AAO (LPD Pt)

Concerning high AR TiO$_x$ structures, Pt peaks are clearly visible and distinct in the CV data for LPD Pt on TiO$_x$ NTs (see Figure 4.3). However, the plain TiO$_x$ NTs showed relatively low currents, given the Pt loading, during CV analysis. The ECSA was calculated to be only 0.67 m$^2$/g$_{Pt}$ or about 1/120$^{th}$ the ECSA of Pt on CB. The DLC at 1600 rpm by contrast was 2.6 mA/cm$^2$ which is about half the DLC of Pt on CB.

This data indicates that the Pt contained in the electrode layer does not appear to be fully utilized. SEM micrographs in Figure 4.4a and Figure 4.4b reveal the occurrence of Pt particle agglomeration which takes place predominantly within the voids created by the high AR TiO$_x$ NTs. Agglomeration appears to be a result of both the structure of the NTs and poor Pt particle adhesion to the TiO$_x$ surfaces.

It is clear that the LPD Pt deposition technique needs to be modified in order to
improve the viability of LPD Pt on TiO$_x$ NTs. For LPD Pt to be fully functional, better particle adhesion to TiO$_x$ surfaces is required.

Since the majority of the LPD Pt deposited on plain TiO$_x$ NTs did not appear to be efficiently utilized, CB was added (see Figure 4.4c) to the material in a 1 to 1 ratio with TiO$_x$ (i.e., 1 mg of CB to 1 mg of TiO$_x$ NTs). This material was then analyzed again using CV and RDE analysis (see Figure 4.5). The addition of CB resulted in a large improvement in the performance over plain TiO$_x$ NTs. The currents observed during CV analysis indicate a much better utilization of the Pt in the electrode material with the ECSA increasing to 19 m$^2$/g$_{Pt}$, which is a 28x improvement over the plain TiO$_x$ NTs. The increase in ECSA confirms the catalytic functionality of the LPD Pt. It also qualitatively demonstrates the significance of Pt particle agglomeration to catalyst efficiency.

![Graphs](image)

Figure 4.3: CV (a) and ORR polarization curves (b) for LPD Pt on TiO$_x$ NTs are shown.
Figure 4.4: SEM micrographs are shown of: (a) LPD Pt deposited on TiO$_x$ NTs, (b) Pt agglomeration within the voids created by the high AR TiO$_x$ NTs, and (c) the Pt on TiO$_x$ NTs with carbon added. Scale bars represent 3µm.

Figure 4.5: CV (a) and ORR polarization curves (b) for LPD Pt on TiO$_x$ NTs are shown with carbon added. It is important to note the large
increase in the area of the H_{ads} region following the addition of carbon to the electrode material.

### 4.1.2.3. Nb_{x}Ti_{y}O_{z} NTs

The LPD Pt coated Nb_{x}Ti_{y}O_{z} NT electrodes measured ECSA values between 0.26 and 0.44 m^{2}/g_{Pt} (see Figure 4.6 and Table 4-1), which were the lowest of all the LPD materials. This is consistent with the conductivity trend which was observed in Chapter 3, where increased Nb concentration resulted in decreased TiO_{x} film conductivity. As with LPD Pt on plain TiO_{x} NTs, these results could likely be improved by modifying the LPD Pt process.

![Figure 4.6](image)

Figure 4.6: CV (a) and ORR polarization curves (b) for LPD Pt on Nb_{x}Ti_{y}O_{z} NTs are shown. Lower currents in CV curve appear to correspond with the lower conductivity measured for the Nb_{x}Ti_{y}O_{z} material.

### 4.1.3. Materials with vapor phase Pt

Due to the highly efficient nature of the PEALD Pt, ultra-low loadings should be
achievable. However, it appears that these low Pt loadings did not always result in a strong Pt signal in either CV or RDE analysis. Only when Pt particles reach much larger sizes (e.g., \(\approx 10\)nm) did a strong Pt signal appear (see Table 4-2). PVD Pt on TiO\(_x\)/SiNWs, by contrast, showed an easily identifiable Pt signal with around 5 nm particles, which suggests that Pt deposited at room temperature is much more active than Pt deposited at high temperatures (e.g., 450°C).

Table 4-2: Results of CV/RDE analysis of vapor phase Pt coated support materials including: mass of the electrode layer (\(M_{\text{electrode}}\)), wt. % Pt loading (\(L_{\text{Pt}}\)), electrochemically active surface area (ECSA), and diffusion limiting current (DLC @ 1600 rpm) values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(L_{\text{Pt}}) (wt. %)</th>
<th>(M_{\text{electrode}}) (µg)</th>
<th>(M_{\text{Pt}}) (µg)</th>
<th>ECSA (m^2/g_{\text{Pt}})</th>
<th>DLC(_{1600}) (mA/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt on CB</td>
<td>20</td>
<td>20</td>
<td>4.0</td>
<td>81</td>
<td>-5.0</td>
</tr>
<tr>
<td>TiO(_x)/CB (PEALD Pt) 1</td>
<td>2.2</td>
<td>20</td>
<td>0.4</td>
<td>32</td>
<td>-3.1</td>
</tr>
<tr>
<td>TiO(_x)/CB (PEALD Pt) 2</td>
<td>2.2</td>
<td>40</td>
<td>0.9</td>
<td>31</td>
<td>-3.8</td>
</tr>
<tr>
<td>TiO(_x)/CB (PEALD Pt) 3</td>
<td>2.2</td>
<td>60</td>
<td>1.3</td>
<td>34</td>
<td>-4.2</td>
</tr>
<tr>
<td>TiO(_x)/CB (PEALD Pt) 4</td>
<td>2.2</td>
<td>80</td>
<td>1.8</td>
<td>30</td>
<td>-4.4</td>
</tr>
<tr>
<td>TiO(_x)/CB (PEALD Pt) 5</td>
<td>2.2</td>
<td>100</td>
<td>2.2</td>
<td>33</td>
<td>-4.6</td>
</tr>
<tr>
<td>TiO(_x)/CB (PEALD Pt) 6</td>
<td>2.2</td>
<td>200</td>
<td>4.4</td>
<td>29</td>
<td>-4.4</td>
</tr>
<tr>
<td>TiO(_x)/SiNWs (PEALD Pt) 1</td>
<td>5.6</td>
<td>200</td>
<td>11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiO(_x)/SiNWs (PEALD Pt) 2</td>
<td>21</td>
<td>200</td>
<td>42</td>
<td>0.05</td>
<td>-1.9</td>
</tr>
<tr>
<td>TiO(_x)/SiNWs (PVD Pt)</td>
<td>2.9</td>
<td>200</td>
<td>5.8</td>
<td>1.7</td>
<td>-3.4</td>
</tr>
</tbody>
</table>
4.1.3.1. PEALD Pt on TiO$_x$ coated CB

For PEALD Pt on TiO$_x$/CB (600 cycles) the calculated Pt loading based on multiple EDS measurements, was just over 2 wt. %. Due to the low loading, CV and RDE analyses required a much higher electrode layer mass to generate a strong Pt signal (e.g., 200 µg vs. 20 µg for Pt on CB). The CV and RDE analyses (see Figure 4.7) indicate ECSA values of around 30 m$^2$/g$_{Pt}$, which is a little less than half what is observed for Pt on CB. This is at least partially due to the large size of the Pt particles (≈ 10 nm) which were deposited on the TiO$_x$/CB surfaces. But even with the reduced Pt efficiency, the stability of TiO$_x$/CB will prove crucial in the long-term performance of this catalyst structure (as will be seen in section 4.2). Also, the DLCs displayed in Figure 4.7b represent 80% of the DLC values observed for Pt on CB.

Figure 4.7: CV (a) and ORR polarization curves (b) for PEALD Pt on TiO$_x$/CB are shown.

4.1.3.2. TiO$_x$ coated SiNW (PEALD Pt)

In contrast to the results observed for PEALD Pt on TiO$_x$/CB, PEALD Pt on
TiO$_x$/SiNW showed no significant Pt activity (see Figure 4.8). The particle size for a 5.6 wt. % Pt loading on these TiO$_x$/SiNWs support structures is likely too small ($\approx 5$ nm) to overcome the SMSI described in section 1.2.2. Hence, the catalytic properties of the deposited Pt particles appear to be inhibited. However, when the PEALD Pt loading was increased to $\approx 20$ wt. % (i.e., 600 PEALD cycles), a small Pt signal was observed. The average Pt particle size for this loading on TiO$_x$/SiNWs was $\approx 10$ nm. The low currents measured during CV analysis (see Figure 4.9a) suggest that the adverse effects of the SMSI remain a factor even for a relatively high Pt loading. The ECSA value was calculated to be $0.05$ m$^2$/g$_{Pt}$, which is only a very small fraction of the value calculated for the Pt on CB standard (i.e., $81$ m$^2$/g$_{Pt}$). The ORR polarization curves support what was observed in the CV data with DLCs less than 40% that of the Pt on CB standard.

![Figure 4.8: CV curve of 5.6 wt. % PEALD Pt on TiO$_x$/SiNWs. No Pt peaks are visible.](image)
Figure 4.9: CV (a) and ORR polarization curves (b) for 21 wt. % PEALD Pt on TiO$_x$/SiNWs are shown.

4.1.3.3. TiO$_x$ coated SiNWs (PVD Pt)

In an attempt to confirm the negative effects of high temperature on Pt coated TiO$_x$ surfaces (i.e., the uncontrolled SMSI [3]), another TiO$_x$/SiNWs sample was prepared with PVD Pt. While PVD Pt does not provide the same degree of coverage as PEALD Pt on high AR structures (see section 1.5 of chapter 1), it has the advantage of being a room temperature process. It was expected that this fact would help relieve the adverse effects of SMSI caused by the deposition process itself. The CV and RDE data appear to support this hypothesis (see Figure 4.10). For a $\approx$ 3 wt. % Pt loading (i.e., particle sizes around 5 nm) the Pt signal was fairly strong, especially in comparison to the 21 wt. % PEALD Pt on TiO$_x$/SiNW material. An ECSA value of 1.7 m$^2$/g$_{Pt}$ was calculated which is still much lower than the Pt on CB standard but is also 20 times higher than the PEALD Pt. This improvement over PEALD Pt is a strong indication that a lower temperature PEALD Pt process should be developed to improve Pt activity.
4.2. Endurance Testing

This section reports the results of the accelerated stress tests (ASTs) performed on each catalyst material defined above. Each material is presented in terms of the measured change in ECSA value in response to CV cycling; these values are compared to the values obtained for the Pt on CB standard. All materials were exposed to 0.5 M sulfuric acid (in water) for 2000 cycles. Each cycle consists of a voltage sweep from 0 to 1.2 V and back to 0 V at a sweep rate of 100 mV/s (as outlined in section 2.7.9 of Chapter 2).

4.2.1. Standard

The 20 wt. % Pt on CB standard showed significant Pt signal loss with increased CV cycling (see Figure 4.11). The changes in the area of the hydrogen adsorption ($H_{ads}$) region indicate that the Pt signal is initially large but decreases rapidly with increased CV cycling. This leads to a low final ECSA value after the AST is completed. It is anticipated
that TiO<sub>x</sub>-based materials will show greater stability (i.e., fractional changes in the ECSA due to the AST are expected to be less).

It should be noted that Pt activity is typically less during ASTs due to the change in electrolyte from HClO<sub>4</sub> to H<sub>2</sub>SO<sub>4</sub>. This is because Pt surfaces are susceptible to HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ion adsorption [2].

Figure 4.11: AST results for Pt on CB. The CV curves (a) following the initial clean, 500, 1000, 1500, and 2000 CV cycles show consistent gradual loses in the H<sub>ads</sub> region (lower left of CV curve). The double layer is subtracted (b) to measure the area of the H<sub>ads</sub> region and calculate the ECSA values for each CV curve.

4.2.2. TiO<sub>x</sub> coated CB (LPD Pt)

Since LPD Pt on TiO<sub>x</sub>/CB exhibited high ECSA and DLC values during CV and RDE analyses, it was predicted that this material would perform well during the AST. This proved to be correct; ECSA values for LPD Pt on TiO<sub>x</sub>/CB were, again, comparable to Pt on CB before the AST but were 2.7x higher after the 2000 cycle AST was finished.
(see Figure 4.12a). The ECSA value reduction resulting from the AST was ≈ 25% for LPD Pt on TiO$_x$/CB and ≈ 70% for Pt on CB (see Figure 4.12b). The raw data collected during the AST is shown in Figure 4.12c.

![Graphs showing ECSA values over cycles](image)

Figure 4.12: AST results for LPD Pt on TiO$_x$/CB are compared to the Pt on CB standard and ECSA results are labeled according to the Pt support material used. The ECSA values (a) following: the initial electrode clean, 500, 1000, 1500 and 2000 CV cycle steps are shown. The percent change in ECSA from the initial cleaned value (b) is also shown for each cycle step. The CV curves which these values are based on can also be seen (c).
4.2.3. TiO$_x$ NTs from AAO (LPD Pt)

The Pt signal for the LPD Pt on TiO$_x$ NT was much lower than expected for a 16 wt. % Pt loading. Even so, the stability of TiO$_x$ NTs was observed to be much higher than Pt on CB (see Figure 4.13a). In fact, the TiO$_x$ NT material showed only a 10% reduction in the ECSA after the 2000 cycle AST (see Figure 4.13b); this is the lowest reduction of all the materials studied in this work. But the high stability could not compensate for the low ECSA values (i.e., the initial ECSA for LPD Pt on TiO$_x$ NTs was lower than the final ECSA of Pt on CB). As observed in section 4.1.2.2, the low ECSA appears to be the result of low Pt utilization due to the agglomeration of Pt particles.

On the other hand, LPD Pt on TiO$_x$ NT with CB added exhibited a significantly improved ECSA, as expected (see Figure 4.14a,c); ECSA was initially 13 m$^2$/g$_{Pt}$ vs. 17 m$^2$/g$_{Pt}$ for Pt on CB. In fact, between 1500 and 2000 CV cycles, the ECSA values for the LPD Pt on TiO$_x$ NTs overtake the Pt on CB values. Hence, with increased cycling the TiO$_x$ NT supports could maintain a higher activity than Pt on CB which suggests simply mixing TiO$_x$ NTs with CB may help to stabilize current Pt on CB technology. This could be a simple, yet promising, first step toward improving current Pt on C technologies.
Figure 4.13: AST results for LPD Pt on TiO$_x$ NTs are compared to the Pt on CB standard and ECSA results are labeled according to the Pt support material used. The ECSA values (a) following: the initial electrode clean, 500, 1000, 1500 and 2000 CV cycle steps are shown. The percent change in ECSA from the initial cleaned value (b) is also shown for each cycle step. The CV curves which these values are based on can also be seen (c).
Figure 4.14: AST results for LPD Pt on TiO$_x$ NTs with CB added are compared to the Pt on CB standard and ECSA results are labeled according to the Pt support material used. The ECSA values (a) following: the initial electrode clean, 500, 1000, 1500 and 2000 CV cycle steps are shown. The percent change in ECSA from the initial cleaned value (b) is also shown for each cycle step. The CV curves which these values are based on can also be seen (c).

4.2.4. Nb$_x$Ti$_{y}$O$_{z}$ NTs (LPD Pt)

Nb$_x$Ti$_{y}$O$_{z}$ NT materials were difficult to evaluate due to both the low Pt signal and
high material resistance. While initial CV peaks are observed, they readily disappear during the AST (see Figure 4.15). The support material resistance also increased with cycling (manifested as a vertical skew in the CV data), making it impractical to calculate ECSA values accurately. This is not alarming since the NbₓTiₙO₂ 2-D films were considerably less conductive than plain TiOₓ films. In order for NbₓTiₙO₂ NTs to become a more viable catalyst support option, a significant improvement in conductivity will be required.

Figure 4.15: AST results for NbₓTiₙO₂ NTs (LPD Pt) are shown. Results indicated material resistance increases with cycling. The vertical skewing of the CV curve prevented accurate assessment of ESCA values.

4.2.5. TiOₓ coated CB (PEALD Pt)

PEALD Pt on TiOₓ/CB exhibit similar activity and stability to LPD Pt on TiOₓ/CB (see Figure 4.16 and Figure 4.12). During the AST, ECSA values decreased by 20% from 16.3 to 13.0 m²/gₚt; this represents an improvement of 2.5x over Pt on CB. While the observed stability was not as high as plain TiOₓ NTs, it was much higher than
TiO$_x$ NTs with CB added. Hence, independent of the Pt deposition method, TiO$_x$/CB supports appear to be an excellent candidate to replace CB in future PEMFC systems.

Figure 4.16: AST results for PEALD Pt on TiO$_x$/CB are compared to the Pt on CB standard and ECSA results are labeled according to the Pt support material used. The ECSA values (a) following: the initial electrode clean, 500, 1000, 1500 and 2000 CV cycle steps are shown. The percent change in ECSA from the initial cleaned value (b) is also shown for each cycle step. The CV curves which these values are based on can also be seen (c).
4.2.6. TiO$_x$ coated SiNW (PEALD Pt)

As shown in the CV and RDE analysis, PEALD Pt on TiO$_x$/SiNWs yielded a low Pt signal. During the AST, the initial ECSA was 0.21 m$^2$/g$_{Pt}$ (1% the ECSA of Pt on CB); after only 1000 cycles of the AST, the catalyst material became dramatically more resistive. This made $H_{ads}$ area measurements impractical to obtain (see Figure 4.17). Hence, the final ECSA value after the partial AST was 0.09 m$^2$/g$_{Pt}$ (a 60% decrease).

Since TiO$_x$ materials have generally exhibited high stability even when the Pt signal was low, it can be assumed that the low activity and instability observed here were due to other influences. One potential influence is the SMSI between the Pt and TiO$_x$ surfaces; if this interaction is too strong, the Pt activity will be reduced. It is also feasible that the SiNW cores are coming in contact with Pt particle surfaces; since Si is known to potentially poison Pt, this contact may reduce activity as well. Hence, it is important to evaluate the electrochemical behavior of the PVD Pt on TiO$_x$/SiNWs; given that PVD Pt is deposited at less than 200°C, it should not be strongly affected by the SMSI.
Figure 4.17: AST results for 21 wt. % PEALD Pt on TiO$_x$/SiNWs are compared to the Pt on CB standard and ECSA results are labeled according to the Pt support material used. The ECSA values (a) following: the initial electrode clean, 500, 1000, 1500 and 2000 CV cycle steps are shown. The percent change in ECSA from the initial cleaned value (b) is also shown for each cycle step. The CV curves which these values are based on can also be seen (c).

4.2.7. TiO$_x$ coated SiNWs (PVD Pt)

In contrast to PEALD Pt, the PVD Pt on TiO$_x$/SiNWs yielded a more defined and
stable Pt signal (see Figure 4.18). ECSA values undergo a 30% decrease after 2000 cycles from 1.7 to 1.2 m²/g Pt. This represents nearly an order of magnitude increase in ECSA and a 30% increase in stability over PEALD Pt on TiOₓ/SiNWs. Hence, the SMSI appears to play a significant role in the activity of PEALD Pt. However, the ECSA values calculated here are still only a fraction of those observed for PEALD Pt on TiOₓ/CB, which indicates that the SMSI alone is not responsible for the low activity of Pt on TiOₓ/SiNWs.

Figure 4.18: AST results for PVD Pt on TiOₓ/SiNWs are compared to the Pt on CB standard and ECSA results are labeled according to the Pt
support material used. The ECSA values (a) following: the initial electrode clean, 500, 1000, 1500 and 2000 CV cycle steps are shown. The percent change in ECSA from the initial cleaned value (b) is also shown for each cycle step. The CV curves which these values are based on can also be seen (c).

4.3. Summary and Discussion of Results

In summary, electrochemical testing was performed on: the Pt on CB standard, TiOₓ/CB (with either LPD or PEALD Pt), TiOₓ NTs (with and without CB added), and TiOₓ/SiNW (with PEALD Pt or PVD Pt). It is evident in the CV and RDE data that the Pt on CB standard initially performed better than all of the TiOₓ materials developed in this work. However, the AST results indicate that TiOₓ-based materials were generally more stable than Pt on CB, and some of the materials maintained a higher activity level after the AST.

In principle, the most desirable material would be one that does not use CB, eliminating the need to consider the effects of carbon corrosion. However, the currently developed TiOₓ materials have benefitted from the incorporation of CB while still demonstrating higher stability than plain Pt on CB. In fact, the LPD and PEALD Pt on TiOₓ/CB materials demonstrated a more than 2x ECSA value advantage over Pt on CB during accelerated stress testing. These were very promising results and perhaps among the most significant of this work.

It has also been observed that Pt adhesion plays a more significant role with high
aspect ratio structures than with semispherical colloidal structures (i.e., TiO\textsubscript{x} NTs vs. TiO\textsubscript{x}/CB). The shape of the TiO\textsubscript{x} NTs appears to have adverse effects on its ability to disperse LPD Pt within the electrode layer; this leads to significant Pt agglomeration. Thus, for LPD Pt to be compatible with TiO\textsubscript{x} NTs, greater adhesion of Pt to TiO\textsubscript{x} surfaces is required.

The development of TiO\textsubscript{x}/SiNW materials here is still in its infancy. It appears that Pt deposited at high temperatures, such as with PEALD Pt, encourages the negative effects of the SMSI to occur. The SMSI is reported to begin at temperatures above 200°C. Hence, the room temperature PVD Pt, deposited onto TiO\textsubscript{x}/SiNWs, appears to be less affected by the SMSI [3, 4].

Another material that could be developed further is Nb\textsubscript{x}Ti\textsubscript{y}O\textsubscript{z}. As mentioned in section 3.6 of Chapter 3, Nb has the potential to act as a stabilizing agent within the TiO\textsubscript{x} film matrix, but it needs to be implemented carefully in order to be fully utilized. The TiO\textsubscript{x} film developed here appears to be incompatible with Nb doping due to the emphasis on post deposition oxygen reduction. Consequently, oxygen rather than Ti vacancies are formed, which can inhibit the functionalization of Nb [5, 6].

Electrode materials composed of Pt coated low aspect ratio structures (e.g., Pt on TiO\textsubscript{x}/CB) exhibited activity values consistently higher than their much larger, high AR counterparts (e.g., TiO\textsubscript{x} NTs or TiO\textsubscript{x}/SiNWs). This is a trend that has been observed elsewhere for catalyst supports [7]. It was reported that increasing the size of the catalyst support structure has adverse effects on the measured activity. Also, the purpose of high AR structures was to address electrode flooding, but this could not be tested using either
CV or RDE analysis. Hence, membrane electrode assembly (MEA) testing is needed to assess the full benefit of high AR structures.

The next chapter will suggest future research which could be performed to extend the conclusions presented in this work.

4.4. References


Chapter 5: Future Directions

This chapter suggests some research that could be performed to further the results reported in this work. These suggested next steps attempt to address the limitations due to the negative effects of the strong metal support interaction (SMSI).

5.1. Future Directions for TiO$_x$ Coated SiNWs

In principle PEALD Pt on TiO$_x$/SiNWs should be a promising replacement electrode material for future PEMFCs; however, the negative effects of the SMSI appear to inhibit most of the activity of PEALD Pt deposited on TiO$_x$/SiNW surfaces. The deposition of ~10 nm Pt particles was required for a signal to be observed during CV analysis, which dramatically reduces the catalyst efficiency. By contrast, PVD Pt (3-5 nm particles) on TiO$_x$/SiNWs deposited at room temperature seems to avoid the negative effects of the SMSI but does not provide the high surface coverage obtainable with PEALD Pt. Hence, the development of a low temperature (<200°C) PEALD (or ALD) Pt process could prove useful at reducing both the required Pt particle size as well as the negative effects of the SMSI.

Also, it has been reported that there is an incompatibility between Pt and Si: when Pt comes into contact with Si it can poison the Pt and thus degrade its catalytic properties [1]. Even though the TiO$_x$ coated SiNWs reported here have a layer of TiO$_x$ between the deposited Pt particles and the SiNW cores, it is still possible that during ink preparation (which involves 60+ minutes of sonication) Si surfaces may become exposed and make contact with the Pt. The TiO$_x$/SiNWs material which utilized PVD Pt in this research
indicates that if cross contamination exists it does not completely deactivate all of the Pt surfaces. The use of alternative nanowire cores coated with TiO$_x$ would eliminate the potential for Si poisoning and may improve upon the Pt on TiO$_x$/SiNWs results reported in this work. Nanowire growth techniques reported in the literature which may be compatible with ALD TiO$_x$ coatings include nickel and aluminum [2, 3]. Multiwalled carbon nanotubes (MWCNTs) have also been reported as a core for ultrathin TiO$_2$ films in catalyst support research with good results [4].

5.2. Addressing the SMSI: Catalyst Modification

Another approach to overcoming the negative effects of the SMSI, while still reducing the Pt loading required to provide adequate catalytic performance in electrode materials, is to investigate the use of mixed metal/core shell catalyst structures.

Since reducing Pt loading is a major factor in decreasing the overall cost of PEMFCs, catalyst coatings which yield smaller Pt particles are desirable. However, due to the negative effects of the SMSI induced by the PEALD Pt process used in this work, dramatically reducing Pt particle size may not be possible. To overcome this limitation, a core shell catalyst material could be developed where less expensive metals (such as ruthenium [5 - 7]) may be coated with a thin layer of Pt. This could allow for larger catalyst particles to be formed while still decreasing the Pt loading of electrode materials. Alternatively, progress has been made using a variety of mixed-metals which have shown great catalytic performance [8 - 12].

Naturally, these methods could be useful for Pt loading reduction in cases where low temperature catalyst deposition processes have been developed, but these methods
should also be considered if the SMSI prevents catalyst particle size reduction.

5.3. References


