## ADVANCEMENTS IN ELECTROCHEMISTRY FOR THE SENSING OF AQUEOUS COMPOUNDS AND PERSISTENT COMPOUND DESTRUCTION

By

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## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Chemical Engineering – Doctor of Philosophy

2020

### ABSTRACT

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A significant research question to address is if existing electrochemical methods can be used to advance the sensing of biological compounds and toxic heavy metals, and to destroy persistent toxic pollutants to benefit the planet and humankind. Using the methods of cyclic voltammetry (CV), square wave voltammetry (SWV), square wave stripping voltammetry (SWSV), and electrochemical oxidation (EO), the sensing of isatin and manganese, and the destruction of perfluoroalkyl compounds was investigated. Each task had the main focus of advancing our understanding of the process and making significant process improvements.

Isatin is an endogenous indole that has potential pharmaceutical applications based on its anticonvulsant abilities through reaction pathways in the human body. Due to its low concentrations in blood, serum, and tissues, it is typically detected using gas chromatography mass spectroscopy (GC/MS) which requires a specialized individual and lengthy measurement times. In order to combat this, researchers have begun investigating electrochemical detection methods for this compound. Here, the investigation of isatin detection on a 3-in-1 boron-doped diamond (BDD) sensor was studied to simplify the electrochemical system requirements and set the ground work for a potential plug and play sensor for isatin. Both sensor configurations tested showed applicability to this application with the lowest limit of detection obtained to be 0.04  $\mu$ M. Not only was isatin able to be detected in a complex sample matrix in a short measurement time with this simplified technical approach, it was done so with the elimination of extensive electrode pretreatment processes that have been required for other electrode materials in the past. This study paves the way for a fully developed BDD sensor that can expand the understanding of isatin reaction pathways and advance its ability to be used in pharmaceuticals. Manganese is an important nutrient but has toxic effects in humans making it imperative to be able to detect it in human blood, urine, and serum as well as drinking water. Indium tin oxide (ITO) has been a typical electrode material for spectroelectrochemical measurements and metal detection experiments on transparent substrates. This study goes through a few process parameters for an ITO film on a non-transparent silicon substrate. It was found that heating and annealing the film created the best film structure for an electrochemical sensing application towards manganese with a limit of detection of 0.1 parts per billion (ppb). This obtained lower detection limit allows for improved accuracy in human serum measurements with no added membranes to the electrode's surface and uses an electrode material that already has the capabilities to be mass produced with good repeatability. This makes ITO an economical sensing solution.

Per- and polyfluoroalkyl substances (PFAS) are toxic to human health and are wide spread in the environment due to their numerous consumer and industrial applications. Most current remediation techniques take advantage of filtration or adsorption technologies to remove these compounds from a water source. However, since they do not destroy the compounds, these remediation techniques yield waste products. This study, utilizing electrochemical oxidation for the destruction of PFAS, looks at tackling waste products from an ion exchange process. By utilizing BDD, a laboratory study showed that PFAS completely mineralize in these complex solutions. Overall, it was found that ammonia based solutions allow for the best mineralization of the most common PFAS using electrochemical oxidation for an ion exchange regenerate solution. This study provides valuable knowledge to ion exchange manufacturers who are looking to solve their residual PFAS waste problem.

All three studies have shown that existing electrochemical techniques can be used to further sensing and remediation knowledge in today's world and provide safer, cleaner technology options for the betterment of human health and the environment.

Copyright by MARY ENSCH 2020 To Mom, Dad, Hannah, and Michaelangelo. The best support system I could have asked for.

#### ACKNOWLEDGEMENTS

First, I would like to thank Dr. Thomas Schuelke for providing financial support through the Fraunhofer USA, Inc. Center for Coatings and Diamond Technologies, which has allowed me to complete my research as well as enable me to present the results at various scientific conferences. I would also like to thank him for his ongoing support and guidance through my PhD studies. Additionally I would like to thank both Michael Becker and Dr. Cory Rusinek for providing day-to-day mentorship and support. I am also very grateful to Dr. Scott Calabrese-Barton, Dr. Greg Swain, Dr. Elias Garratt, and Dr. Richard Lunt for serving as committee members and offering valuable insights and advice. Finally, I want to thank all of the dedicated researchers at Fraunhofer USA as well as staff members, interns, and MSU graduate and undergraduate students for all of their help along the way.

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# **CHAPTER 1**

# **MOTIVATION OF WORK**

#### 1.1 Overview

An important question to consider is if electrochemical techniques can be advanced to improve upon biological compound sensing, toxic compound sensing, and toxic compound destruction to benefit the planet and humankind. The ability to improve upon biological sensing is important to advance pharmaceuticals based on how compounds react in the body and to understand the levels at which they can be manipulated to better treat or prevent disease. Isatin's first detection was in 1991 with a gas chromatographic mass spectroscopy (GC/MS) method and a few years later by high performance liquid chromatography measurements (HPLC). [1, 2] UV detection methods were being coupled with HPLC to detect isatin, but only were successful at obtaining limits of detection in the mg/L ranges. [3] These are not relevant to concentrations seen in the human body. [4, 5] Application of electrochemical detection for HPLC was utilized to gain insight on how isatin effected the levels of neurotransmitters in rats that had Parkinson's disease, and although it provided promising results, the three electrode setup comprised of a chemically modified working electrode material that required a multiple step preparation procedure. [6] Isatin's detection would be greatly advanced by removing the need of multiple sample pre-treatments, providing a measurement technique that is accurate and portable without extensive electrode processing, and obtaining limits of detection that allow understanding of isatin's reactions in the human body.

Toxic heavy metals are persistent in the environment and have been shown to cause harm to humans when above a required threshold. If these metals go undetected in drinking and other water sources, they can become a substantial health issue. Electrochemical heavy metal analysis dates back to 1996 with the development of a microfabricated analysis system. [7] Since this time, electrochemical sensors and biosensors have been developed with different materials, configurations, and styles. For manganese detection specifically, electrode materials that have been used include carbon, lithium doped or polymer coated indium tin oxide, bismuth, copper based palladium, or platinum. [8–16] The main advancement that the field is relying on is the ability to mass produce reliable sensors, that require minimal pretreatment, at a low cost without hindering

on the obtained limits of detection.

Finally, the use of electrochemical methods to destroy organic compounds that are toxic to humans are of utmost importance to mineralize the contaminants once and for all and prohibit a contamination cycle from continuing. Using electrochemistry aimed at remediating organic contaminants has been around since the early 1960s. These contaminated solutions include textile dyes, petrochemicals, paper industry effluents, tannery effluents, and other industrial wastewater. [17] As industry advances and develops new chemicals, the risks associated with them, and their need for remediation, also increases. To improve upon this technique for modern times, a system would need to be adapted to allow for the removal of ultra low concentrations of contaminants, in a true environmental matrix, that are unable to be broken down by competing technologies in a way that remains energy efficient.

These three important tasks can be accomplished using the electrochemical methods of cyclic voltammetry, square wave voltammetry, square wave stripping voltammetry, and electrochemical oxidation.

### 1.2 Electrochemical Methods

The main electrochemical methods used in this dissertation include those of cyclic voltammetry (CV), square wave voltammetry (SWV), square wave stripping voltammetry (SWSV), and electrochemical oxidation (EO). The next few sections outline the basic underlying principles that are important in further chapters. Each of the voltammetry measurements utilizes a three-electrode setup comprised of a working, reference and auxiliary electrode shown either of the configurations in Figure 1.1. The three electrodes are connected to a potentiostat. Electrochemical oxidation utilizes a two-electrode setup with the use of an anode and a cathode that are connected to a powersupply. The setup for an electrochemical oxidation experiment is shown in Figure 1.2.



Figure 1.1: (left) diagram of a beaker setup for electrochemical measurements and (right) a clamp cell setup that can also be used alternatively. Each has (A) a working electrode, (B) a reference electrode, and (C) a counter/ auxiliary electrode



Figure 1.2: Setup used for an electrochemical oxidation experiment including an (A) anode, (B) cathode, and (C) stir bar

## 1.2.1 Cyclic Voltammetry

CV is performed by scanning the potential between the working and reference electrodes in a negative or positive direction and measuring the resulting current response. Typically, an experiment would start at one potential, scan out in either direction to a further potential in a linear fashion,

and return to the starting point to complete one cycle. During this time, the current is measured. A figure depicting the potential waveform used in CV and the corresponding current response curve is shown in Figure 1.3. In order to understand repeatability and monitor change over time, typically 4 to 6 cycles are performed. The rate at which the scan is performed is also an important experimental parameter.



Figure 1.3: (left) Potential waveform for cyclic voltammetry and (right) the corresponding current response

There is a relationship between the scan rate and the current that is measured on the working electrode that is known as the capacitance, Equation 1.1. [18]

$$i = C * \frac{dV}{dt} \tag{1.1}$$

Where *i* is the current (A), *V* is the potential in V, *t* is the time in seconds, and *C* is the capacitance (F). By selecting a potential and recording the current output at various scan rates, a plot of the current versus the scan rate can be generated which provides the capacitance as the slope (A\*s/V or F). CV is also important to determine at which potentials chemical reactions take place and how fast they occur on the working electrode's surface. Since most electrolytes are aqueous, the workable potential window of a specific electrode material can be determined by measuring the potentials between the water oxidation and reduction reactions. This will also provide knowledge on if the electrode can be oxidized or reduced and thus hinder its ability to detect other compounds in solution.

How fast a reaction occurs on a given electrode can also be determined using CV. This allows for the determination of the heterogenous rate constant for the material and allows characterization and comparison of different electrode materials. Using a common redox couple, such as potassium ferrocyanide, a CV experiment can be performed and the Randles-Sevcik equation can be used that relates the peak heights measured, the area of the working electrode exposed in solution, the scan rate used, and the diffusion coefficient of the redox couple as seen in Equation 1.2.

$$i_{\rm p} = (2.69x10^5) * n^{\frac{3}{2}} * D^{\frac{1}{2}} * C * A * v^{\frac{1}{2}}$$
(1.2)

Where  $i_p$  is the peak current (A), *n* is the number of electrons in the reaction, *D* is the diffusion coefficient (cm<sup>2</sup>/s), *C* is the concentration of the redox compound (mol/cm<sup>3</sup>), *A* is the exposed area of the electrode (cm<sup>2</sup>), and *v* is the scan rate (V/s). Once the diffusion coefficient is determined from this equation it can be used in two different methods to determine the rate constants for a redox couple on an electrode material.

The first method is known as the Nicholson Shain method and can be utilized when the separation between the oxidation and reduction peaks is less than 212 mV. [19] The equation that describes this method is provided as Equation 1.3.

$$k^{o} = \varphi \frac{(\pi D_{\text{ox}} v \frac{nF}{RT})^{\frac{1}{2}}}{(\frac{D_{ox}}{D_{red}})^{\frac{\alpha}{2}}}$$
(1.3)

Where  $k^o$  is the heterogeneous rate constant (cm/s),  $\varphi$  is a kinetic parameter that is tabulated based on peak potential separation at a set temperature for a one electron process and can be found in a table in reference [19],  $D_{red}$  and  $D_{ox}$  are the diffusion coefficients for the reduced and oxidized form of the redox couple, respectively (cm<sup>2</sup>/s), and  $\alpha$  is the transfer coefficient that usually has a value of 0.5. The type of diffusion that a redox couple has on a working electrode material can be determined based on graphing the peak currents obtained from multiple scan rates against the square root of the scan rate. If this relationship is linear, there is semi-infinite linear diffusion. The second method used for rate constant determination is the Klinger and Kochi method that utilizes fast scan CV for compounds that traditionally have peak separations larger than 212 mV or those that show a steady state response. [20] Fast scan CV refers to using scan rates that are >100 V/s compared to traditional scans in the mV/s range. The equation for this method is provided as Equation 1.4. [20]

$$k^{o} = 2.18(D\alpha nv \frac{F}{RT})^{\frac{1}{2}} e^{-(\alpha^{2}n \frac{F}{RT})(E_{p}^{ox} - E_{p}^{red})}$$
(1.4)

Where  $E_p^{ox}$  and  $E_p^{red}$  are the peak potentials for the oxidation and reduction peaks, respectively. This method will also provide information on the diffusion of the process and again shows semiinfinite linear diffusion when the forward peak currents have a linear relationship with the square root of the scan rate.

The method of CV provides the tools to characterize and compare different working electrode materials. It is being utilized in the following chapters to advance knowledge on the properties that boron-doped diamond has as a quasi-reference material, what factors change the electrochemical responses seen with indium tin oxide, and if there are surface adsorption reactions occurring with fluoride in the use of BDD for PFAS oxidation. To further use these materials for sensing and oxidation experiments, more advanced methods need to be utilized.

## 1.2.2 Square Wave Voltammetry

Square wave voltammetry (SWV) is similar to CV in that a potential range is scanned and an output current is measured, however, this method utilizes a staircase waveform. This allows for background noise suppression, high sensitivity, and the diagnostic ability of normal pulse voltammetry. [21] The current is recorded at the first pulse per cycle and at the end of the second pulse allowing for a difference current between the two points to be calculated. [21] A figure depicting this waveform in provided in Figure 1.4 as well as the corresponding graph depicting a typical current response. This pause after the potential step, before the current is measured, allows for non-faradaic current to dissipate so that there is a lower background current and, subsequently, lower limits of detection for

the specified compound can be obtained. Non-faradaic current is the current that is not associated with a the direct consumption of reactants to form products describes by Faraday's law such as the current from the formation of the double layer at the electrode's surface. [18] Due to the sensitivity of this technique care must be taken to ensure the cleanliness of the analysis equipment to avoid interference from other compounds.



Figure 1.4: (left) Potential waveform and (right) typical forward, reverse, and difference current response for square wave voltammetry

This method can be utilized in combination with the standard addition method to obtain the limit of detection (LOD) for a given compound when using a specific working electrode material. In order to do this, a scan is performed with the desired working electrode in a pure electrolyte solution. Next a set concentration of analyte is added to the solution and the scan is repeated. After this, an additional concentration is added and the scan is performed again. The cycle of adding analyte and scanning the potential range continues until there are enough scans that a graph can be generated for the current obtained versus the added concentration. This graph should provide a linear relationship between the concentration and the measured current. The slope of this line provides the sensitivity (m) that the electrode has towards the specific compound detection. In order to find the LOD, the scan for the lowest concentration of analyte is repeated 3 times. [22] The standard deviation of the peak height (s) is then multiplied by 3 and divided by the obtained sensitivity to find the LOD, Equation 1.5. In order to get statistical data, the experiment can be repeated multiple times in order to obtain a standard deviation. This method is utilized in the

following chapters to show that full BDD sensors, comprising of a working, auxiliary, and quasi reference electrode, can be developed to reach lower detection limits for a biological compound is a shorter amount of time than other techniques.

$$LOD = \frac{(3s)}{m} \tag{1.5}$$

This method is sufficient for a variety of biological compounds, but in order to do heavy metal analysis an additional step is needed. This leads to the method of square wave stripping voltammetry.

### 1.2.3 Square Wave Stripping Voltammetry

Stripping voltammetry advances SWV by adding in a pre-concentration or deposition step. In this pre-concentration/deposition step of anodic stripping voltammetry (ASV), the metal ion is reduced from its ionic state to its elemental state onto the working electrode's surface. In cathodic stripping voltammetry (CVS), the metal ion is oxidized from its ionic state to a higher oxidation state and plates onto the electrode's surface as an oxide. After sufficient pre-concentration, the analyte is effectively removed, or stripped, from the electrode surface by a potential sweep in the opposite direction from the pre-concentration potential. In general, these methods are known as square wave stripping voltammetry (SWSV) when they use the same square wave waveform as previously mentioned. The solution is stirred during the preconditioning step where a sufficient potential is applied to plate the analyte on the electrode's surface, the solution settles during a few second rest, then the analyte is removed from the electrode's surface through scanning the potential in the opposite direction. The important parameters for this method include the deposition potential and time. These must be carefully chosen to ensure adequate deposition of the metal onto the electrode's surface without sacrificing on measurement time.

Not only can this method be used to determine the concentration of ions in solution, but it can also provide information about the electrochemical activity of an electrode based on where the ions are depositing onto the surface. For example, a metal can be plated onto the surface using the pre-conditioning/ deposition step before removing the electrode from solutions and imaging the surface to determine where the metal was actually deposited. When using anodic or cathodic stripping voltammetry, the same approach used for SWV to determine the LOD of a compound can be used. This method is utilized in the following chapters to advance the understanding of indium tin oxide (ITO) as an electrode material for sensing applications in a way that lowers costs of sensor fabrication with the ability to mass produce sensors from this material and allows for repeatable and reliable results with minimal pretreatments.

## 1.2.4 Electrochemical Oxidation

Electrochemical oxidation (EO) has been used for wastewater treatment studies and commercial applications throughout history. [23-30] This method works by direct or indirect oxidation at atmospheric conditions with no additional chemicals. The oxidation occurs with the transfer of one electron from the species in solution to the anode or the generation of oxidizing agents at the anodes surface that can then oxidize the contaminant in the bulk solution. There is no need for a reference electrode in this experimental setup. An anode and a cathode are directly connected to a power supply that controls the applied current or voltage. Oxidation occurs at the anode and involves the transfer of an electron from the species of interest in the electrolyte solution to the electrode, subsequently oxidizing the species in solution through a direct electron transfer process. In order for this exchange to occur in a direct process, the species is required to be within an appropriate distance from the electrode surface before diffusing away. Therefore, both mass transport and electron transfer are important. This oxidation can also happen by having other compounds in solution transform into oxidizing agents, such as hydroxyl radicals, that can oxidize the compound of interest away from the electrode's surface. This is known as indirect oxidation. This method is utilized in the following chapters to advance the management of PFAS waste from ion exchange processes in order to stop the contamination cycle from continuing to endanger the population, while exploring energy conscious techniques.

### **1.3 Background on Electrochemical Sensing**

The three classifications of electrochemical sensing are conductimetric, potentiometric, and voltammetric. The work here focused on voltammetric sensing which is based on recording a current-voltage curve over the course of time. Advantages of these electrochemical sensors include the choice of electrode material having an influence on the ability to separate two similarly oxidizable or reducible species, having high selectivity and specificity due to species undergoing a reaction at a specific potential, having the ability to apply complex potential waveforms leading to sensors with low detection limits, and the ability to miniaturize these sensors. [31] The first instance of voltammetric sensing came about after the invention of the dropping mercury electrode (DME) in 1922. [31] This electrode allowed for the study of reducible species due to its wide negative potential window. Shortly after in 1925, a polarograph was invented that allowed for a currentvoltage curve to be recorded photographically, but it was not until 1939 that the first commercial instrument became available. [32] In order to advance sensing from the negative potential range to cover both the negative and the positive potential range, more advanced solid electrode materials began to be investigated. These included materials such as platinum, gold, or carbon based films. In the 1950s more advanced polarography appeared, including the use of square wave, when circuits became available. [31] Once the development of the instrumentation became widely available, work in stripping analysis began to be investigated and compared to the standard voltammetric analysis that was previously performed. [32]

Both linear scan voltammetry and cyclic voltammetry grew in popularity in the 1960s. [32] Microelectrodes began to make an appearance after this time and the first comprehensive review of them was written in 1981. [32] It was found that microelectrodes have advantageous properties such as immunity to solution resistance, an increase in current density, and a lower double-layer capacitance. [32] Additionally, in the 1980s fast-scan linear sweep voltammetry and cyclic voltammetry were added to high performance liquid chromatography (HPLC) to extend the range of analytes that could be detected. [32] All these advancements require the understanding of the

material being used as the working electrode. The ability for a material to be applicable as a good electrode material for voltammetric sensing can rely on its structure. Two newer electrode materials are that of boron-doped diamond (BDD) and indium tin oxide (ITO). Discussed further in Section 1.3.1 are the structures of the electrode materials of BDD and ITO and how they play a role in the properties that each material possesses.

#### 1.3.1 Structure-property Connections

#### 1.3.1.1 Boron-doped Diamond

The process parameters used when depositing a BDD film can have an influence on its physiochemical properties. These parameters include the level of boron dopant. The boron doping level of a diamond film can have an influence on the surface and physical properties such as the electrical conductivity, sp<sup>2</sup> carbon content, surface termination, and surface area. [33] Boron content influences the grain size of the material with films that have a higher boron concentration have smaller grain sizes. [33, 34] The wetting ability of the electrode's surface is also an influence of the boron content of the film. It has been shown that film's with a lower boron concentration have a hydrophobic surface whereas those with a higher boron content show characteristics of an oxygen terminated film. [33, 34] A lower boron concentration allows for electrodes with an increased electrochemical potential window due to their higher resistivity. [34, 35] In addition, a higher boron content allows for a higher carrier mobility, a necessary parameter for electrochemical sensing. [35]

One can also relate the boron content of a diamond film to its ability to be used in certain electrochemical applications. For example, electrochemical nitrate reduction has been shown to have a larger peak potential and occur at a more positive potential for a BDD film with a higher boron content that has been attributed to a higher conductivity value. [33]. The highly doped film ultimately had a higher sensitivity and lower detection limit for nitrate compared to the other that was not as heavily doped. The boron content has also been related to the detection of uric acid on BDD films. An increase in the linear detection range and a decrease in the detection limit is

obtained with an increase in boron concentration. [34] For the oxidation of sulphamerazine on BDD, a higher concentration of boron to carbon was more effective. [35] Similarly, the efficiency of the electrochemical oxidation of azo dyes was influenced by the boron concentration of the film. An increase the doping level increased the efficiency of the process. [36]

#### 1.3.1.2 Indium Tin Oxide

Similar to BDD, the deposition parameters used when depositing ITO through sputtering can affect the structural, electrical, and optical properties of ITO that can come into play when utilizing the material as an electrode for a sensing application. The first process dependent report on the use of ITO for electrochemical applications was published in 1992. [37] More recently, a report detailing how the microstructure and doping of the film can have an influence on it's electrochemical properties was published in 2002. [38]

An electrochemical comparison between an as grown ITO film and one with the application of vacuum annealing has been made. It was found that more reversible behavior was obtained on the film that was vacuum annealed compared to the as-grown film. [37] This is suggested to be due to the fact that the resistivity decreases with annealing and increases the free carrier concentration. [37] The vacuum annealed films also allowed for a lower peak separation in peak potential than those obtained on as-grown films due to their increase in oxygen vacancies. [37] Although this study had very limited film characterization, it showed that the film that went through post-deposition annealing in a vacuum had a superior performance than the as-grown film.

ITO can have an amorphous or crystalline microstructure. The shift to crystallinity comes from the application of heat during deposition. In amorphous films, the carrier concentration is low with a high mobility due to the absence of crystal defects, but upon crystallization, the carrier density increases and the mobility decreases. [38] It has also been shown that the tin in an amorphous state is not electrically active in contrast to the crystalline material [38] The electron transfer rates for three common redox couples were lower for the amorphous film with lower peak currents and larger peak separations. [38] This study provided evidence that the amorphous ITO film was not an adequate electrode for the oxidation of guanine. This study provides evidence that the microstructure of the film has an influence on its ability to be used in electrochemical applications such as voltammetric sensing.

### 1.3.2 Prior State of the Art

Since this report will cover three distinct topics related to electrochemistry, it is important to provide the prior state of the art for each. When considering the electrochemical detection of isatin, there are three primary works prior to this investigation. Two of which cover the electrochemical detection of isatin after an initial system such as high-performance liquid chromatography (HPLC) or flow injection analysis (FIA), whereas, the third looks directly at the first attempt to detect isatin solely based on electrochemical methods. [6, 39, 40] Table 1.1 shows each study and the figures of merit that were obtained. The differential pulse study obtained similar limits of detections (LOD) to both the electrodes used after FIA and the glassy carbon electrode used after HPLC. The lowest obtained LOD was from using the chemically modified palladium hexacyanoferrate electrode after HPLC. However, it is important to simplify the electrode requirements for this process to make it more accessible.

Manganese detection using electrochemistry is not a new topic. To consolidate the prior state of the art research, the detection of only manganese specifically using cathodic stripping voltammetry in the last 25 years was researched. Working electrodes without any use of membranes or additional techniques, such as ultrasonic or prior column methods, were focused on that had no other interfering metals. The prior art scope was also limited to manganese detection in simulated solutions so that it would be more applicable to the study performed here. Electrode materials in this prior art research include modified carbon paste, glassy carbon, carbon film, graphite composite, boron-doped diamond, palladium, carbon nanotube, indium tin oxide, graphite, and platinum.[41, 42, 8, 43–46, 14, 47–49] Table 1.2 compares the obtained limit of detection and linear range for each study as well as the pretreatment the working electrode went through and the electrochemical parameters used. It is important to consider an economical working

Method	Electrodes Used	Electrode Pretreatment	Isatin Pretreatment	Electrolyte	Figures of Merit	Reference
Differential pulse voltammetry (DPV)	Working: Glassy carbon Counter: platinum wire Reference: silver/ silver chloride	<ol> <li>Polishing with diamond spray, sonicating in ultrasonic, then performing voltammetric sweeps until a stable baseline was obtained between every measurement.</li> <li>Pretreated the same as 1 but the measurements were recorded consecutively without pretreatment in between</li> </ol>	Obtained from Loba- Chemie Indoaustranal Co. with no further purification.	0.2 M phosphate buffer with pH 7.0 saturated with nitrogen	<ol> <li>Sensitivity         <ul> <li>: 11.72 +/- 0.60</li> <li>nA/uM, LOD: 0.211</li> <li>uM, R2 0.984, S.D.</li> <li>0.835, Linearity</li> <li>range: 10 uM</li> </ul> </li> <li>Sensitivity: 10.96 +/-         <ul> <li>0.24 nA/uM, LOD:</li> <li>0.194 uM, R2: 0.992,</li> <li>S.D. 0.709, Linearity</li> <li>range: 5 uM</li> </ul> </li> </ol>	[40]
High-performance liquid chromatography with electrochemical detection	Working: 1. Glassy carbon 2. Palladium hexacyanoferrate chemically modified electrode Counter: gold wire Reference: saturated calomel	Pretreatment after fabrication and before measurements is unavailable. Detection potential: 0.9 V	Obtained from Sigma Chemicals and sent through HPLC before the electrochemical detection	0.2 M phosphate buffer with pH of 5.0 containing 8% methanol saturated with nitrogen	<ol> <li>Limit of detection: 1.0 x 10<sup>-7</sup> M</li> <li>Limit of detection: 2.5 x 10<sup>-8</sup> M</li> </ol>	[6]
Flow injection analysis with electrochemical detection	Working: 1. boron-doped nanocrystalline diamond 2. Tetrahedral amorphous carbon Counter: stainless steel Reference: silver/ silver chloride	Both working electrodes were soaked for 20 minutes in ultrapure isopropanol and dried with nitrogen gas	Obtained from Sigma Aldrich with and sent through flow injection analysis system prior to detection	0.1 M phosphate buffer with pH of 7.2 saturates with nitrogen	<ol> <li>Sensitivity: 19.7 mA/M, linear range: 100 – 0.1 uM, limit of detection 1.0 x 10<sup>-7</sup> M</li> <li>Sensitivity: 18.1 mA/M, linear range: 100 – 0.1 uM, limit of detection: 1.0 x 10<sup>-7</sup> M</li> </ol>	[39]

Table 1.1: Summary table outlining the prior art for the electrochemical detection of isatin

electrode material for this application with minimal pretreatments to be able to advance this sensing technology to a single use sensor for the medical or environmental field.

The prior art research focused on perfluoroalkyl substance (PFAS) oxidation with electrochemistry focused on the studies that looked at using BDD as the anode material. There are five categories included in this review: those involving industrial waste waters, those in natural water matrix or ground water, simulated solutions with only perfluorooctanoic acid (PFOA), simulated solutions starting with perfluorooctane sulfonate (PFOS) or perfluorobutane sulfonic acid (PFBS), and studies that start with a mixture of PFAS. These categories are split into two tables, Table 1.3 that covers the simulated solutions studies and Table 1.4 that shows the PFAS studies performed in industrial or ground water solutions.

Table 1.3 covers four studies with just PFOA, one study with just PFOS, one study with just

Table 1.2: Summary table outlining the prior art for the electrochemical detection of manganese in simulated buffer solutions

Working Electrode	Additional Electrodes	Working electrode Pretreatment	Electrolyte	Type of manganese	CSV Parameters	Figures of Merit	Reference
1-(2-Pyridylazo)-2- Naphthol-Modified Carbon Paste electrode	Reference : silver / silver chloride (Ag/AgCl) Counter: platinum disk	Extruded out of tube and scrapped off then polished on white paper	Phosphate-borax buffer pH 8.7 for accumulation, NH <sub>3</sub> -(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> pH 9.4 for oxidation and stripping	$ \begin{array}{llllllllllllllllllllllllllllllllllll$		Limit of detection: 6.9 x 10 <sup>-9</sup> M Linear range: 1.0 x 10 <sup>-8</sup> to 1.0 x 10 <sup>-7</sup> and 8.0 x 10 <sup>-7</sup> to 1.0 x 10 <sup>-5</sup> M	[41]
Rotating glassy carbon	Reference: Ag/AgCl Counter : platinum wire	Polished with alumina powder followed by a rotation for 2 minutes in a hydrochloric acid rinse.	Seawater oxidized by ultraviolet radiation and passed through resins	Manganese Fisher Scientific standard	Deposition time: 10 min Deposition potential: 0.75 V	Limit of detection: 6 nM	[42]
Carbon film	Reference : saturated calomel electrode (SCE) Counter: platinum foil	Cycling in 1 M perchloric acid solution three times at 100 mV/s	0.2 M H3BO3 with 0.1 KCl at pH 7.2	Manganese sulfate	Deposition time: 120 s Deposition potential: 0.8 V	Limit of detection: 3.9 nM	[8]
Graphite/ Styrene- Acrylonitrile Copolymer Composite	Reference : Ag/AgCl Counter : platinum wire	Polished with fine emery paper followed by alumina suspension and an ultrasonic bath	0.1 M acetate ammonium buffer solution with pH 9	Manganese atomic absorption standard stock solution from Wako, Japan	Deposition time: 180 s Deposition potential: 0.5 V	Limit of detection: 3.6 x 10 <sup>-9</sup> M Linear range: 0.5 – 20 ug/L	[43]
Boron-doped diamond	Reference : SCE Counter : platinum wire	Polished with diamond lapping compounds in between measurements	0.5 M ammonium nitrite at pH 7 degassed with nitrogen	N/A	Deposition time: 60 s Deposition potential: 0.85V	Limit of detection: 7.4 x 10 <sup>-7</sup> M Linear range: 1.25 – 25 uM	[44]
Palladium on top of copper	Reference: copper/ copper chloride Counter: palladium on copper	N/A	0.1 M Borate buffer at pH 9	Manganese stock solution from Fluka Analytical	Deposition time: 600 s Deposition potential: 0.7 V	Limit of detection: 334 nM Linear range: 455 nM - 109 uM	[45]
Metal catalyst free carbon nanotube	Reference : Ag/AgCl Counter: platinum wire	Purchased and used with no pretreatment	0.1 M borate buffer at pH 8.5	Manganese atomic absorption standard with 2% nitric acid from Fisher Scientific	Deposition time: 60 s Deposition potential: 0.6 V	Limit of detection: 93 nM Linear range: 0.6 to 6.7 uM	[46]
Indium tin oxide	Reference e: Ag/AgCl Counter e: platinum wire	N/A	Acetate buffer pH 5	Manganese atomic absorption standard from Acros Organics	Deposition time: 10 min Deposition potential: 1.2 V	Limit of detection: 6 nM Linear range: 0.5 -7.5 ppb	[14]
Edge plane pyrolytic graphite	Reference : SCE Counter : platinum wire	Polished using alumina lapping compounds of decreasing size	0.5 mol/dm <sup>3</sup> ammonium nitrate buffer at pH 7	Manganese perchlorate from Aldrich	Deposition time: 120 s Deposition potential: 0.85 V	Limit of detection: 14.2 nmol/dm <sup>3</sup> Linear range: 25 – 250 nmol/dm <sup>3</sup>	[47]
Bare carbon paste	Reference: SCE Counter: carbon rod	Renewed by wiping with paper	0.1 M phosphate buffer pH 7.4	Magnesium chloride	Deposition time: 120 s Deposition potential: 0.85 V	Limit of detection: 1 x 10 <sup>-7</sup> M Linear range: 1 x 10 <sup>-6</sup> – 12 x 10 <sup>-6 M</sup>	[48]
Platinum thin-film	Reference: Ag/AgCl Counter: platinum	Electrochemically cleaned with 10 cycles in the +/-1.5V range in 0.1 M potassium chloride	0.2 M acetate buffer at pH 5.5	Manganese atomic absorption standard with 2% nitric acid from Arcos Organics	Deposition time: 900 s Deposition potential: 0.7V	Limit of detection: 16.3 nM Linear range: 91 -910 nM	[49]

PFBS, and one study with a mixture of a few chain lengths. [50–55, 27] Some of the removal percentages were estimated based on the provided figures in the literature. Most studies achieved greater than 50 % degradation for their perspective compound in under 10 hours.

Table 1.4 shows the studies that were performed in complex solutions. These include those of industrial wastewater and contaminated groundwater. [56–61] All of those obtained removal percentages of greater than 90 %. In terms of advancing the prior state of the art, it is important to look at minimizing the treatment time needed for these solutions while also reducing the energy consumption that is required.

Table 1 3.	Summary tab	le outlining the	prior art for the	e simulated PFAS	Solutions
	Summary lab	ie outilling the	prior art for the	c sinulated I TAL	5 solutions

Solution	Cell Configuration	Type of BDD	Cathode Material	Active Anode Area	Volume (L)	Flow or Stir Rate	Current Density (mA/cm <sup>2</sup> )	Time (h)	Removal %	Reference
8 mM PFOA, 10 mM NaClO4	flow cell, gap of 10 mm	Condias, Germany	Pt-deposited Ti plate	77.4 cm <sup>2</sup>	0.3	0.2 L/min	0.15	8	~50% estimated from figure	[50]
100 ppm of PFOA in either NaClO₄ or Na2SO4	undivided, flow- by cell, electrode gap of 8 x 10 <sup>-3</sup> m	Advanced Diamond Technologies	Tungsten	$42 \times 10^{-4} \text{ m}^2$	5 x 10 <sup>-4</sup> m <sup>3</sup>	1.11 x 10 <sup>-4</sup> m <sup>3</sup> /s	5, 10, and 20	6	5 mA/cm <sup>2</sup> : 55.8%, 10 mA/cm <sup>2</sup> : 84.1%, 20 mA/cm <sup>2</sup> : 94.9%	[51]
200 ppm of PFOA, 0.05 M NaSO₄	Teflon-lined stainless steel autoclave electrochemical cell, 2 cm electrode gap	Fabricated by chemical vapor deposition on silicon	Pt	5.5 cm <sup>2</sup>	0.4	1000 rpm	20	6	93.6%	[52]
0.24 mM PFOA, 5 g/L NaSO₄	undivided cell with parallel electrodes, 5 mm gap for MCD, 8 mm gap for UNCD	MCD from Adamant Technologies Switzerland, UNCD from Advanced Diamond Technologies USA	Stainless steel with MCD, tungsten with UNCD	MCD 70 cm <sup>2</sup> , UNCD 42 cm <sup>2</sup>	1 L for MCD, 0.5 L for UNCD	5 x 10 <sup>-5</sup> m/s for MCD, 1.1 x 10 <sup>-4</sup> m/s for UNCD	1, 2, 5, 10, 20	4	Complete degradation by MCD at 5 mA/cm <sup>2</sup> , only 21% for UNCD at 5 mA/cm <sup>2</sup>	[53]
0.4 mM PFOS in 5.5 and 10 mM NaClO4	Rotating disk electrode and flow-through reactor	RDE and flow through from Adamant Technologies, Switzerland	RDE: Pt wire. Flow through: BDD	RDE 1.1 cm diameter Flow through reactor: 25 cm <sup>2</sup>	Flow through: 2 L	Flow through reactor: 100 ml/min RDE 3000 rpm	20 mA/cm <sup>2</sup>	RDE: 20 Flow through: 28	~ 50% in RDE and 98% in flow through estimated from graph	[54]
0.4 mM PFBS in 10 mM NaClO4	RDE in a glass cell with a circulating water jacket / a flow through reactor electrode gap of 0.3 cm	Adamant technologies	Platinum wire	1.13 cm diameter disk for RDE 25 cm <sup>2</sup> for flow through	350 ml or 600 ml RDE Flow through: 1 L	3,000 rpm 10 ml/min in flow through	5 - 20 mA/cm2	1.7	~ 99% in flow through at 10 mA/cm <sup>2</sup> and ~ 50% at RDE	[55]
0.114 mM of PFBA, PFHxA, PFOA, PFDeA, PFBS, PFHxS, and PFOS in 1.4 g/L NaClO4	Batch, 3 electrode quartz cell, 30 mm distance between anode and cathode	Technical institute of physics and chemistry, Chinese Academy of Sciences	Titanium sheet	25 mm x 35 mm	0.04	1500 rpm	23.24 mA/cm <sup>2</sup>	2	PFOA: ~ 55% defluorination	[27]

### Table 1.4: Summary table outlining the prior art for the complex solutions containing PFAS

Solutions	Cell Configuration	BDD	Cathode Material	Active Anode Area (cm <sup>2</sup> )	Volume (L)	Flow or Stir Rate	Current Density (mA/cm <sup>2</sup> )	Time (h)	Removal %	Reference
Raw industrial wastewater	undivided, two circular parallel plates, gap of 5 mm	Adamant Technologies, Switzerland	Stainless steel	70	2	N/A	50	8	97.1%	[56]
Industrial wastewater	undivided flow by cell, two circular parallel plates, gap of 5 mm	Adamant Technologies, Switzerland	Stainless steel	70	2	3 L/min	50	10	99.7%,	[57]
Contaminated Ground Water and reverse osmosis concentrate	batch mode, 21x7x7 cm cell, 2 cm electrode spacing	Condias, Germany	Nb/ BDD	35	1	300 rpm	2.3	Ground water: 120 Reverse Osmosis: 18	Ground water: ~95.6% Reverse Osmosis: ~90.0% Estimated from figures	[58]
Nanofiltration concentrate	undivided cell, 1 mm gap. 2 parallel flow by compartments	Adamant Technolgies	BDD	70	1	6 L/min	5	6	98%	[59]
Natural ground water	Single compartment cell, 4 mm electrode spacing	Advanced diamond technologies	Tungsten	38	0.25	250 ml/min	15	8	~90% estimated from graph	[60]
Natural ground water	Single compartment Microflow cell, 4 mm spacing between electrodes	Condias, Germany	Stainless steel	10	0.25	0.10 L/min	25	8	91.0%	[61]

## 1.3.3 Deficiencies of Technology

Although electrochemical voltammetric sensing has advanced substantially over the years, there are still a few deficiencies in the technology. Noble metals and advanced diamond materials can be costly. In addition, in order to be more convenient, electrodes themselves need to be miniaturized

as well as the necessary equipment. For example the development of sensors that comprise of the working, counter, and auxiliary electrodes all on a single platform. Both cost effective materials and miniaturization of the sensing technology will allow for more accessible sensors and more single use sensors. In addition, the reduction in time and energy for PFAS remediation will play an important role for it to be used in industry.

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# CHAPTER 2

# ISATIN DETECTION USING A BORON-DOPED DIAMOND 3-IN-1 SENSING PLATFORM

#### 2.1 Introduction

This work has been published in Analytical Chemistry<sup>1</sup>. Indole-2,3-dione, or isatin, has attractive properties as an endogenous indole that could be applied in the treatment of Parkinson's Disease, tremors, or epilepsy. [1–3] Its structure is shown in Figure 2.1. Isatin has a large amount of biological activity and is found in the tissues and fluids of mammals. [4–7] In 1988 scientists discovered this compound using the technique of gas chromatography mass spectroscopy (GCMS). [4] Concentrations of isatin range from above 1  $\mu$ mol/L in blood to 0.1 to 10  $\mu$ mol/l in tissues and greater than 1 mmol/L in urine samples. [6, 8, 7] This compound has been of interest due to its ability to bring on stress and anxiety, the inhibition of sodium in rat intestines, and the potential link it may provide between a person's mood, the natriuretic peptide system, and monoamine neurotransmitter levels. [6, 9, 10] Moderate concentrations of isatin, 15-20 mg/kg of body weight, have been found to be anxiogenic but a higher dose, 50 mg/kg of body weight, can induce sedation in rats and larger mammals such as monkeys. [9] To gain a better understanding of all the interactions isatin is capable of and how to take advantage of it as a pharmaceutical drug, a more complete understanding of how it interacts in the human body and the mechanisms it goes through is essential. To achieve this, precise measurement techniques for the detection of isatin are necessary.

Since the discovery of isatin using GCMS, liquid chromatography (LC) coupled with UV-vis spectroscopy or an electrochemical voltammetric method have been used as detection methods. [1, 8, 7, 11–14] A downside to GCMS is the long measurement times required. [14] A research group using high performance liquid chromatography (HPLC) with UV-vis measured isatin's absorbance peak at 242 nm with a limit of detection (LOD) of 2  $\mu$ mol/L. [14] Another group using LC with electrochemical detection with a palladium hexacyanoferrate modified electrode measured isatin in rat brains with a LOD of 0.03  $\mu$ mol/L. [1] Diculescu et al. used UV-vis with a found LOD of 0.8  $\mu$ mol/L and began to study the detection possibilities of using electrochemical techniques without the addition of a chromatography techniques. [11]

<sup>&</sup>lt;sup>1</sup>Analytical Chemistry 2018, DOI:10.1021/acs.analchem.7b04045



Figure 2.1: Molecular structure for isatin

Isatin has both an oxidation and reduction reaction that are irreversible and dependent on pH that can be detected via electrochemistry. [11] When utilizing a glassy carbon (GC) electrode, isatin displays an oxidation peak at +1.08 V and a reduction peak -0.48 V. [7, 11] One group used a GC electrode and multiple voltammetry techniques to study isatin and were able to obtain a LOD of 0.19  $\mu$ M when using differential pulse voltammetry. [11] Other groups have also studied isatin on GC electrodes. [3, 7, 12]

Boron-doped diamond (BDD) is another electrode material known for its outstanding properties when used for the electrochemical detection of biological compounds. [15–17] BDD has many electrochemical advantages such as its wide potential window, low background current, chemical inertness, and its good chemical and electrochemical stability. [18, 19] The wide potential window that is characteristic of BDD offers the ability to detect compounds that have higher positive or negative redox potentials. BDD electrodes have excellent microstructure stability even at these extreme potential values. [18, 19] With minimal preconditioning steps, BDD displays quasi-reversible redox systems with resistance to deactivation and fouling. [20, 21] Additionally, BDD can be fabricated into different electrode microstructures such as micro electrode arrays (MEAs)

that can then be used as micro-sensors for free hydroxyl radical generation and neural activity measurements. [21–29]

One factor that can produce unwanted results in experiments is the potential drop due to solution resistance which can shift peak potential and increase peak separation. MEAs fabricated out of BDD offer a lower electrical potential difference, or IR drop, due to their lower electrode surface area compared to typical macro (MAC) electrodes and they can provide steady state current responses that MAC electrodes can not. [23, 24] After a potential step, MEAs require a short time to reach equilibrium. [24] One group reported that an ultramicroelectrode array (UMEA) showed 50-100 times better sensitivity than a traditional MAC electrode with a superior reproducibility. [30] In order to simplify the usability of MEAs and prevent breakage and loss, sensing platforms have been fabricated that consist of the working, auxiliary, and reference electrodes. [30–40]

Previously, A 3-in-1 sensor was made from silver (Ag) and gold (Au) electrodes to detect nitrate  $(NO_3^-)$  and another was fabricated with carbon nanotubes for the detection of glucose. [39, 40] Many of these sensors use Ag/AgCl or Ag/Ag<sup>+</sup> as a reference or quasi-reference electrode material. [34, 37, 39, 40] One research group fabricated a device with a BDD quasi-reference material but failed to mention how it behaved. [35] However, two groups using sensors made with all BDD components, demonstrated that BDD could behave as an acceptable quasi-reference material. [38, 30] To evaluate BDD's performance as a reference material, potential controlled experiments were performed to determine its stability for 57 hours and showed that the potential only drifted by +/- 8 mV. [38]

For the remainder of this chapeter, two fully BDD 3-in-1 sensors, one MAC and one MEA, were fabricated and characterized. Both sensors were assessed for their ability to detect isatin. The BDD quasi-reference material was characterized based on its potential stability over time compared to a standard Ag/AgCl reference electrode in pH solutions of 4.0 to 7.4. The BDD MAC electrode had a working area of  $3.14 \times 10^{-2} \text{ cm}^2$ . The MEA's total working area amounted to 1.71 x  $10^{-4} \text{ cm}^2$ . The BDD material was characterized with Raman spectroscopy and scanning electron microscopy (SEM). The development of such a BDD sensing platform could be used in future

work to detect isatin in applications involving liquid chromatography coupled to electrochemical detection methods while removing the need for three separate electrodes and simplifying the required electrode pretreatment.

#### 2.2 Experimental Section

### 2.2.1 Chemicals and Materials

Potassium ferrocyanide (K<sub>4</sub>Fe(CN)<sub>6</sub>) and potassium ferricyanide (K<sub>3</sub>Fe(CN)<sub>6</sub>) were purchased from Mallinckrodt Specialty Chemicals and J.T. Baker, respectively. Isatin and hexaamineruthenium(III) chloride (Ru(NH<sub>3</sub>)<sub>6</sub>Cl) were purchased from Sigma Aldrich. A potassium chloride (KCl) solution of 1.0 M was prepared with DI water and salt from ChemPure Brand Chemicals. The KCl solution was used to prepare stock solutions of Fe(CN)<sub>6</sub><sup>3-/4-</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+/2+</sup>. A 10x phosphate buffered saline (PBS) solution (10.6 mM monobasic potassium phosphate, 1551 mM sodium chloride, 29.7 mM dibasic sodium phosphate) was purchased from Gibco and diluted to 1x using DI water (1.1 mM monobasic potassium phosphate, 155 mM sodium chloride, 3.0 mM dibasic sodium phosphate) to a final pH of 7.4. The 10x PBS was also diluted and pH adjusted with hydrochloric acid from Fisher Scientific to obtain pH values of 4, 5, 6, and 7. The 0.1 M PBS was used to make a stock isatin solution. Surine Negative Urine Control was purchased from a Simga-Aldrich Company, Ceriliant.

## 2.2.2 Instrumentation

A VCA Optima from AST Productions, Inc. was used to perform contact angle measurements with a drop size of 1  $\mu$ L of water. The systems software determined the contact angles of each water drop on the sample's surface. This measurement was repeated 3 times to obtain a mean value and a standard deviation. A single compartment glass cell with 5 mL of solution was used for cyclic and square wave voltammetry measurements. A clamp held each sensor in place once immersed in solution. Each 3-in-1 sensor was electrically connected via a micro USB connector to the leads from the potentiostat. Parameters for capacitance measurements using cyclic voltammetry

were: scan rates: 100-500 mV s<sup>-1</sup>, electrolyte: 1.0 M KCl. Square wave voltammetry parameters were: frequency: 15 Hz; Amplitude, 0.05 V; increment E, 0.004 V. A CHI660C analyzer from CH Instruments, Inc. was used. Nitrogen (N<sub>2</sub>) was bubbled for 5 minutes prior to the start of the isatin experiments unless stated otherwise. Response curves for isatin were generated using the standard addition method. the reproducibility of each electrode was determined from 4 scans at each concentration. The spectrophotometric analysis was performed using a UV-vis-NIR spectrophotoeter (UV-3600) from Simadzu with quartz cuvettes that had a 10 mm path length.

### 2.2.3 3-in-1 Electrode Fabrication

Both the MAC and MEA were fabricated on the same conductive silicon (Si) wafer through multiple processing steps. Microwave plasma-assisted chemical vapor deposition (MP-CVD) was first used to grow the BDD layer on top of the 3 inch diameter Si/SiO<sub>2</sub> wafer. This wafer was p-type with a thickness off 350  $\mu$ m and a resistivity between 1-5 Ohm cm. This was then coated with an insulating SiO<sub>2</sub> top layer that was 1  $\mu$ m thick. The sensors were patterned using a photolithography mask that allowed for the deposition of an insulating interlayer to be deposited on their surface using plasma-enhanced chemical vapor deposition (PE-CVD). Through all of these steps, the exposed BDD, which could be electrically connected at the top of each sensor, was the only electrochemically active surface on the face of the sensor.

A second photoresist mask defined the MAC and MEA configurations and allowed for the three distinct electrodes on each to be patterned. The spacing between each electrode in the MEA was carefully decided. If the micro discs were too close together the advantages of the single small electrodes would be lost as their depletion layers would overlap. [22, 23] Each 3-in-1 sensor was released from the wafer by laser cutting. An earlier publication goes in to more detail on the fabrication process. [22] Figure 2.2 shows optical micrographs of both the MEA (left) and MAC (right) 3-in-1 sensors. The active surface area of the MAC was  $3.14 \times 10^{-2} \text{ cm}^2$  and the 97 electrodes that comprised the hexagonal patterned MEA had a total active anode area of  $1.71 \times 10^{-4} \text{ cm}^2$ .



Figure 2.2: Optical micrograph of the MEA (left) and MAC (right) 3-in-1 sensors with exposed BDD

## 2.3 Results and Discussion

## 2.3.1 Electrode Characterization

Boron is typically used as a dopant for diamond to charge carrier concentrations greater than  $10^{20}$  cm<sup>-3</sup> to obtain metal-like electrical conductivity. [41–45] The surfaces of the MAC and MEA were characterized using Raman spectroscopy and scanning electron microscopy (SEM). Figure 2.3 shows a Raman spectrum and SEM micrograph taken from the diamond-coated wafer that both sensors were fabricated from.

The SEM micrograph, Figure 2.3 (A) shows grain sizes around 1-2  $\mu$ m for the polycrystalline diamond film that was used for all sensors. The film has no visual evidence of cracks or other defects. The Raman spectrum has large peaks around 500 and 1200 cm<sup>-1</sup> that are indicative of highly doped BDD. [41, 46–48] These peaks grow in intensity with higher boron concentrations. The boron concentration of the film was determined by using a fitting program in Matlab; providing a concentration of 0.3 %.

Cyclic voltammetry was used to generate a current vs voltage curve to determine the capacitance



Figure 2.3: (A) An SEM micrograph of the polycrystalline BDD surface that was used to fabricate the two 3-in-1 sensors with no defects or large cracks in the films structure and (B) the corresponding Raman spectrum analysis for the BDD wafer

values of the sensors. The MAC had a capacitance of 721 nF and the MEA had a capacitance of 5.3 nF. The drastic difference between the two comes from the different surface areas that are exposed to solution. If the capacitances are normalized to each corresponding surface area they are  $25 \,\mu\text{F/cm}^2$  and  $31 \,\mu\text{F/cm}^2$  for the MAC and MEA, respectively. These capacitance values are in a similar range to those reported for BDD in literature, 20-40  $\mu$ F/cm. [49]

Cyclic voltammetry (CV) was used further to determine the electron-transfer kinetics for the two redox couples of  $Fe(CN)_6^{3-/4-}$  and  $Ru(NH_3)_6^{3+/2+}$ .  $Fe(CN)_6^{4-}$  was used for the MAC electrode configuration whereas the MEA used a 1:1 ratio of  $Fe(CN)_6^{3-}$  and  $Fe(CN)_6^{4-}$ . The concentrations of the redox couples were 1.0 mM in 1.0 M KCl. The peaks were analyzed after manual background subtraction. [50, 51] The cyclic voltammograms for both redox couples on each 3-in-1 sensor are shown in Figure 2.4.

Each electrode was first conditioned in 1 M sulfuric acid ( $H_2SO_4$ ) from -2.0 V to +2.8 V at 0.5 V/s for 30 scans to condition the electrode surface. This was decided based on the investigation



Figure 2.4: (A) Cyclic voltammograms of 1 mM  $Fe(CN)_6^{3-}$  and 1 mM  $Ru(NH_3)_6Cl$  on the MAC 3-in-1 BDD sensor oth dissolved in 1 M KCl and (B) of a 1:1 ratio of  $Fe(CN)_6^{3-/4-}$  and 1 mM of  $Ru(NH_3)_6Cl$ , both dissolved in KCl, on the 3-in-1 BDD MEA sensor. Scan rate: 0.1 V/s.

into surface chemistry effects as discussed next. For obtaining different surface terminations, three different pretreatments were used: hydrogen termination (HT), oxygen termination (OT) and electrochemical cycling (ET). The ET was done in 1.0 M H<sub>2</sub>SO<sub>4</sub> using the procedure stated above. For HT, the electrodes were placed in a microwave plasma system in ultra-pure hydrogen (H<sub>2</sub>) for 10 minutes. For the OT pretreatment, electrodes were placed in an oxygen (O<sub>2</sub>) atmosphere for 1 minute in a reactive ion etcher (RIE). Contact angle measurements were used to evaluate each pretreatment process based on the obtained angle. Contact angles of 90 +/- 4.5° were measured for HT whereas angles of 0° were measured for the OT pretreatments. These trends align with those seen in literature for BDD surfaces. [52] The contact angles for the ET pretreatment were predominantly oxygen terminated at 13 +/-  $3.3^\circ$ . However, these are slightly more hydrophobic than the OT contact angles, suggesting different functional groups and surface coverage. The ET process may be generating a slightly more hydrophilic surfaces due to a stepwise mechanism

involving bond breakage and carbon-oxygen bond formation. [53] Because of this, and the cleaning of the surface impurities, the ET process was selected as the pretreatment for the remainder of this study. It is also important to point out that this pretreatment procedure wold be accessible to the users of the sensing technology. Not all users would have access to specialty equipment to perform the hydrogen or oxygen termination procedures. Since the ET uses the same technology as the method its-self, it is accessible to the common user. This pretreatment was only performed on the electrodes before beginning a set of measurements. It was not performed between measurements for the same calibration curve.

For the cyclic voltammograms of the redox couples, Figure 2.4, the MAC electrode provided the expected semi-infinite linear diffusion response and the typical bell shaped curves. Peak separations,  $\Delta E_p$ , for Fe(CN)<sub>6</sub><sup>3-/4-</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+/2+</sup> were 86 mV and 67 mV, respectively.  $\Delta E_p$  for Fe(CN)<sub>6</sub><sup>3-/4-</sup> on BDD electrodes is sensitive to the surface chemistry and cleanliness whereas Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+/2+</sup> is insensitive to the surface chemistry, inner sphere or outer-sphere electron transfer, respectively. [53–57] The heterogeneous rate constants for both of these redox couples was determined using the Nicholson and Shain method. [58, 59] The rate constants on the MAC for Fe(CN)<sub>6</sub><sup>3-/4-</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+/3+</sup> were 1.74 +/- 0.10 x 10<sup>-3</sup> cm/s and 1.17 +/- 0.09 x 10<sup>-2</sup> cm/s, respectively. Both redox couples indicated semi-linear diffusion due to the peak currents on the forward scans showing a linear relationship with the square root of the scan rate.

The CVs for the MEA was different from the MAC's in that they displayed a sigmoidal shape for both the oxidation and reduction of the redox couples. This shows that the reaction is limited by diffusion of the reactants to the electrodes surface due to the lack of overlap in the molecular diffusion towards each individual microelectrode causing the overall output current to be the sum of all the elements in the array. [23, 24] Due to the small size of the microelectrodes, the reactant transport is dominated by hemispherical diffusion, improving the signal-to-noise ratio. [18, 21, 23] This diffusion profile can shift back to semi-infinite diffusion behavior if the spacing between the microelectrodes is too small. [22, 23]

The CV's for the MEA are shown in Figure 2.4 (B). The rate constants for this sensor con-

figuration were determined using fast-scan CV (FSCV) measurements and the Klinger and Kochi method. [60] This was due to the fact that the peak separations were above the maximum limit for the Nicholson and Shain method preciously used. The  $\Delta E_p$  value at 100 V/s were 560 mV and 127 mV for Fe(CN)<sub>6</sub><sup>3-/4-</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+/3+</sup>, respectively. The rate constants for Fe(CN)<sub>6</sub><sup>3-/4-</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+/3+</sup> were 5.21 +/- 1.03 x 10<sup>-3</sup> cm/s and 1.40 +/- 0.13 <sup>-1</sup> cm/s, respectively. Both redox couples displayed a linear relationship between the forward peak current and the square root of the scan rate.

Surface morphology and cleanliness is a determining factor for  $Fe(CN)_6^{3-/4-}$  reaction kinetics. This is due to the fact that the reaction proceeds through surface sites which can become blocked by adsorbed oxygen. [61, 47] Hydrogen terminated films typically show rate heterogeneous rate constants between 0.01 and 0.1 cm/s compared to oxygen terminated films that can be 2 orders of magnitude lower. [61, 47, 48] The resulting rate constants for both the MAC and MEA were in the range typically displayed for oxygen terminated films, being consistent with the studies into surface termination after the ET pretreatment.

For  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ , the rate constant is influenced by the density of electronic states near its formal potential. [57] Diamond films have shown rate constants between 0.01 and 0.1 cm/s for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ .[47] Both the MAC and MEA fell within this range.

### 2.3.2 BDD as a Quasi-Reference Electrode

Since the three electrodes making up the two sensor configurations are made completely of BDD, two questions needed to be addressed: (1) Does this BDD film have a stable potential in solutions of differing pH values? (2) Is the potential stable over an extended period of measurement time?

These two questions were investigates using the MAC sensor by measuring its reference electrode's potential in solutions of various pH values compared to the potential of a Ag/AgCl electrode. Figure 2.5 shows the potential-time curves at a pH of 4.0-7.4 over a 12 hour period of time. The BDD's steady-state potential shifts in a negative direction with increasing pH. This phenomenon was reported in literature previously for diamond. [30] The potential stabilizes quickly in all the tested electrolyte solutions regardless of the pH.



Figure 2.5: The BDD's reference potential in 0.1M phosphate buffered saline at various pH values measured against a Ag/AgCl reference electrode for 12 hours.

Ponnuswamy attributed the change in BDD's potential in different pH solutions to the reactions between protons in the electrolyte solution and the surface. [38] The results found here are applicable to their suggestion that the change in proton concentration and interaction with the diamond surface causes the shift in potential. At each pH value, the potential stabilized after the first hour and remained relatively unchanged for the full 12 hour period. These results indicate that the quasi-reference material of BDD is suitable for a sensing application for a 3-in-1 device. To further evaluate the quasi-reference material in this device, a 28 hour stability experiment was performed. The average potential was -0.197 V with a standard deviation of 0.015 V as shown in Figure 2.6. Although the response fluctuated in the first 4 hours, it reached a stable potential where it remained for the remaining time. This shows that the BDD quasi reference can have a stable response for an extended measurement time.

### 2.3.3 Isatin Detection

Due to the stability of the 0.1 M phosphate buffered saline solution at pH 7.4, and its biological relevance, it was chosen to be used for the isatin voltammetric studies. Before each measurement, oxygen was removed from the solution by nitrogen ( $N_2$ ) bubbling. To further prevent oxygen from re-entering the environment, a  $N_2$  blanket was used on top of the solution during a measurement.



Figure 2.6: The BDD's reference potential for the extended 28 hours in 0.1M phosphate buffered saline at a pH of 7.4 measured against a Ag/AgCl electrode.

Figure 2.7 shows the CVs for 350  $\mu$ M of isatin on both the (A) MAC and (B) MEA sensor configurations at a scan rate of 0.1 V/s. Preconditioning of the sensors was done using the ET pretreatment process as previously mentioned.

The CV for the MAC electrode, Figure 2.7 (A), shows the independent anodic and cathodic peaks that have been reported previously. [11] The anodic peak is located at +0.832 V; -0.2 V from the peak location reported in literature against a Ag/AgCl reference electrode. [11] This shift seen on this electrode is due to the fact that the BDD quasi-reference displays a potential that is -0.2 V when referenced against a Ag/AgCl reference electrode. This same phenomenon occurs with the cathodic peak for isatin. The formal potential and half wave potential were determined as -0.034 V and -0.686 V, respectively.

The MEA CV, Figure 2.7 (B), shows a sigmoidal response for the reactions occurring for isatin. This sensor configuration also displays a lower faradaic current and background current. Since both sensor configurations clearly display the cathodic process and the cathodic process avoids interferences with other compounds such as ascorbic acid and glucose, it was chosen for the electrochemical detection comparison. [11]

Before performing the detection experiments the possible adsorption of isatin and its reduction products were studied on the BDD surface using CV and the MAC sensor configuration. The CV



Figure 2.7: Current versus voltage cyclic voltammogram curves for 350  $\mu$ M isatin in 0.1 M PBS at pH 7.4 on the 3-in-1 (A) MAC sensor and (B) MEA sensor. Scan rate of 0.1 V/s.

was measured for 350  $\mu$ M of isatin on the sensor before removing it from solution and rinsing it with DI water and immediately placing the sensor into a clean solution of 0.1 M PBS. N<sub>2</sub> was bubbled before measuring the original isatin CV and the following CV in the clean PBS buffer for 5 minutes. Figure 2.8 shows the results from this study. It was determined that there was no adsorption on the BDD's surface from isatin or its reduction products even at these elevated levels. This result coincides with that described by Diculescu et al. where they found the lack of adsorption of isatin on a glassy carbon electrode.

Square wave voltammetry was used to study the reduction of isatin based on the standard addition method with concentrations from 0.3 to 12  $\mu$ M in 5 mL of 0.1 M PBS at a pH of 7.4. N<sub>2</sub> bubbling was performed and blanketed on top the electrolyte solution. Both sensor configurations



Figure 2.8: Current versus voltage cyclic voltammogram curves of 350  $\mu$ M isatin in 0.1 M PBS at pH 7.4 (red) and after rinsing the 3-in-1 MAC electrode and rescanning the same electrode in clean electrolyte solution (black). Scan rate of 0.1 V/s.

showed a linear range from 0 to 12  $\mu$ M of isatin and a second linear range from 20 to 100  $\mu$ M. In order to determine the sensitivity, limit of detection (LOD), and limit of quantification (LOQ) of each sensor, three tests were performed. The LOD and LOQ were calculated using  $3\sigma$ / m and  $10\sigma$  /m, respectively where  $\sigma$  represents the standard deviation of the current for the lowest concentration measured and *m* is the slope of the obtained calibration curve.  $\sigma$  values for the MAC and MEA were 7.3 nA and 0.01 nA, respectively.

After each standard addition of isatin, the solution was stirred for 10 seconds. Figure 2.9 shows the voltammograms for 0.3 to 12  $\mu$ M of isatin on the MAC (A) and MEA (B) sensors. The peak heights at each concentration were measured from drawing a line at the background current level and determining the distance from the background to the peak maximum. [62, 50, 51]

From Figure 2.9 two different peak shapes can be seen; one for the MEA and one for the MAC electrode. The shape of the peak produced by the MEA sensor is much wider with a steep rise on the leading edge of the peak and a drawn out decay peak. The MAC had a full width half max (FWHM) of 0.23 V at 12  $\mu$ M whereas the MEA had a FWHM of 0.26 V. The irreversibility of the reduction of isatin is presumed to be the cause of these broad peak shapes for both sensor configurations. SWV has been shown to result in wider peaks when analyzing irreversible systems. [62] This phenomenon occurs due to the reverse pulse peak being more broad than the forward



Figure 2.9: Squarewave voltammograms for various concentrations of isatin on the 3-in-1 (A) MAC and (B) MEA sensor configurations in 0.1 M phosphate buffered saline with pH of 7.4.

pulse peak whereas in a reversible system they would be nearly mirror images of one another. [63, 64, 52] The broader peak shape for these sensors can also be a result of the charge transfer coefficient ( $\alpha$ ) being below 0.2.  $\alpha$  values this low have been shown to distort peak shapes as seen with those for the MAC configuration. [50, 51]

The difference in peak shapes could also be a result of the different diffusive properties between the two electrode configurations. On a literature reported MAC made of glassy carbon, isatin reduction occurred in a two step reaction where the products reduced to isatide. [11] This reduction appeared as a shoulder in their detection scans. In the study presented here, the MAC sensors have a tail at the end of the stripping peak which could be related to the reduction of the products to isatide on this BDD surface. The MEA does not display this same characteristic tail suggesting the reduction products diffuse away faster on this sensor configuration and do not become further reduced. It has been shown that analytes diffuse away from MEA's faster than they do when using an MAC. [21–29]



Figure 2.10: Calibration curves for (A) the MAC and (B) the MEA in 0.1 M phosphate buffered saline with a pH of 7.4

Ultimately the MEA exhibited a lower sensitivity due to the standard deviation of the current measurement being 2 orders of magnitude lower at 0.3  $\mu$ M compared to the MAC. The calibration curves for both sensor configurations are shown in Figure 2.10. The calculated LOD and LOQ were both lower for the MEA due to this. The LOD of the MEA was 0.04  $\mu$ M and that of the MAC was 0.22  $\mu$ M. Both the MEA and MAC sensors displayed linearity with an excellent  $R^2$  value. These values can be seen in Table 2.1.

Also shown in Table 2.1 is the comparison of the electrochemical results to those obtained with UV-vis spectroscopy and other literature studies. The wavelength used for UV-Vis measurements

Table 2.1: Figures of merit for isatin detection using the 3-in-1 MAC and MEA sensors compared to other reported literature studies on different detection methods. Standard deviations calculated at lowest concentration detected for this study

Detection Method	Sensitivity μΑ/μΜ, Abs/μΜ	LOD, $\frac{3\sigma}{m}$ (µmol L <sup>-1</sup> )	LOQ, $\frac{10\sigma}{m}$ (µmol L <sup>-1</sup> )	R <sup>2</sup>
3-in-1 Macro	$9.31  x  10^{-2}$	0.221	0.735	0.999
3-in-1 MEA	9.81 x 10 <sup>-4</sup>	0.041	0.137	0.999
UV-Vis	1.57 x 10 <sup>-2</sup>	0.573	1.911	0.999
HPLC-UV [14]	-	2.000	-	1.000
LC-ED at PdHCF CME [1]	-	0.025	-	0.999
Differential Pulse [11]	1.10 x 10 <sup>-2</sup>	0.646	-	0.992

was from 200 to 450 nm and the absorbance of isatin was recorded for concentrations of 0.3-12  $\mu$ M. The absorbance spectra for these concentrations is provided as Figure 2.11. The LOD was determined by generating a calibration curve from the peak absorbance at 242 nm. This value was higher than that obtained for the electrochemical detection mainly due to the large standard deviation of the signal between each test. In fact, this differentiation is orders of magnitude higher than that seen with both electrochemical sensors. Due to this, both the MEA and MAC have proven to have lower detection limits than the UV-vis detection. Compared to the other electrochemical sensing study that did not involve a pretreatment between concentration measurements, the study performed here obtains a lower LOD and LOQ with a higher linear correlation coefficient and linear range of concentrations. [11] The study here also advances this technology by removing the need of separate counter and reference electrodes. Further, the use of BDD can be more reproducible with the ET pretreatment compared to having to polish a glassy carbon electrode before each day of measurements. Polishing drastically changes the surface of the electrode and can cause large fluctuations in data and a higher degree of uncertainty in the actual concentrations measured. BDD is more suitable for understanding the concentrations in the human body and how the reactions are occurring. This more advanced sensing technology will allow for a quicker turn around on information related to the advancement of pharmaceuticals.



Figure 2.11: UV-vis absorbance spectra for isatin in 0.1 M of PBS pH 7.4

### 2.3.4 Urine Simulant Study

To further advance the understanding of this compound using electrochemical methods, calibration experiments were performed in a urine simulant with no N<sub>2</sub> bubbling prior to measurement for evaluation in a more complex sample matrix. Isatin was studied in the range of  $1.8 - 12 \mu$ M due to the lower concentrations being hidden in the background of the new matrix. Due to the increased complexity of this study, the sensitivity of the MAC decreased by 10x with an increase in the LOD to 0.82  $\mu$ M. The calibration curve still displayed linearity of 0.995. The MEA sensitivity only decreased by a factor of 3 and the LOD increased to 0.80  $\mu$ M but this sensor also displayed linearity with an *R*<sup>2</sup> value of 0.994. Figure 2.12 shows the voltammograms for both the MEA and MAC.

The calibration curves for both sensors are shown in Figure 2.13. The calculated LODs are higher than those that were determined in the buffered solutions, but most LC methods use pretreatment methods as well as extraction procedures before determining isatin concentrations that include diluting the complex matrix, pH adjustments, and using ethyl acetate for extraction. [8, 14, 65] Even with these pretreatment procedures, the LOD when using LC-MS was well above that obtained for the two electrochemical sensors at 2  $\mu$ M. No studies of isatin had previously been performed in synthetic urine solution. This study allows further understanding of the capability to use electrochemistry in the measurement of real samples.



Figure 2.12: Squarewave voltammograms for the 3-in-1 MAC sensor (A) and MEA sensor (B) in Surine Negative Urine Control with no additional  $N^2$  bubbling



Figure 2.13: Calibration curves for the (A) MAC and (B) MEA for isatin in Surine Negative Urine Control with no  $N^2$  bubbling

#### 2.3.5 Repeatability Study

A 5-day repeatability study was performed to analyze the repeatability of the BDD sensors. The measured data is shown in Figure 2.14. The ET pretreatment procedure was used on the first day of the study for both sensors. Square wave voltammetry was then performed in a 3  $\mu$ M solution of isatin in PBS buffer of pH 7.4. Over the next 3 days, each sensor was used to rest a fresh solution for 7 total trials without repeating the pretreatment method. Both sensors had a decrease in signal; 63% for the MEA and 73% for the MAC. The ET process was the repeated and the sensor were retested. The MEA regained 64% of the original signal it had and the MAC regained 76%. Over the course of the 7 trails, the MEA remained stable and regained full signal strength in trial 6. The MAC showed a similar trend for those without the ET method applies but the signal did not decrease as significantly with the ET procedure compared to without. This study suggests that there are substantial changes with the signal response over the course of a few days and additional research is required to better understand how the surface regeneration works.



Figure 2.14: Repeatability data for the 3-in-1 (A) MAC and (B) MEA sensors with the discussed electrochemical pretreatment and without any addition of a pretreatment

#### 2.3.6 Key Advancements Obtained from Study

The advancements obtained from this study include:

- Simplified technical equipment for the electrochemical detection of isatin by removing the need for three separate electrodes with a 3-in-1 sensor
- Time savings in the analysis of isatin samples by implementing one sample pretreatment process compared to the previous complicated and multistep processes used on other electrode materials
- The ability to directly detect isatin in a complex sample, such as a urine simulant, without the necessary extraction methods typically used for analysis with gas chromatography.
- Using the MEA sensor configuration obtained a sensitivity that was two orders of magnitude lower than the MAC resulting in a lower LOD in simulated solution and as overall more repeatable with the electrochemical pretreatment method compared to the MAC.

### 2.4 Summary

Two sensors were fabricated to have a reference, auxiliary, and working electrode, all comprised of BDD, and were fully characterized. The reference electrode had a potential variation with pH, but stabilized quickly and remained stable over the course of 30 hours. Both sensors, one comprising of a MEA and one comprising of a macro electrode, were characterized with a surface sensitive and surface insensitive redox couples and displayed comparable rate constant values. Adsorption of isatin and its reduction products were evaluated and no adsorption was found for the BDD surface. Comparison of the MEA and MAC lead to the MEA having a LOD of 0.04  $\mu$ M whereas the MAC had a LOD 0.22  $\mu$ M; both below the LOD of UV-vis spectroscopy measurements. Both sensors were further evaluated in a urine simulant study as well as repeatability tests. This work concludes that the fully BDD devices can be feasible for the measurement of isatin. Future applications of these sensors include the detection following a flow injection analysis system.

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# **CHAPTER 3**

# INDIUM TIN OXIDE FILM CHARACTERISTICS FOR CATHODIC STRIPPING VOLTAMMETRY

#### 3.1 Introduction

This work has been published in ACS Applied Materials and Interfaces<sup>1</sup>. Indium tin oxide, or ITO, is a common conductive and optically transparent film that is used in applications such as transparent electrodes for solar cells, surface heaters for windows, liquid-crystal displays, and spectroelectrochemical applications. [1–10] Although sputtering is the most common deposition method for ITO films, it can also be performed using chemical vapor deposition, ion beam evaporation, and spray pyrolysis. [1, 2, 4–7, 11–17] ITO films can be tailored to having different optical and electrical properties and can be deposited as amorphous or crystalline films.

The wide range of characteristics that each film can possess comes from the changes in the ordered structure of the film due to the generation of oxygen vacancies. [7] The tunable process parameters that allow these changes include gas pressures, substrate temperatures, deposition time, film thickness, and post processing annealing steps in different gases and at different temperatures. [2, 4, 5, 7, 11, 18, 19] Between the temperatures of 100 and 150 °C, there is an amorphous to crystalline transition for ITO. [19] This shift causes films to differ in their presence of oxygen and conducting carrier concentration. [1, 7, 19, 20] When the substrate temperature is above 100 °C the film's resistivity drops leading to an increase in carrier concentration and mobility. [6, 19] A film thickness of greater than 200 nm, deposited at room temperature, are typically crystalline, but those below 100 nm are typically amorphous. [4] All of these process parameters can be tuned to create unique films for specific applications. [2, 4, 7, 11, 19, 21]

Post deposition process parameters can also have an effect on the ITO film's characteristics. dc-sputtered post deposition annealed films show an increase in grain size, decrease in electrical resistivity, and a decrease in intrinsic strain. [4, 5, 11, 20] The temperature needed for crystallization during annealing is higher for films that were deposited on non-heated substates compared to those deposited on heated substrates. [4, 7] The optical properties of the film are also affected by annealing. It can lead to an increased band gap and a steeper cutoff absorption. [4] Various

<sup>&</sup>lt;sup>1</sup>ACS Applied Materials and Interfaces 2019, DOI:10.1021/acsami.8b22157

studies have been carried out to study the changes in the ITO film based on annealing atmosphere, temperature, and if vacuum is used. [1, 7, 11, 20, 22]

The most common use of ITO in the field of electrochemistry is as an optically transparent film for spectroelectrochemical measurements. [9, 23, 24] It has been used to detect analytes including Azure A, total alkaline phosphate in human blood, potassium ferricyanicde, and iron using complexation with 2,2'-bipyridine. [2, 23, 25, 26] This application is primarily due to this ITO film possessing a large positive potential window beyond +1.5 V while remaining transparent in the range of 390-700 nm. [23, 27, 28] Since the film is already in its oxidized form, it does not react in this positive potential range. [25] Several metals including cadmium (Cd), lead (Pb), copper (Cu), cerium (Ce), mercury (Hg), and manganese (Mn), has also been detected with ITO, by using the method of stripping voltammetry. [27–30] Cd and Cu had their signal monitored as they were plated onto the electrode surface using attenuated total internal reflectance stripping voltammetry. [29] Ce additionally has been detected using cathodic stripping voltammetry (CSV) and ITO. [27] Recently, bare ITO was used to detect Pb, Cu, and Hg simultaneously using this method. [30]

Mn has been investigated on ITO also using CSV. [28] This was performed using an ITO coated with polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-sulfonate (SSEBS) as well as compared to a bare ITO electrode. [28] This study was followed up with a paper reporting the detection of Mn in digested bovine blood samples that obtained similar detection capabilities as inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectroscopy (GF-AAS). [31] The detection of Mn is important due to it having toxic effects and a maximum contaminant level (MCL) in drinking water of 50 parts per billion (ppb) set by the United States Environmental Protection Agency (EPA). It is also significant to test human blood, urine, and serum levels when monitoring its effects. [32, 33]

Palladium (Pd) on Cu, boron-doped diamond (BDD), and various other carbon materials have also been used to detect Mn with CSV. [34–39] Compared to these other materials, the positive potential window of ITO makes it more beneficial for CSV. Cu-based Pd electrodes obtained a
LOD at 19 ppb which is below the MCL in drinking water but higher than the typically biological concentrations. [32, 33, 35] The BDD sensor was evaluated in sea water and required the use of ultrasound, but only obtained a LOD of 5.5 ppb which is still not sensitive enough for serum analysis. [36] Additionally BDD had a higher resistivity compared to ITO and can be expensive to fabricate into sensor designs. [40] The bare carbon paste electrode previously studied obtained the same LOD as the BDD sensor. [39] The most promising electrode material for Mn detecting using CSV was edge plane pyrolytic graphite that obtained a LOD of 0.80 ppb. [37] However, the previously studied ITO films reached an even lower LOD compared to this material which may be due to the metal oxide surface of ITO being beneficial in the deposition of manganese dioxide (MnO<sub>2</sub>) on the surface.

Sensors being used for metal detection ultimately do not require the use of optical transparency when utilizing the method of CSV. ITO has been deposited on opaque substrates before, but never has then been applied to CSV metal detection. [27, 41] Fabrication of such a sensor on silicon (Si) is much safer and easier than the process used for sensor fabrication on transparent substrates due to avoiding the use of hydrofluoric acid (HF). [42] Si can utilize dry etching processes for fabrication allowing for faster and more precise etching without putting fabricators lives in jeopardy. ITO is already mass produced for other applications on non-transparent substrates that would also allow for an economical mass production of sensors. In addition to the unique electrochemical properties that ITO possess, it is already widely used in mass production for solar cells which means it is available at much lower costs, and is more reproducible than other electrode materials used in CSV.

This study reports on the optimization of ITO working electrodes on Si substrates for the application of metal detection using CSV. At this time, there is no report in literature using opaque substrates for this technique. Several processing parameters such as heated and non-heated deposition and the effects of post deposition annealing were investigated. Each corresponding film was thoroughly characterized and evaluated before using each to detect Mn by CSV.

#### **3.2 Experimental Section**

#### 3.2.1 Chemicals and Materials

A stock solution of potassium ferrocyanide ( $K_4Fe(CN)_6$ ) was prepared using powder purchased from J.T Baker and deionized (DI) water. Manganese (Mn) was purchased from Acros Organics. Deionized (DI) water and acetic acid (Fisher Scientific) were used to prepare a 0.2 M acetate buffer with 0.2M sodium acetate purchased from Sigma-Aldrich. Ferrocene (Aldrich Chemical Company Inc.) was prepared in acetonitrile (Sigma-Aldrich) using a 1mM solution with 0.1 M tetrabutylammonium hexafluorophosphate.

#### 3.2.2 Instrumentation

An AFM5100 from Hitachi was used in tapping mode to complete the atomic force microscopy (AFM) measurements on an area of 4  $\mu$ m<sup>2</sup> with a scan frequency of 0.84 Hz. The roughness of each sample was determined using the open source software of Gwyddion using three evaluation lines that were placed across the top, middle, and bottom of the scanned area. A cutoff length of one-fifth of the scan length was used in these calculations.

X-Ray diffraction (XRD) measurements were performed with a Rigaku SmartLab 3 kW Cu source generating a parallel beam with electron current of 44 mA and an acceleration voltage of 40 kV. Out of frame diffraction peaks were collected at 4° /min using symmetric ( $2\theta - \omega$ ) scanning stepping at 0.02° over a range of 30° - 90°. Diffracted X-rays were collected through collimating slits at 0.5° pitch and aperture of 20 mm using a 0D SC-70 photomultiplier tube. An area of 10 x 12 mm was set to limit the X-ray beam spot on the sample.

A Shimadzu UV-vis-NIR spectrophotometer with a wavelength of 190-2500 nm was used for all optical measurements. A 414513 semiconductor parameter analyzed from Hewlett-Packard was used for the four-point probe measurements with a correction factor of 4.3. [43]

An Epsilon Eclipse from Bioanalytical Systems, Inc. (BASi) was used in a three electrode setup for all electrochemical measurements. Each film was used as a working electrode with a 0.5

mm circle diameter exposed to the electrolyte solution. Inside the cell was a silver/silver chloride (Ag/AgCl) reference electrode and either a platinum (Pt) or graphite auxiliary electrode. A silver quasi-reference was used for the chronoamperometry (CA) experiments in ferrocene. Each CV experiment utilized 0.1 mM Fe(CN)<sub>6</sub><sup>4-</sup> in 1.0 M KCl by scanning the potential from -0.1 to 0.6 V. Peak height measurements were performed with an extrapolated baseline method described in literature. [44–46]

#### 3.2.3 Electrode Fabrication

Pulsed dc magnetron sputtering was utilized for all fabrication runs. Each run was performed for 20 minutes using a Kurt J. Lesker PVD 775 system. One set was performed at room temperature and one utilized a set substrate temperature of 190 °C. An ITO target  $(In_{90}/Sn_{10})$  with a 1.6% oxygen  $(O_2)$  to argon (Ar) ratio was used. The power density was 20 W/in. Two groups of microscope slides and nonconductive Si substrates were formed: those annealed and not annealed. The annealing was done at 400 °C for 1 hour in ambient air. Four final samples were evaluated; heated and annealed (HA), heated and not annealed (HNA), not heated and annealed (NHA), and not heated and not annealed (NHNA). All film's thicknesses were in the range of 230 and 250 nm.

# **3.3 Results and Discussion**

#### 3.3.1 Physical and Optical Characterization: Atomic Force Microscopy

Atomic force microscopy (AFM) was used to evaluate each electrode film's surface morphology. Figure 3.1 shows the two dimensional topography views for HA, HNA, NHA, and NHNA on nonconductive silicon (Si) substrates. From this Figure, visual similarities can be seen between the two heated samples and the two non-heated samples.

NHA and NHNA, shown in (C) and (D) respectively, are comprised of smaller grain sizes that appear to be more inhomogeneous than the two heated samples. Also between these two films, the annealing is noted to cause a significant appearance of taller gains shown in the lighter color. HA and HNA, shown in (A) and (B) respectively, have larger grain sizes compared to the non-heated



Figure 3.1: Tapping mode atomic force microscopy (AFM) images for the four analyzed ITO films (A) HA, (B) HNA, (C) NHA, and (D) NHNA.

samples. Annealing the heated sample (A) also brings about higher grain structures compared to the not annealed heated sample.

The AFM data also provided the root-mean-square (rms) roughness values for each film. NHNA had the lowest rms value with HA having the highest value. All the film's rms values are provided in Table 3.1. The roughness values are affected more by the heating than the annealing, but all the films are smooth overall. There is a benefit to having a greater roughness to electrode materials. A higher roughness leads to a greater microscopic surface area which can lead to a greater sensitivity and lower limit of detection (LOD) in CSV measurements.[44–46] From this physical and optical characterization, HA and HNA are potentially more advantageous as a sensing material than the other two films.

	HA	HNA	NHA	NHNA
rms (nm) (n = 3)	$1.45 \pm 0.07$	$1.22 \pm 0.08$	0.62 ± 0.05	$0.54 \pm 0.03$
sheet resistance (Ω)	9.22	19.22	18.36	43.85
resistivity (Ω·cm)	$2.1 \times 10^{-4}$	$4.4 \times 10^{-4}$	$4.2 \times 10^{-4}$	$10.1 \times 10^{-4}$
capacitance $(F/cm^2)$ $(n = 3)$	$2.7 \times 10^{-5} \pm 9.7 \times 10^{-8}$	$2.2 \times 10^{-5} \pm 1.1 \times 10^{-7}$	$2.7 \times 10^{-5} \pm 2.5 \times 10^{-7}$	$2.0 \times 10^{-5} \pm 1.1 \times 10^{-6}$
FeCN Ko $(cm/s)$ $(n = 3)$	$1.5 \times 10^{-1} \pm 1.7 \times 10^{-2}$	$1.5 \times 10^{-1} \pm 2.8 \times 10^{-2}$	$1.1\times10^{-1}\pm1.1\times10^{-2}$	$8.7\times 10^{-3}\pm 6.4\times 10^{-5}$
direct optical Band gap (eV)	4.08	3.96	3.98	3.67
Ohm's plot resistance $(\Omega)$	1318 ± 126	2461 ± 156	2941 ± 172	26976 ± 2187
Mn CSV sensitivity (A/ppb) (n = 3)	$-3.4\times10^{-8}\pm1.2\times10^{-9}$	$-3.0 \times 10^{-8} \pm 3.4 \times 10^{-9}$	$-3.3 \times 10^{-8} \pm 3.5 \times 10^{-9}$	N/A
Mn LOD (ppb) $(n = 3)$	0.1 ± 0.05	$0.3 \pm 0.08$	0.8 ± 0.04	N/A

Table 3.1: Comparison of each of the figures of merit for each of the four ITO films that were investigated.

## 3.3.2 Physical and Optical Characterization: XRD

All four films were confirmed as polycrystalline from the presence of multiple peaks in the diffraction pattern performed with symmetric scans. The peaks were identified as Ia3 ITO using the crystallography open data base. [47–50]

In Figure 3.2 (A) the (222) peak decreases as a function of heat treatment, regardless if performed by deposition or annealing. The (400) peak, Figure 3.2 (B), shows an opposite trend by increasing with heat treatment. Literature states that the (400) peak decreases when there is increasing oxygen in the ITO film suggesting that the heated deposition promotes the (400) orientation of the film. [50] The center of the (222) orientation shifts during both heating during deposition, and annealing a non heated film displaying a change in the strain of this phase. Using the NHNA film as a zero point, the NHA peak center is +0.16 °and the HNA film's is -0.2 °. HA's center of the (222) orientation peak is in roughly the same position as NHNA's.

The ratio of the (222) and (400) peaks,  $I_{(222)}/I_{(400)}$ , for NHNA is 23 times greater than HNA's, indicating a transition to a preferred orientation (Figure 3.3 (left)). The full width half-maximum (fwhm) of the (222) and (400) peaks is also a function of heat treatment. In general, the fwhm decreases from both heating and annealing as shown in Figure 3.3 (right). This trend shows that either during heating or after annealing, the crystalline quality improves. Without the application of heat during processing, the mobility of the tin and indium-oxygen clusters is restricted and limits



Figure 3.2: XRD scans for the (A) (222) peak and (B) (400) peak for each ITO film investigated.

the likelihood of miss-orientations leading to bond distortions.



Figure 3.3: (left) ITO crystal quality  $(I_{(222)}/I_{(400)})$  ratio obtained from XRD analysis, and (right) the full width half max (FWHM) data for each film from XRD analysis pertaining to either the (222) or (400) peak

The FWHM for NHNA is caused by this process. The application of heat above 150 °C during deposition enables the mobility of the tin and indium oxide clusters. [51] An exception is the jump in FWHM from the (400) in NHNA and the (400) in NHA and the reverse FWHM positions of (222) and (400) for HNA. This may be the result of having frozen clusters when using room temperature deposition for NHA. Annealing has shown the ability to unfreeze these sites but the diffusion through the film is limited and restricts their chance of occupying favorable lattice positions. However, with heated deposition HNA allows the clusters a higher mobility and increases the probability of stable bond formations and a lower FWHM.



Figure 3.4: ITO crystal size derived using the Scherrer equation and the (222) and (400) peak of each film

HA supports all the conclusions drawn when combining heating and annealing by having the smallest FWHM, least amount of stress or strain, and the largest (400) crystallite size as seen in Figure 3.4. This leads to the conclusion that HA could be the best film for Mn detection due to its larger grain size and increased conductivity. [19] This could also suggest that HNA may be the optimum film due to its mirrored properties for the FWHM and crystal size compared to HA. Additionally, The  $I_{(222)}/I_{(400)}$  of HNA is lower than that of HA.

# 3.3.3 Physical and Optical Characterization: UV-Vis Spectroscopy

To gain insight into the charge carriers of the films, microscope slides were included in each run and analyzed using UV-Vis Spectroscopy. The Transmittance (T%) spectra of a blank microscope slide, for reference, and each of the four films is shown in Figure 3.5 The T% spectrums of HNA and NHNA are similar to one another as well as HA and NHA, suggesting that the annealing step changes the optical properties of the films. Literature states that annealing of ITO films shifts the absorption edge to a lower wavelength, and this is the same trend seen with the films in this study. [4] HA and NHA are shifted to lower wavelengths and HNA is also seen shifted in this direction which may be due to the heating of the substrate. Compared to NHNA, it is presumed that these three films will have a lower defect density and higher crystallinity due to this shift in their T% spectra. [4]



Figure 3.5: Transmittance spectra measured with UV/Vis for each of the four films deposited on a transparent microscope slide

In the wavelength range of 1500-2500 nm, NHNA has the highest T% value with HA displaying the lowest. Due to the fact that literature has shown that a higher carrier concentration displays a lower T% in this wavelength, it is assumed that HA has the highest carrier concentration. [4, 52] The direct optical band gap of each film was also determined from the T% data using the reflectance spectrum as well. The direct optical band gap provides information about the crystallinity of each film due to the relation between an increase in band gap with a decrease in localized state density. [53, 54] In order to calculate the band gap, the energy gap ( $E_g$ ) was first determined using Equation 2.1. [55, 56]

$$\alpha * h * v = (h * v - E_g)^r \tag{3.1}$$

Where *hv* is the photon energy,  $\alpha$  is the absorption coefficient, and *r* is the transition coefficient with a value of either 0.5 or 2 for a direct band gap or indirect band gap, respectively.  $\alpha$  is determined using Equation 2.2.

$$T = (1 - R)e^{(-\alpha \mathbf{d})} \tag{3.2}$$

Where d is the film's thickness. By extrapolating the linear region of the Tauc Plot, Figure 3.6, the direct optical band gap was determined for each film. All of the fitting parameters are displayed in Table 3.2.



Figure 3.6: Tauc graph used to determine the direct optical band gap for the four ITO films studied

Table 3.2: Fitting parameters for the band gap determination from the Tauc plot of each film.

Sample	Fit Function	R <sup>2</sup>	Band Gap (eV)
HA	0.152x-0.622	0.9824	4.08
HNA	0.104x-0.412	0.9826	3.96
NHA	0.125x-0.496	0.9834	3.98
NHNA	0.067x-0.244	0.9677	3.67

The lowest and highest optical band gap belonged to NHNA and HA, respectively. The band gap was increased by both heating and annealing. According to the density of states model by Mott and Davis, the process of annealing or heating removes the defects that were present in the amorphous film and forms saturated bonds that increase the band gap. [56] This trend agrees with the FWHM trend from the XRD analysis.

Since HA has the highest band gap followed by NHA and HNA, these three films are highly likely to be applicable for a sensing application. All the optical band gaps determined for these films compare well with literature values for other reported ITO films. [5, 7, 21]

#### 3.3.4 Electrical Properties

In terms of having a good electrode material for electrochemical sensing applications, low resistance is necessary. For each film, the resistance and resistivity values are summarized in Table 3.1. NHNA had the highest resistivity and sheet resistance and HA had the lowest. NHA and HNA had almost the same sheet resistance and resistivity as one another. According to literature the resistivity of an ITO film decreases when it is heated or annealed to temperatures above 100  $^{\circ}$ C. [4, 7, 11, 19] Compared to other electrodes used for Mn detection, the ITO films have a higher resistivity than carbon, but lower than boron-doped diamond. [40, 38, 57] The results for the electrical properties suggest that HA should be expected to perform as the best electrochemical sensor; agreeing with the optical property analysis performed earlier.

#### 3.3.5 Electrochemical Characterization

Cyclic voltammograms (CVs) and Ohm's resistance plots were generated to investigate each film's electrochemical behavior. The CVs allowed for the double layer capacitance of each film to be determined in 1 M potassium chloride (KCl) with a scan rate range of 0.1 to 0.4 V/s. Each current value at 0.0V was recorded and was graphed against its corresponding scan rate, Figure 3.7. The slope of this graph provided the capacitance of each film that could then be divided by the exposed area to obtain the typical units of  $F/cm^2$ .

The inner sphere electron transfer redox couple of potassium ferrocyanide was used to evaluate each ITO film. This was chosen since it has a surface sensitive nature and can be used to compare to other electrode materials although it is believed that the reaction of this redox on the surface varies with its monolayer adsorption and does not vary with surface oxide coverage. [58] Figure 3.8(A) shows the CV for each film obtained from a scan rate of 0.1 V/s.



Figure 3.7: Graph showing the current vs scan rate study of each of the ITO films used to determine their corresponding capacitance values

The peak separations determined at 0.1 V/s were 90 mV, 83 mV, 89 mV, and 95 mV for HA, HNA, NHA, and NHNA, respectively compared to previously published at 160 mV. [59] Potassium ferrocyanide is a common redox couple used to characterize boron doped diamond (BDD) and glassy carbon. The peak separations on these materials are 70-85 mV for BDD and 61-65 mV for glassy carbon. [59–61] Depending on pretreatments, carbon electrode materials can have drastically different peak separations including values of closer to 145 mV. [59, 61] The ITO films investigated here are similar to the peak separations for BDD.



Figure 3.8: (A) CV curves of 0.1 mM ferrocyanide in 1.0M KCl with a scan rate of 0.1 V/s. (B) Potential windoe study performed in acetate buffer of pH 5.0. (C) CSV od 25 ppb of Mn in acetate buffer of pH 5.0, deposition time of 3 minutes and a deposition potential of +1.2 V.

The rate constant of ferrocyanide on each ITO film was determined using the Nicholson Shain method for electrodes that display low peak separation with exact psi values that were interpolated from the supplied table in the reference. [62] In terms of peak current, Figure 3.8(A), HA had the highest followed by HNA and NHA with very similar responses. NHNA displayed the lowest current value out of the four films. This trend of peak current matches the trend for the conductivity of each film. The rate constants for each film are shown in Table 3.1. HA and HNA had the fastest rate constant and NHNA has the slowest. This result suggests, again, that HA or HNA would make a great electrochemical sensor since a high current response and a fast rate constant are desired.

Each ITO film's electrochemical potential window was also studied; Figure 3.8 (B). The potential began at 0.0V and was scanned anodically to +2.5 V before being reversed and scanned to -1.75 V and then back to 0.0V. All four films display an excellent anodic potential window, but have several peaks in the cathodic scan. These peaks are believed to be from the reduction of oxygen and ITO to metallic indium (In) and tin (Sn) as studied by Liu et al. [63] The peak at -0.3 V is the largest on HA and is likely due to the reduction of oxygen in each film. This would also support the claim that the reduction of the (400) XRD peak is due to increasing oxygen in the films. According to all four scans, it appears that both heating and annealing ITO can cause an increase of oxygen incorporation into the films. The other peaks at around -1.2 V are also largest in HA and are related to the reduction of the ITO films. [63] This film with the In- and Sn- terminated phases and larger crystallite size has an important roll for the electrode performance.

Plotting the change in peak potential  $(E_p)$  versus the change in peak current  $(i_p)$  for each film allowed for the generation of Ohm's resistance plots. The slope of these plots is the resistance in the electrochemical cell in Ohm. All four film's resistance plots are shown in Figure 3.9. These plots were generated since the resistance values from the four-point-probe only provide information of the resistance through the film between the probes in air. Whereas these plots measure the resistance when exposed to an electrolyte solution as the films would be in a practical application.

Each of the four film's has a constant resistance when the temperature is constant and are ohmic resistors. HA had the lowest resistance calculated and NHNA had the highest. NHA and HNA were



Figure 3.9: Plots for the Ohm's resistance of each of the four ITO films investigated

very similar to each other once again. All the values obtained from these plots is also displayed in Table 3.1. The trends seen from the Ohm's plots are expected based on the four-point-probe measurements.

Chronoamperometry measurements were performed to determine the microscopic surface area of each film by using an applied potential step and the Cottrell equation. [44] All calculations were performed with a constant diffusion coefficient of 2.24 x  $10^{-5}$  cm/s. all four films displayed microscopic surface areas that were statistically similar at roughly 0.20 cm<sup>2</sup>. The geometric surface area of 0.196 cm<sup>2</sup> is almost identical to this value; probably due to the smoothness of each film provided in Table 3.1. From this, it was determined that the surface roughness may not be a critical parameter in discriminating between the films.

#### 3.3.6 CSV of Manganese

Manganese was used to further test the applicability of each ITO film by doing CSV with 25 ppb of Mn with a deposition potential of +1.2V for 3 min, based on previous Mn experience when using ITO. [28] The stripping voltammograms of each film were performed a total of three times and an average for each is plotted in Figure 3.8 (C). NHNA is the only film that did not have a response peak at this Mn concentration. HNA and HA displayed a comparable peak to one another

and NHA was visually comparable to them as well, but showed a smaller magnitude of current. Table 3.1 displays the peak current responses for each film. These results, and previous, support the hypothesis that the heated deposition run makes the most appropriate ITO film for Mn analysis, but further investigation into HA and HNA still needs to be performed to decide between them.

3.3.7 Calibration and Figures of Merit



Figure 3.10: Mn stripping voltammograms for the full concentration range on HA (A1) and the smaller range (A2), for the full range on HNA (B1) and the smaller range (B2), and for the full range on NHA (C1) and smaller range (C2). Performed in pH 5.0 acetate buffer with a deposition potential of 1.2 V and a deposition time of 3 min

Mn concentrations of 1, 5, 10, 25, and 50 ppb were used to generate calibration curves performed in triplicate. Figure 3.10 shows the stripping voltammograms for the HA, NHA, and HNA films. Calibration curves pertaining to the full concentration range investigated are sown in Figure 3.11. The uncertainty in the slope, y-intercept, and the uncertainty in the y and correlation coefficient  $(R^2)$  values were determined using a Linest function in Excel. The equation for propagation of uncertainty in the best fit line was used to determine the uncertainty in the LOD for each calibration curve. [64] NHNA was excluded from both Figure 3.10 and Figure 3.11 due to its inability to perform for this application resulting from an  $R^2$  value of 0.663.



Figure 3.11: Calibration curves for Mn on HA (A), HNA (B), and NHA (C)

The overall average response of NHA was  $[I(A) = (-3.3 \times 10^{-8} + /-3.5 \times 10^{-9})c (A/ppb) + (1.2 \times 10^{-7} + /-8.9 \times 10^{-8}) (A) R^2 = 0.967]$  with a LOD of 0.8 ppb. The downsides to this film were that the background shifted slightly throughout the measurements and the lowest concentration of 1 ppb was hard to distinguish from the background, as seen in Figure 3.10(C2). HNA had a response of  $[I(A) = (-3.0 \times 10^{-8} + /-3.4 \times 10^{-9})c (A/ppb) + (1.4 \times 10^{-7} + /-8.6 \times 10^{-8}) (A) R^2 = 0.964]$  and a LOD of 0.3 ppb. Compared to the peaks obtained in NHA, the peaks on HNA are more symmetric and the background level shifts less. The lowest concentration is still hard to distinguish from the background in Figure 3.10(B2). HNA also exhibited an improved reproducibility and lower

standard deviation at 1 ppb compared to NHA. HA had an overall response with the lowest LOD, highest sensitivity, and greatest correlation coefficient;  $[I(A) = (-3.4 \times 10^{-8} + / - 1.2 \times 10^{-9})c (A/ppb) + (8.2 \times 10^{-8} + / - 3.1 \times 10^{-8}) (A) R^2 = 0.996]$ . The LOD on HA was 0.1 ppb which is 3x lower than that of HNA. The R<sup>2</sup> value for this film was the only analytically acceptable value. Previously recorded LODs for Mn on bare ITO are reported at 0.27 ppb, making the film studied here superior. [28] The lowest concentration of 1 ppb on this film displays a clear and distinct peak compared to HNA and NHA. The background also remains the most stable and appears the flattest from the other films. HA was also the most reproducible film overall.

The LODs obtained on HA, HNA, and NHA are lower than the MCL of 50 ppb for Mn in drinking water, blood (4-15 ppb), urine (1-8 ppb), and serum (0.4-0.85 ppb). [32, 33] It is also worth noting that the films investigated here did not undergo a deposition time optimization which can lead to even lower LOD values if necessary.

## 3.3.8 Possible Metals Interference

Since manganese is not the only metal that is present in environmental and biological samples, it is important to consider if other metals may have an affect on the sensors Mn detection response. These metals can include cadmium, chromium, copper, iron, lead, and nickel. Table 3.3 shows each of these metals reaction potentials. By using cathodic stripping voltammetry and the application of a positive deposition potential, the interference from most metals plating onto the working electrode's surface is avoided due to them having a negative reduction potential. In other literature it has been shows that cadmium chromium and zinc do not interfere with the manganese detection when using a carbon film electrode. [38] They also found that at elevated concentrations nickel, copper and lead had an influence on the manganese signal. Since lead does have a positive redox potential to form an oxide, this could also plate onto the electrode's surface during the deposition of manganese. Additionally iron has been shown to influence the ability to detect manganese on both the carbon film electrode and an ITO electrode. [38, 28] This interference is possibly due to the fact that iron chemically strips the manganese oxide back off the electrode before the potential

sweep can be performed. [28] However, a previous study showed that typically  $Fe^{2+}$  concentrations in drinking water do not cause a concern for the ITO electrodes. Additionally anion interferences can be reduced with a negatively charged polymer placed onto the ITO's surface. [28] A literature report also shows that using sodium citrate can help to eliminate this potential interference in waters that have high iron concentrations. [65]

Table 3.3:	Redox	potentials for	or other	metals	that are	potentially	y in envi	ronmental	and	biolog	gical
samples											

Metal	Symbol	Reaction	Reduction Potential (V)
Cadmium	Cd	$Cd^{2+} + 2e^{-} \leftrightarrow Cd_{(s)}$	-0.402
Chromium	Cr	$Cr^{2+} + 2e^{-} \leftrightarrow Cr_{(s)}$ $Cr^{3+} + 3e^{-} \leftrightarrow Cr_{(s)}$	-0.890 -0.740
Copper	Cu	$Cu^{+} + e^{-} \leftrightarrow Cu_{(s)}$ $Cu^{2+} + 2e^{-} \leftrightarrow Cu_{(s)}$	0.518 0.339
Iron	Fe	$Fe^{2+} + 2e^{-} \leftrightarrow Fe_{(s)}$	-0.440
Lead	Pb	$\begin{array}{c} Pb^{2+} + 2e^- \leftrightarrow Pb_{(s)} \\ PbO_{2(s)} + 4H^+ + 2e^- \leftrightarrow Pb^{2+} + 2H_2O \end{array}$	-0.126 1.458
Manganese	Mn	$MnO_{2(s)} + 4H^{+} + 2e^{-} \leftrightarrow Mn^{2+} + 2H_2O$ $Mn^{2+} + 2e^{-} \leftrightarrow Mn_{(s)}$	1.230 -1.182
Nickel	Ni	$Ni^{2+} + 2e^{-} \leftrightarrow Ni_{(s)}$	-0.236

# 3.3.9 Key Advancements from Study

Key advancements from this study include:

- Development of an economically viable and consistent film material for metal sensing applications that is already mass produced for other applications
- Lower detection limits for manganese that allows for improved accuracy in human serum measurements
- Understanding that heating and annealing of ITO film's create the best film structure to be used as an electrode for electrochemical sensing applications

#### 3.4 Summary

The performance of four different indium tin dioxide films were investigated to determine which film would be the optimum electrode material for sensing manganese (Mn) with cathodic stripping voltammetry. Two samples were heated at 190 °C during deposition and two samples were annealed in air for 1 hour at 400 °C; generating one heated and annealed (HA), one heated and not annealed (HNA), one not heated and annealed (NHA), and one not heated and not annealed (NHNA). All films were thoroughly characterized.

The samples that were heated showed comparable trends using AFM and XRD analysis. Both of these samples (HA and HNA) also showed higher roughness, crystallite sizes, and (400) XRD peaks with lower fwhm values compared to the non-heated films. The annealed samples had higher optical band gap values and carrier concentrations than those not annealed. 4-point-probe measurements displayed NHNA having the highest resistance and resistivity with HA having the lowest. HA, HNA, and NHA all exhibited good electrochemical detection ability for Mn. Only the HA film displayed a calibration curve that was analytically in acceptable range for the linear correlation coefficient of 0.996. It can be concluded that heating during the deposition of ITO and post deposition annealing creates an optimum film for the CSV detection of Mn. The key parameters of the film may be its roughness, crystallite size, resistivity, and  $I_{(222)}/I_{(400)}$  obtained from XRD analysis. This study expands previous understanding of ITO and lays the ground work for further analyte detection on this material using CSV for an economical way to mass produce sensors.

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# **CHAPTER 4**

# ELECTROCHEMICAL OXIDATION FOR THE MINERALIZATION OF PER- AND POLYFLUOROALKYL SUBSTANCES

#### 4.1 Introduction

A portion of this work has been published in Water and Environment Journal<sup>1</sup>. Per- and polyfluoroalkyl substances (PFAS) are man-made chemicals that began production in the early 1950's. Since their discovery, they were used heavily in customer and industrial applications that took advantage of their oil and water repelling properties. [1–9] The main property of this class of chemicals that sets them apart from others are their fully fluorinated carbon chains or "tails". Under the broad term of PFAS, which now encompasses more than 4,000 compounds, there is a main group of perfluoroalkyl acids (PFAA) which encompasses the perfluoroalkylcarboxylic Acids (PFCA) and Perfluoroalkylsulfonates (PFSA) with each group comprising of compounds with four to 18 carbons in their background. The differences between the PFCA and PFSA are the head groups that are attached to the carbon chain tails. The two most popular chains that are being studied in recent literature are perfluoroactanoic acid (PFOA) and perfluoroactane sulfonate (PFOS) since they are widely distributed and have potentially negative health effects. The molecular structures of PFOA and PFOS in shown in Figure 4.1. Due to their fully fluorinated carbon chain, they are stable in the environment and bioaccumulate rapidly. Both compounds have been phased out by industry but wide spread contamination still remains an issue for human exposure.

Few standard water treatment methods have been successful at remediating these compounds. Those that have been can be divided into two classes, that of adsorption and filtration and that of destruction. Methods for adsorption and filtration include ion exchange columns, nanofiltration, ultrafiltration, and reverse osmosis. Ion exchange (IX) columns have the added ability of being regenerated for reuse which saves on cost. Some of the resins researched for PFAS include Purolite A600E, A5202E, A532E, PAD500, PAD428, MN102, Sorbix A3F, PFA300, IRA67, IRA958, and IRA67 [10–15]. However, although they can remove PFAS from a certain source, they do not destroy the compounds. Ultimately, the PFAS is just concentrated into a secondary waste product. With improper disposal of this waste, the contamination cycle can continue. Due to this being the

<sup>&</sup>lt;sup>1</sup> Water and Environment Journal 2020, DOI:10.1111/wej.12616



Figure 4.1: Molecular structure of (top) PFOA and (bottom) PFOS

case will all filtration and adsorption techniques, there is a need for a destructive treatment method to destroy the PFAS once and for all.

Destructive methods include thermal, plasma based water treatment, and electrochemical oxidation. Thermal destruction utilizes temperatures above 1000° C and may not completely combust of all the PFAS chains. [4, 6, 3] In addition, the use of thermal techniques lead to the generation of various undesirable green house gasses. [3] Plasma treatment is new for PFAS, but has obtained promising results for PFCA utilizing a laminar jet bubbling reactor and argon gas. [16, 17] Electrochemical oxidation (EO) does not require the use of additional gasses or chemicals. It operates using applied current to perform direct and indirect oxidation of contaminant species. [18] Electrode materials are limited for water based remediation of PFAS due to the need of high current and voltage. Boron-doped diamond (BDD) has been a widely explored material for these applications. [5, 19–31] It can withstand the high current and potential while promoting hydroxyl radicals which can be of benefit in indirect oxidation of co-contaminants. [18] EO has been applied in literature studies to address PFAS contamination using current densities from 0.04 - 50 mA/cm<sup>2</sup>. [5, 28, 22, 23, 27, 21, 25, 24, 26, 19, 20, 29, 31] Time frames for these treatment experiments have ranged from minutes up to 120 hours.[21, 29, 26]. One of the daunting concerns with EO can be the high cost of the electrode material and high energy consumption, but it is important to remember that EO is one of the only remediation techniques that has proven to provide complete mineralization of PFAS. [27] All possibilities to reduce operating costs should be considered. The following sections discuss using EO independently and in conjunction with a regenerable IX column. [3, 4, 6, 1] There is a focus on combining current densities to evaluate if the overall energy associated with the process can be lowered while still obtaining the desired level of compound destruction.

# 4.2 Electrode Stack Characterization

Before performing electrochemical oxidation experiments for the destruction of PFAS, the electrode stack being used needed to be characterized. This stack was comprised of two double side coated BDD on niobium (Nb) anode plates and three double side coated BDD on Nb cathode plates. The two anodes were sandwiched in between the cathodes and an exposed anodic surface area of 105 cm<sup>2</sup> was used with 3 mm distance in between each plate. Characterization was done using scanning electron microscopy (SEM), Raman spectroscopy, and electrochemical methods to determine the capacitance and rate constants for two redox couples. The SEM image in Figure 4.2 shows a high surface area film with no cracks on the surface.

Raman spectroscopy was used to determine the boron content of the film. The spectrum is shown in Figure 4.3 and the total boron content was  $4.88 \times 10^{20} \text{ cm}^{-3}$  +/- 5.7 x  $10^{19} \text{ cm}^{-3}$ . This classifies this film as highly doped.

In order to find the electrochemical capacitance of the film, cyclic voltammetry (CV) was used. This experiment was performed by exposing a small area of the electrode to a 1 M potassium chloride (KCl) solution and measuring the current as the potential was scanned using a laboratory potentiostat. After each scan, the scan rate was increased and the measurement was performed again. The current was then recorded at 0 V and plotted against the scan rate at which is was



Figure 4.2: Scanning electron microscopy (SEM) image of the BDD surface



Figure 4.3: Raman spectroscopy of BDD electrodes

obtained, Figure 4.4. The scan rates of 0.1 - 0.5 V/s were used and three sets of each were performed. The capacitance of the film was 2.66  $\times 10^{-04}$  F/cm<sup>2</sup> +/- 4.88  $\times 10^{-07}$  F/cm<sup>2</sup>, which was obtained from the slope of the graph relating the current and scan rate.

The electrochemical characterization was completed by determining the rate constants of the BDD for an inner and outer sphere electron redox couple. The inner sphere redox couple that was chosen was potassium ferrocyanide (FeCN) and the outer sphere redox couple that was chosen was ruthenium hexaammine (RuHX). Each redox couple was used in a 1 M KCl solution and the current



Figure 4.4: Current versus scan rate plots to determine the capacitance of BDD

was measured as the potential was scanned for scan rates of 0.05 to 1.0 V/s. The Nicholson and Shain method was used to determine each rate constant. All together, each scan rate was performed a total of three times so an average could be taken. Figure 4.5 shows a CV for both redox couples. The rate constant for FeCN was  $3.96 \times 10^{-04}$  +/-  $4.47 \times 10^{-06}$  and the rate constant for RuHx was  $9.00 \times 10^{-04}$  +/-  $3.28 \times 10^{-05}$ .



Figure 4.5: Cyclic voltammogram of both ferrocyanide and ruthenium hexamine on the BDD surface

#### 4.3 Constant Current

#### 4.3.1 Methods

All electrochemical experiments were performed with a 180W multi range 60V/8A DC power supply from BK Precision Instruments. All solution matrices were made with analytical grade sodium sulfate ( $Na_2SO_4$ ) from J.T. Baker Inc. at a concentration of 50 mM. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) were purchased from Sigma Aldrich. Nalgene bottles were used for all solutions and testing volumes were 750 ml. Solutions were constantly stirred during testing using a Hanna Instruments magnetic stirrer HI 190M on max. A pH probe, temperature probe, and fluoride ion selective electrode (ISE) were purchased from Thermofisher Scientific and a fluoride standard that was used to calibrate the ISE was purchased from Sigma Aldrich.

2ml of sample was removed and stored in the refrigerator in polyethylene vials at 4° C until analysis was performed with the fluoride ISE. A total ionic strength buffer (TISAB) was made using glacial acetic acid (Fisher Chemical), reagent grade sodium chloride (NaCl) (Sigma Aldrich), sodium hydroxide (NaOH) (Spectrum Quality Products Inc.) and DI water and used to dilute each sample 1:1. The Michigan State University College of Natural Science Research Technology Support Facility performed the liquid chromatography mass spectroscopy (LC/MS) measurements for the samples spiked with only PFOA.

## 4.3.2 Results and Discussion

# 4.3.2.1 PFOS

PFOS studies were performed with the previously characterized electrode stack. Constant current densities of 5, 10, 25, and 50 mA/cm<sup>2</sup> were used. Each experiment was performed in triplicate. The current densities of 5 and 10 mA/cm<sup>2</sup> were performed for 1.5 hours but the current densities of 25 and 50 mA/cm<sup>2</sup> were only performed for 1 hour. The starting concentration of



PFOS was 10 parts per million (ppm) as calculated for the amount of powder that was added. With increasing current density the initial temperature, pH, and potential of each system also increased.

Figure 4.6: PFOS Temperature, pH, and voltage trends for the constant current density studies

These figures are shown in Figure 4.6. pH for all tests began at 6 and increased over time. The pH for 10, 25, and 50 mA/cm<sup>2</sup> increased to 10.5 whereas the pH of the 5 mA/cm<sup>2</sup> solution has an upwards trend tending towards 10.5 but does not reach there in 1.5 hour. BDD in a known efficient producer of hydroxyl radicals and previous studies using BDD have shown that the pH could increase by 5 units depending on the applied current density. [32, 33] The temperature started at room temperature for all tests and increased with time and potential for the low current densities of 5 and 10 mA/cm<sup>2</sup> remained constant, whereas, the potential for both 25 and 50 mA/cm<sup>2</sup> both slightly decreased over time. PFOS degradation was monitored with the F- ISE and the concentration of free F- was used to calculate the percentage of defluorination. Figure 4.7 shows the percent of

defluorination for the current densities studied.



Figure 4.7: PFOS reduction overtime with each current density tested

The three tests at each current density are taken into account and an average is graphed with its corresponding error. It is clear that the PFOS degradation is independent of current density for these studies. Each current density also had a standard deviation of 4 % at each time point. The 1st order rate constants for each current density were also determined and graphed as an average value. The PFOS concentrations were calculated based on the percentage of fluoride released under the assumption that no shorter chains were being formed due to lack of analysis equipment. The rate constants for each were  $0.39 + -0.02 h^{-1}$ ,  $0.39 + -0.07 h^{-1}$ ,  $0.45 + -0.10 h^{-1}$ , and  $0.45 + -0.10 h^{-1}$ , for 5 at 1.5 hours, 10 at 1.5 hours, 25 at 1 hour, and 50 mA/cm<sup>2</sup> at 1 hour respectively. Each rate constant had a linear correlation coefficient ( $R^2$ ) above 0.85. The average linear correlations were 0.9821, 0.958, 0.951, and 0.8628 for 5, 10, 25, and 50 mA/cm<sup>2</sup>, respectively. 5 and 10 mA/cm<sup>2</sup> share the same rate constant as do 25 and 50 mA/cm<sup>2</sup>.

To ensure the validity of the PFOS results, a quality assurance check was performed with the ISE. To do this, each of the 1 hour time points from the three  $25 \text{ mA/cm}^2$  runs were retested with the ISE at the end of the complete study. The repeatability in the results obtained was 105 +/- 5.6 %, validating that the ISE measurements were accurate. To advance our understanding of how



Figure 4.8: PFOS 1st order rate constants

PFAS behave in electrochemical experiments, perfluorooctanoic acid (PFOA) was studied with the addition of LC/MS analysis.

#### 4.3.2.2 PFOA

The degradation of PFOA was studied at different applied current densities using the previously characterized electrode stack. Current densities included 1, 5, 10, 25, and 50 mA/cm<sup>2</sup>. All tests were performed for 1 hour. The stack was lowered into 750 ml of 50 mM sodium sulfate that the PFOA was spiked into using a concentrate made from the dissolved powder. Cell voltages spanned rom +4 V to +9 V at the lowest and highest current density, respectively. All solutions were started at room temperature and experiences an increase to 40 °C at 50 mA/cm<sup>2</sup>. All testing solutions began at a pH of 5, one pH unit lower than the PFOS solutions, and increased over time to 10.5 except for the current density of 1 mA/cm<sup>2</sup>, where the pH remained constant. The current densities chosen here suggest that the reactions affecting the pH may be different between 1 mA/cm<sup>2</sup> and the rest of the current densities. Graphs showing the change in temperature, pH, and potential for each current density are shown in Figure 4.9.

The temperature increased over time for all current densities studied with the highest having the largest increase. The potentials were stable across the full testing time for all current densities except for 50 mA/cm<sup>2</sup> where a slight increase was observed. The starting concentration of PFOA was 6.5 parts per million (ppm) as determined by liquid chromatography mass spectroscopy (LC/MS) measurements. A graph representing the PFOA degradation over time, in terms of percent defluorination obtained by using the F<sup>-</sup> ISE, is shown in Figure 4.10. The release of fluoride increases over time with increasing current density. The five tests also show good repeatability between the three sets that were performed.

Each current density study was also fit to first order kinetics using the PFOA degradation over time from the LC/MS analysis. This way the direct rate constant relating to PFOA can be determined instead of inferring from the ISE analysis as was done for PFOS. These plots are shown in Figure 4.11. All current densities has a linear correlation coefficient of greater than 0.90 with both 5 and 10 mA/cm<sup>2</sup> being above 0.99. The rate is increasing as current density is increased. the values for  $k_1$  are as follows: 0.34, 1.35, 2.04, 3.77, and 6.27 h<sup>-1</sup>, for 1, 5, 10, 25, and 50 mA/cm<sup>2</sup>, respectively.


Figure 4.9: PFOA Temperature, pH, and voltage trends for the constant current density studies



Figure 4.10: PFOA degradation over time at each current density value

Another interesting takeaway from this constant current density study comes from taking a closer look at Figure 4.10. This being that the slopes of the PFOA defluorination lines only seem



Figure 4.11: 1st order rate constants for PFOA based on LC/MS measurements for each current density study.

to differ in the first 0.25 h of each test. For the remaining time of each, the slopes are relatively the same. For instance, for the first 0.25 hours of the test,  $1 \text{ mA/cm}^2$  had a slope of 0.28 %/h that increased to 2.0 %/h at 50 mA/cm<sup>2</sup>. However, for 0.25h untill the end of 1 hour, the slope for 5 through 50 mA/cm<sup>2</sup> were 0.54, 0.58, 0.62, and 0.49 %/h for 5, 10, 25, and 50 mA/cm<sup>2</sup>, respectively. This raises the question as too if the higher current density is truly only beneficial in the first 0.25 h of each study and could then be lowered to save on energy consumption.

Fluoride quality analysis was also performed for PFOA using the 1 hour time sample from each 25 mA/cm<sup>2</sup> test. The obtained concentration of fluoride was 99.7 +/- 1.3 % of what the original tested value was. This verified the F- ISE measurements were accurate over time for this study.

### 4.3.2.3 Comparison of ISE Results to LC/MS Results

At the time of analysis, the Michigan State University mass spectroscopy facility could only analyze for the single compound of PFOA. Due to this limitation, shorter chain compounds could not be directly identified, but by determining if there was a difference in the concentration of PFOA that remained from ISE analysis and what the LC/MS provided, it could be assumed that any difference was from the generation of shorter chain fluorinated carboxylic acids. All five current densities that were used were tested with LC/MS and the PFOA concentrations were graphed against those calculated from the ISE.



Figure 4.12: Comparison of the PFOA concentration obtained by the F- ISE and LC/MS

Figure 4.12 shows the comparison of the concentrations obtained using the two different analysis methods. The concentrations for both methods overlap for the lowest current density of 1 mA/cm<sup>2</sup> at 4.3 +/- 0.2 ppm from the ISE and 4.4 from LC/MS after 1 hour, but as the current density is increased, the two concentrations begin to differ. The differences between the two methods are shown in Table 4.1. Since there is a smaller amount of PFOA detected with LC/MS than there is free fluoride that would pertain to that amount of degradation, the remaining PFOA is assumed to have converted to shorter chains through an unzipping mechanism.

Current Density (mA/cm²)	Remaining PFOA from ISE (ppm)	Remaining PFOA from LC/MS (ppm)
1	4.3 +/- 0.2	4.42
5	2.6 +/- 0.2	1.61
10	2.0 +/- 0.3	0.81
25	1.4 +/- 0.5	0.11
50	0.9 +/- 0.2	0.02

Table 4.1: Comparison of remaining concentration of PFOA obtained from the ISE analysis and LC/MS analysis

## 4.3.3 Fluorination of BDD

It has been shown in literature that perfluoroalkyl compounds can be used to fluorinate a BDD surface. [34, 35] As such, it is important to consider that some of the fluoride released during the decomposition of PFAS could adsorb onto the BDD surface. This was investigated in three ways: (1) determining the contact angles between a unused and used BDD electrode for PFAS remediation (2) measuring a potassium ferrocyanide (FeCN) CV on a used and unused electrode, and (3) investigating the potential window changes between a used and unused electrode.

The contact angle measurements were done using a 0.5  $\mu$ L drop of water on the surface of each anode. The part of each electrode that was submerged into solution was labeled as "used" and the part that was not submerged and remained above the solution volume was labeled as "unused". For the anodes, the used electrodes displayed an average contact angle of 84° +/- 5.6° and the unused portion displayed 75° +/- 4.9°.

The FeCN study was used due to its behavior as an inner sphere redox couple. If the fluoride was deposited onto the BDD surface, the surface sensitive reaction of ferrocyanide could be effected. Cyclic voltammetry was performed in 1 mM FeCN in 1M KCl at 0.1 V/s on the used and unused portion of the BDD anode used in the previous PFOA degradation studies. Figure 4.13 shows the voltammogram for both electrode portions. It is immediately apparent that the response from the two differs. The unused portion has a characteristic shape showing the oxidation and reduction of ferrocyanide whereas the used portion has no visible peaks. This is indicative that there was a

change to the surface of the BDD anode during the remediation experiments with PFOS and PFOA. To investigate this further, the potential windows of the used and unused portions were compared.



Figure 4.13: 1mM ferrocyanide in 1 M KCl measured on both the used and unused portion of the anode that was used for the constant current density PFOA degradation studies

The potential window of each anode surface was investigated in 1 M sulfuric acid at a scan rate of 0.1 V/s to determine if there was a shift in the hydrogen or oxygen evolution potentials. Four scans were performed with the last two being graphed for each in Figure 4.14. It can be seen that the used anode has a slightly larger oxygen evolution potential and a further negative hydrogen evolution potential. According to literature, fluorinated BDD electrodes have a larger window compared to diamond electrodes and can show a potential window of 5 V [36–38]. There is a larger difference in the hydrogen evolution between a fluorinated BDD and non fluorinated BDD compared to the oxygen evolution due to the fact that the fluorinated surface is more hydrophobic, seen with contact angles, which decreases the adsorption strength of water and atomic hydrogen shifting the reaction more negative [37]. Between the contact angle measurements, investigation into the redox couple of ferrocyanide, and the comparison of the potential window for the used and unused BDD, it is confirmed that there was fluorination of the diamond surface during the electrochemical oxidation experiments.

In an attempt to bring the BDD surface back to its original non-fluorinated state, it underwent



Figure 4.14: CV in 1 M sulfuric acid for both the used and unused portion of the anode

a hydrogen termination process and re-evaluation of the FeCN CV and potential window study. Hydrogen termination of the used surface was performed by placing it into a hydrogen atmosphere in a hot filament chemical vapor deposition reactor for one minute. The resulting ferrocyanide voltammogram and potential window scan are shown in Figures 4.15 in (A) and (B), respectively.



Figure 4.15: (A) CV comparison in1 mM ferrocyanide in 1 M KCl for the used anode, unused anode, and used anode post hydrogen termination and (B) CV in 1 M sulfuric acid for the used, unused, and used electrode post hydrogen termination

It can be seen that the FeCN peak showed a significant current response and clear oxidation and reduction peaks for the hydrogen terminated used sample. The current response after hydrogen termination was greater than the response from the unused sample potentially due to now being cleaner and fully hydrogen terminated whereas the unused portion may have become partially oxygen terminated over time. In addition, the potential window shifted closer to the unused electrode by having the hydrogen evolution reaction shift to more positive values and the oxygen evolution reaction shift to more negative values. Both of these tests verified that the fluorination of the BDD surface could be removed by placing the electrode in a hydrogen plasma after being used for the degradation experiments.

### 4.4 Combined Current Density

To further evaluate on the ability of electrochemical oxidation to degrade PFOA over time and to begin to investigate how to save on energy costs, a combined current density technique was investigated. This technique employed the use of a high current density for the first 15 minutes of each test before lowering it down for the remaining 75 minutes. This decision came from the fact that the most significant benefit for the high current density application seen with the constant current densities was in the first 15 min of each test. The experimental conditions used in the previous constant current density section were employed again in this study. The high current density chosen was 50 mA/cm<sup>2</sup> as it showed the greatest initial change in PFOA concentration from Section 4.3.2.2. Three lower current densities of 1, 5, and 10 mA/cm<sup>2</sup> were investigated for the remaining time frame of each test. Throughout each test, samples were removed at 0.25, 0.5, 0.75, and 1 hours and stored in the refrigerator until analysis was performed.

Graphs showing the change in temperature, pH, and potential for each current density are shown in Figure 4.16. The temperature from all three combined tests increases in the first hour before steadily decreasing with the reduction in applied current. The pH for all three tests also mirrored one another with an increase before stabilizing out at 10.5. The potential slightly decreased during the higher current density application and then remained stable during the lower current density application for all three tests. Each PFOA sample was evaluated with the fluoride ISE as used previously. The starting concentration of PFOA was 6.5 ppm in 50 mM sodium sulfate determined from LC/MS experiments. There was 750 ml of solution placed in a Nalgene bottle and stirred continuously. The PFOA reduction in terms of defluorination percentage over time for



Figure 4.16: Temperature, pH, and voltage trends for the combined current density studies

each combined current density compared to the constant current density of  $50 \text{ mA/cm}^2$  provided as Figure 4.17.



Figure 4.17: PFOA reduction overtime with each combined current densities tested together as well at the standard 50 mA/cm<sup>2</sup> for comparison

It can be seen that the 50 mA/cm<sup>2</sup> combined with 1 mA/cm<sup>2</sup> (50&1), has the lowest evolution of fluoride between each run, but a low standard deviation (n=3) between each run. The 50&10 run also has a low standard deviation between sample sets. For the run using 50&5, the points line up close to those of 50&10, and even overtake them at 1 h, but there is a much larger standard deviation between the tests. As such, using 50&5 could outperform 50&10 as well as be very similar to the degradation that is obtained with the constant current density run of 50 mA/cm<sup>2</sup>. In order to evaluate the rate constants of each combined current density test, two sequential rate constants were used to analyze the fluoride ISE data.  $k_1$  for the rate constant from time 0 to 0.25 hours, and  $k_2$  from 0.25 hours until the end of the study, 1.5 hours.



Figure 4.18: First order rate constant fits for the first 0.25 h, k1, and the remainder of each test, k2.

Figure 4.18 shows the fitted rate constants for the three combined current density studies. Table 4.2 shows the numerical values for each of the rate constants and their obtained linear fits. It is noted that  $k_1$  is only based off of time 0 and 15 min. With only two points the linear coefficient will always be equal to 1.  $k_2$  is based off of 5 points allowing for a better understanding of if a linear relationship exists.

 $k_1$  is the same for both 50&1 and 50&5 with 50&10 having a slightly lower value. Overall, since this time point it taken based solely on the applied high current density of 50 mA/cm<sup>2</sup>, it shows good repeatability. 50&5 had the largest standard deviation in the  $k_1$  value. For  $k_2$  all the

Combined CD	50&1	50&5	50&10
k <sub>1</sub> (h <sup>-1</sup> )	2.51+/-0.2	2.58 +/- 0.4	2.08 +/- 0.3
R <sup>2</sup>	1	1	1
k₂ (h⁻¹)	0.51 +/- 0.1	1.15 +/- 0.3	1.11 +/- 0.1
R <sup>2</sup>	0.9908	0.9953	0.9864

Table 4.2: Rate constants and their linear fits for the three tested combined current densities

linear coefficients are all above 0.98 with 50&1 and 50&5 being greater than 0.99. 50&1 and 50&10 have a lower standard deviation in their values compared to 50&5. Due to this the  $k_2$  value for 50&5 and 50&10 are similar. The  $k_2$  value for 50&1 is roughly half in comparison.

## 4.4.1 Comparison of ISE and LC/MS

As performed for the constant current density study, a LC/MS and F- ISE comparison was done for the best combined current density study of 50&5. The difference in PFOA concentrations over time for each analysis technique are shown in Figure 4.19. The same trend seen before is shown with this data. The concentration of PFOA obtained from the LC/MS data is lower than that determined from the ISE analysis. Again, this suggests that the remaining fluoride not detected from the ISE is bound in other short chains that were formed as part of the degradation process, or have fluorinated the anode's surface. 1.71 +/- 0.1 ppm of PFOA was estimated to be remaining by the ISE analysis but LC/MS provided a final concentration of 0.40 ppm showing the increased ability in electrochemical oxidation to break apart PFOA. The rate constant was also determined for 50&5 based on LC/MS measurements. For time 0 to 0.25h the rate constant was 4.20 h<sup>-1</sup> and from 0.25 to 1 h the rate constant was 2.85 h<sup>-1</sup>. These rate constants are much higher than those corresponding to the ISE analysis. This again suggests that PFOA may be degrading quickly into shorter chain PFAS.



Figure 4.19: Comparison of the PFOA concentration obtained by the F- ISE and LC/MS

### 4.4.2 Remediation of Simulated Ion Exchange Regenerate Solutions

To advance the application of the combined current density method, a treatment train approach that can enhance an existing technology would be beneficial. One of the most promising remediation techniques is adsorption using ion exchange (IX). This has been shown successful in literature for removing a wide array of PFAS. Some of these columns that remove PFAS in particular have the ability to be regenerated and re-used. [10, 5, 13–15, 11, 12] This is a huge cost benefit, but has the downside of generating a concentrated waste product. The regenerate solution out of an IX process can comprise of PFAS in the parts per million (ppm) range in a complex matrix of a brine with an alcohol. [12] Due to difficulties in disposal of this waste, and the potential to continue the contamination cycle with improper disposal, a destruction method is needed to remove the PFAS once and for all. However, due to the nature of the regenerate solution, i.e. high PFAS concentration and high salt, it is a perfect electrolyte solution to apply electrochemical oxidation (EO). In order to determine if EO is an appropriate treatment technology for these solutions, those currently existing in literature to regenerate PFAS specific columns need to be tested.

The four main ion exchange (IX) regenerate solutions that were simulated in the laboratory include: 6% ammonium hydroxide (NH<sub>4</sub>OH) with 2% methanol (MeOH), 6% sodium chloride (NaCl) with 2% MeOH, 6% sodium hydroxide (NaOH) with 2% MeOH, and 0.5% NH<sub>4</sub>OH with

0.5% ammonium chloride (NH<sub>4</sub>Cl). The solutions with MeOH were done at 2% MeOH due to the ability to distill off the majority in a distillation process that can then be reused for future regeneration.[12] NH<sub>4</sub>OH with MeOH was chosen due to its ability to remove PFOA from the IX columns of PUROSORB PAD 500 and MACRONET MN102. [11] NaCl with MeOH was chosen for its ability to remove PFOS from IX columns of PFA300, IRA958, and BAC. [14, 13, 15] NaOH with methanol was chosen for its ability to regenerate PFA300 and IRA67 for PFOS removal. [14, 13] The mixture of NH<sub>4</sub>OH and NH<sub>4</sub>Cl was chosen for its ability to regenerate Purolite A600E and A520E with PFOA, PFBA, PFOS, and PFBS. [10, 11] Each solution was spiked with greater than 10 ppm of PFOA and PFOS due to both being in the tens of ppm range in known ion exchange solutions. [39] The high current density application time was increased from 15 minutes, from the earlier studies, to 1 hour due to the high chemical oxygen demand (COD) present in most of the simulated regenerate solutions. At 2% MeOH, the COD values for these solutions were around 30,000 ppm. The total testing time was also increased to 12 hours to account for the additional competing COD content and higher initial PFAS concentrations.

# 4.4.2.1 Comparison of 50 mA/cm<sup>2</sup> to 50&5 mA/cm<sup>2</sup>

The first IX regenerate solution comparison performed utilized the solution of 6% NH<sub>4</sub>OH with 2% MeOH was to compare the use of 50 mA/cm<sup>2</sup> for an entire test to using a combination of 50&5 mA/cm<sup>2</sup>. This was done by using the higher current density for an extended time of 1 hour before lowering the current density for the remainder of the test. Graphs showing the change in temperature, pH, and potential for each current density are shown in Figure 4.20. The pH for the 50&5 solution decreases much more rapidly in the first 1.5 hours although both tests employed 50 mA/cm<sup>2</sup> for the 1st hour. 50&5 then showed an increase in pH where it ended at about 10 compared to the constant current density that had a continued gradual decrease and ended closer to 8. The temperature for moth tests mirrored on another for the higher current density application. after 50&5 was lowered to 5 mA/cm<sup>2</sup>, the temperature fell and stabled out. The 50 mA/cm<sup>2</sup> run only displayed a slight decrease in temperature over time. The potential for other tests started

relatively high and fell rapidly in the first our before relatively stabling out. The 50&5 test had a lower potential for the lower applied current.



Figure 4.20: Temperature, pH, and voltage trends for the comparison of 50 and 50&5 in IX simulated solution



Figure 4.21: Comparison of the PFOA (left) and PFOS (right) degradation using 50 mA/cm<sup>2</sup> and 50&5 mA/cm<sup>2</sup>

The change of PFOA and PFOS over time are shown in Figure 4.21 left and right, respectively.

When using the constant current density of 50 mA/cm<sup>2</sup> for the entire test, the COD was reduced by 72% and the ammonia was reduced by 88% compared to 43% and 47% for the combined current density of 50&5, respectively. The PFOA concentration in the constant current density test decreased by greater that 99% in 12 hours. Based on the dilution factor used when sending samples for analysis, it is known that there is <66 parts per billion (ppb) remaining, but the exact number is unknown. The PFOS degradation was also greater than 99% for this constant current density study after 12 h. For the 50&5 study, the PFOA concentration degraded 90% and the PFOS degraded 59% in the same total time frame. It can be seen from the PFOS degradation graph (Figure 4.21) that PFOS reached a higher degradation percent in 8 hours then at 12 hours using the combined current density. This may be due to a number of factors including, generation of PFOS from precursors or an outlier in the measurement technique. Generation from precursors is unlikely since the solutions were spiked with purchased powders. However, these powders are not 100% pure. The human error in removing a sample and diluting x100 may have caused for the discrepancy. Overall, 50&5 obtained good degradation results for PFOA and PFOS in the same time frame as using  $50 \text{ mA/cm}^2$  for the entire time. Since this is only one potential IX regenerate solution, it is of importance to test the other solutions researched in industry with a further analysis into the degradation of PFAS.

### 4.4.2.2 Comparison of four different regenerate solutions

In order to compare the ability of using 50&5 further, each of the simulated solutions were tested using 50&5 for the degradation of primarily PFOA and PFOS. Graphs showing the change in temperature, pH, and potential for each current density are shown in Figure 4.22. The highest pH belonged to the NaOH and MeOH solution at 14 compared to all of the others that fluctuated at levels below 10. The temperature increased for all solutions during the high current density application and lowered once the current density was lowered. The highest temperature of 60 °C was reached with the NH<sub>4</sub>OH and MeOH solution. This was also the solution that had the highest starting potential out of all those tested. The other three solutions had similar potentials at the high

and low current density applications.



Figure 4.22: Temperature, pH, and voltage trends for the comparison of the four IX simulated solutions



Figure 4.23: Comparison of the PFOA (left) and PFOS (right) degradation using the four tested simulated IX solutions

The change in PFOA and PFOS for each solution over the 12 hours is shown in Figure 4.23 with PFOA degradation on the left, and PFOS degradation on the right. PFOA degradation was obtained in three out of the four tested solutions. Its degradation was 90% in the  $NH_4OH$  and

MeOH solution, 52% in the NaCl and MeOH solution, and >99% in the NH<sub>4</sub>OH with NH<sub>4</sub>Cl solution. It was not degraded in the NaOH based solution. This lack of degradation in NaOH may be due to the significantly higher pH that was characteristic of this solution compared to the others (Figure 4.22). It has been shown in literature that the degradation of PFOA can be inhibited in solutions with alkaline pH. [40, 29, 31] Each PFOA experiment was fit to sequential 1st order reaction kinetics, Figure 4.24.



Figure 4.24: 1st order rate constant kinetics for PFOA in each simulated solution

For the first hour, the PFOA rate constants were 1.93, 0.06, 0.75, and 1.5 h<sup>-1</sup> for NH<sub>4</sub>OH and MeOH, NaOH and MeOH, NaCl and MeOH, and NH<sub>4</sub>OH with NH<sub>4</sub>Cl, respectively. After one hour, the rate constant for every solution expect for NH<sub>4</sub>OH with NH<sub>4</sub>Cl was 0 h<sup>-1</sup>. That of NH<sub>4</sub>OH with NH<sub>4</sub>Cl was 0.37 h<sup>-1</sup>. These results show that there is no additional degradation in the simulated solutions for the majority of the tests after the current density is lowered. It is interesting to note that out of the two solutions with the highest degradation for PFOA, the NH<sub>4</sub>OH solution with MeOH obtains all of that degradation at the higher current density. Whereas, the combination of NH<sub>4</sub>OH and NH<sub>4</sub>Cl does have slow continued degradation. In the first hour, the NH<sub>4</sub>OH with MeOH solution also has the lowest pH value during this time and the highest achieved temperature which both may contribute to the increased degradation of PFOA. The other ammonia based solution may have ultimately outperformed the solutions with MeOH due to the fact that

this solution does not have the competing COD that the other solutions contain. Table 4.3 lists the PFOA concentrations, rate constants, and linear fits obtained from the studied solutions at 1h and 12 h. This table shows that there is no added benefit, in terms of PFOA degradation, to continue to run the test past 1 h for all solutions except for that based on  $NH_4OH$  and  $NH_4Cl$ . It is also noticeable that in 1h the  $NH_4OH$  solution with MeOH obtained the most PFOA degradation with the fastest rate constant despite having the added competition of COD although this rate constant does not have a nice linear fit.

Solution	PFOA Degradation at 1 h (%)	k1 (h-1)	1 h R <sup>2</sup>	PFOA Degradation at 12 h (%)	k <sub>2</sub> (h <sup>-1</sup> )	1-12 h R <sup>2</sup>
NH4OH w MeOH	85	1.93	0.662	89	0.02	0.3513
NaOH w MeOH	0	0	-	0	0	-
NaCl w MeOH	53	0.75	0.9919	52	0	-
NH4OH w NH4Cl	78	1.5	0.8993	99	0.37	0.9947

Table 4.3: Comparison of 1 h PFOA degradation and 12 h PFOA degradation

For PFOS, only three out of the four solutions obtained degradation. However, the solution that PFOS did not degrade in is different from the one that PFOA did not degrade in. PFOS did not degrade in the NaCl with MeOH solution. In addition it obtained a much lower degradation in the NaOH with MeOH compared to the two ammonia based solutions. The degradation was 40% in the NaOH solution, 59% in the NH<sub>4</sub>OH with MeOH solution, and 91% in the NH<sub>4</sub>OH with NH<sub>4</sub>Cl solution at the end of 12 hours. Sequential first order rate constants were also determined for PFOS for the first hour followed by the remainder of the study. The two solutions with non zero rate constants for the 1st hour of the study were the two NH<sub>4</sub>OH based solutions with 0.29 h<sup>-1</sup> and 2.73 h<sup>-1</sup> for that with MeOH and that with NH<sub>4</sub>Cl, respectively. They had a linear correlation of 0.089 and 0.59 for NH<sub>4</sub>OH with MeOH and NH<sub>4</sub>Cl, respectively. For the remaining portion of the test, 1-12h, the rate constants were 0.05 hr<sup>-1</sup> for both NH<sub>4</sub>OH and NaOH with MeOH and 0.02 for NH<sub>4</sub>OH with NH<sub>4</sub>Cl. The fittings for each rate constant can be shown in Figure 4.25. It is also

interesting to note that the  $NH_4OH$  solution with  $NH_4Cl$  now had the highest degradation in the first hour for PFOS compared to the  $NH_4OH$  solution with MeOH; opposite of the PFOA trend. In addition the mixed ammonia solution did not have continued degradation past this point whereas the ammonia based MeOH solution did.



Figure 4.25: Sequential 1st order rate constant kinetics for PFOS in each simulated solution

A literature study on a different electrode materials also found that PFOS did not degrade in their electrolyte of sodium perchlorate (NaClO<sub>4</sub>) when starting with 20 ppm and applying roughly 7 mA/cm<sup>2</sup>. [41] It has been proposed in the literature that PFOS prefers the gas-liquid interface which may inhibit its degradation. [42] To investigate this electrochemically, the oxygen evolution reaction for each solution on the BDD surface was studied. The oxygen evolution reaction was investigated in each IX solution using a clamp cell placed on top of the used BDD anode. A counter electrode of graphite and a reference electrode of Ag/AgCl was used. The exposed surface area was  $0.13 \text{ cm}^2$ . A graph of the current density compared to potential is shown in Figure 4.26

The two solutions with the lowest PFOS degradation have the earliest onset of the OER, the NaCl and NaOH based electrolytes. The two solutions with the highest PFOS degradation had the furthest potential where the OER began. This suggests that the oxygen evolution could play a role in inhibiting the PFOS from reaching the anode surface to degrade. A report comparing two different electrode materials in the same solution looked into the OER compared to the degradation % that



Figure 4.26: Oxygen evolution reaction performed for all four solutions

was achieved. The authors found that the electrode with the further onset of the OER had a greater PFOS degradation. [43] Table 4.4 provides a summary of the PFOS concentrations, rate constants, and linear fits at 1h and 12h. In these complex solutions, the best electrolyte for treating both PFOA and PFOS are ammonia based solutions. It has also been discovered that there is minimal benefit from running these tests passed the 1 h time point at the higher current density except to gain a continued slow degradation of either PFOA or PFOS depending on the ammonia based solution used.

Solution	PFOS Degradation at 1 h (%)	k1 (h-1)	1 h R <sup>2</sup>	PFOS Degradation at 12 h (%)	k <sub>2</sub> (h <sup>-1</sup> )	1-12 h R <sup>2</sup>
NH₄OH w MeOH	25	0.29	0.0891	58	0.05	0.0783
NaOH w MeOH	6	0.06	0.0039	40	0.05	0.8061
NaCl w MeOH	0	0.06	0.0215	0	0	0.0174
NH4OH w NH4Cl	94	2.73	0.5933	91	0.02	0.6272

Table 4.4: Comparison of 1 h PFOA degradation and 12 h PFOA degradation

### 4.4.2.3 Byproduct Formation Investigation

Since the majority of the IX solutions are comprised of a salt or a base and methanol, it is important to look at the oxidation by-products from these constituents. For example, methanol can be oxidized to for formaldehyde and chloride can be oxidized to perchlorate, both of which are undesirable products. Formaldehyde is classified as a hazardous substance. The calorimetric formaldehyde detection method used was performed by mixing formaldehyde with the Nash reagent. [44] Formaldehyde reacts with the Nash reagent to form diacetyldihydrolutidine which is a yellow compound whose absorbance can be detected at 410 nm using a UV/vis spectrophotometer. The Nash reagent is a mixture of ammonium acetate, acetic acid, acetylacetone and DI water. Once the solutions are mixed they are heated and kept in the dark too cool before analysis with the UV/vis. Using this method solutions containing less than 8  $\mu$ g of formaldehyde per ml can be analyzed. [44] Those of higher concentrations can be diluted prior to analysis. A standard calibration curve can be made for known concentrations of formaldehyde and then used to determine the value of an unknown sample.

Methanol can be oxidized by hydroxyl radicals in the Equations 4.1-4.4 where formaldehyde is generated in Equation 4.3.

$$CH_3OH + OH \rightarrow CH_2OH + H_2O \tag{4.1}$$

$$CH_3OH + OH \rightarrow CH_3O + H_2O \tag{4.2}$$

$$CH_2OH + OH \rightarrow HCHO + H_2O$$
 (4.3)

$$HCHO + CH_3O' \to HCOOCH_3 + H^+ + e^-$$
(4.4)

The constant current density study in  $NH_4OH$  with MeOH and the three combined current density studies in solutions containing MeOH were all investigated for their formaldehyde content at the end of 12 hours. A calibration curve was generated for formaldehyde concentrations of 1 to 8 ppm, shown in Figure 4.27.



Figure 4.27: Calibration curve for formaldehyde detection

The formaldehyde concentrations were 0 ppm, 134 ppm, 104 ppm, 57 ppm, and 0 ppm for  $NH_4OH$  with MeOH at 50 mA/cm<sup>2</sup>,  $NH_4OH$  with MeOH combined current density, NaCl with MeOH, NaOH with MeOH, and  $NH_4OH$  with  $NH_4Cl$ , respectively.

The oxidation of chloride to perchlorate is another oxidation byproduct reaction that is undesirable. Perchlorate generation was analyzed using ion chromatography measurements for the two solutions that contained chloride species, NaCl with MeOH and NH<sub>4</sub>OH with NH<sub>4</sub>Cl. Each solution was diluted by 200x and 500x and an average perchlorate concentration was taken as an estimated value for each 12 hour sample. Both solutions had generated 600-700 ppm of perchlorate in 12 hours. This concentration is substantial and well above the water quality standard for perchlorate. However, there are existing remediation methods that could follow the electrochemical treatment to remove this undesirable product. [45] If the tests in each solution were only ran for 1 h based on achieving the most degradation for both PFOA and PFOS in that time, the byproduct formation may also be significantly reduced and will need to be further evaluated.

### 4.4.3 Energy Usage and Cost Comparison

The overall energy for each PFOA constant current density study and combined current density study of 50&5 was determined using Equation (4.5).

$$Q = \frac{A*J}{v} \int E dt \tag{4.5}$$

Where Q is the total energy in kW\*h/m<sup>3</sup>, J is the applied current density in A/cm<sup>2</sup>, A is the active anodic surface area of the anode in cm<sup>2</sup>, v is the volume of the solution in m<sup>3</sup>, and E is the potential of the system in V. The energy usage for 50&5 was calculated as the sum of two integrals. One pertaining to the first time frame with the higher current density and one pertaining to the time with the applied lower current density. The energy value for each simulated sodium sulfate solution study to reach 75% defluorination are provided in Table 4.5. In terms of comparing the constant current densities to the combined current density, we see that 50&5 has a lower energy consumption for 75% defluorination and at 1 h compared to 50 mA/cm<sup>2</sup>. In addition to consuming similar energy than the process at 25 mA/cm<sup>2</sup>, 50&5 also only required an additional 0.1 h time. The time to reach 75% defluorination was determined by extrapolating the percentage of PFOA defluorination over time graph for 1, 5, and 10 mA/cm<sup>2</sup> on a log scale as they did not reach it in under 1 hour. These graphs are included as Figure 4.28. It is also noted that these measurements should be taken as a rough estimate.

Current Density (mA/cm²)	Defluorination % at 1 hour	Time to reach 75% defluorination (h)	Energy at 75% conversion (kWh/m <sup>3</sup> )	Energy at 1h (J/defluorination %)
1	35	1.8	2.5	92
5	61	1.2	6.5	244
10	70	1.1	10.8	422
25	80	0.8	15.6	473
50	88	0.5	19.6	878
50&5	77	0.9	17.3	622

Table 4.5: Energy requirements of each PFOA study to reach 75% defluorination or at 1 hour

For the 12 hour simulated IX regenerate solutions, the energy was only determined for the two ammonia based solutions as they degraded both PFOA and PFOS successfully. Since one solution obtained the most degradation of PFOA in the first hour and no additional degradation post 1h and the other obtained the most degradation of PFOS in the first hour and no additional decomposition



Figure 4.28: Extrapolation plots used to determine the time to 75% defluorination for (A) 1 mA/cm<sup>2</sup>, (B) 5 mA/cm<sup>2</sup>, and (C) 10 mA/cm<sup>2</sup>

after, the 1 h marked was used as the energy comparison time. Since this is the length of the high current density application, both solutions had the same current applied for the duration of this time. However, the two solutions had different voltage values. In fact the voltage integral over time for the NH<sub>4</sub>OH and MeOH was roughly double that of the NH<sub>4</sub>OH and NH<sub>4</sub>Cl solution leading to

an energy consumption of 106 kW\*h/m<sup>3</sup> compared to 53 kW\*h/m<sup>3</sup>.

To further compare the four IX solutions, the electric energy per order has been determined. The electric energy per order ( $E_{EO}$ ) is the total energy normalized per log removal of contaminant, Equation 4.6. [46] The initial and final contaminant concentrations are based on the total number of PFAS chains in each solution, not just PFOA or PFOS.

$$E_{EO} = \frac{Q}{\log(C_i/C_f)} \tag{4.6}$$

Where  $C_i$  is the initial total PFAS concentration present in the solution and  $C_f$  is the final total PFAS concentration present in the solution. The  $E_{EO}$  values at the 12 hour time point for the NH<sub>4</sub>OH with MeOH, NaOH with MeOH, NaCl with MeOH, and NH<sub>4</sub>OH with NH<sub>4</sub>Cl were 362, 569, 2032, and 84 kW\*h/m<sup>3</sup>, respectively. A bar graph for a visual comparison of these values is provided as Figure 4.29. This confirms that the mixed ammonia solution required the lowest energy per log removal of total PFAS compared to the other three solutions. It is also interesting to note that the NaCl and MeOH solution required the most energy per log removal of total PFAS.



Figure 4.29: Bar graph comparing the conversion efficiency values for the simulated IX regenerate solutions

## 4.5 Key Advancements from Bench Top PFAS Studies

The key advancement from the bench top PFAS studies include the following:

• Step down current density techniques do save on energy without inhibiting PFOA degradation

in simulated solutions with the combination of 50&5 showing improved energy consumption compared to 50 mA/cm<sup>2</sup>

- BDD can become fluorinated from the treatment of PFAS, but this has yet to inhibit its ability to remediate PFAS in these studies
- PFOA and PFOS can be broken down in different complex ion exchange regenerate solutions
- The optimum regeneration solutions to be treated with electrochemical oxidation are those that are ammonia based
- Byproducts are generated from ion exchange regenerate solution treatments that will need to be investigated further

### 4.6 Summary

Investigation into electrochemical oxidation of PFAS began at the bench scale in a beaker less than 1 L. Initial studies that utilized constant current densities showed that there may be a way to take advantage of the step down current density technique for these compounds even though they do not fit the traditional model. Further investigations in simulated solutions showed that one step down current density method of 50&5 did indeed provide energy savings over a constant current density method. Parameters were slightly adjusted when adapting this procedure to complex simulated ion exchange regenerate solutions, showing that in the first hour of high current density application, most solutions reached a mass transport limit for PFOA or PFOS. Although there were a few exceptions to this rule. Due to the generation of unwanted byproducts, further investigation into limiting their development should be completed.

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# **CHAPTER 5**

# CONCLUSION

### 5.1 Conclusion

This report outlines three important studies that advance the field of electrochemistry. The first uses a boron-doped diamond (BDD) sensor that is comprised of a working, counter, and auxiliary electrode. This sensor is used to demonstrate its ability to detect isatin while eliminating pretreatment procedures that require additional time and additional equipment, simplifying the three electrode set up into one plug and play sensor, and obtaining limits of detection (LOD) applicable to biological fluids. This study also demonstrated the additional benefits of using a microelectrode array (MEA) as the working electrode in the sensor due to its lower sensitivity and more repeatable results. The second study focused on using a material that would allow for economical mass production of sensors for heavy metal detection. Indium tin oxide (ITO) is already used in industry for solar cells and does not require a transparent substrate for the detection of heavy metals, ideally manganese (Mn), using cathodic stripping voltammetry (CSV). Investigating the use of heating during deposition and post deposition annealing led to the discovery that a heated and annealed film had ideal properties to detect Mn in environmentally relevant concentrations due to its larger grain sizes and increased conductivity. This led to the concluding that ITO can be an economic sensor material for such applications. Finally, electrochemical oxidation was investigated to advance the understanding of remediation for per- and polyfluoroalkyl substances (PFAS). Current remediation techniques focus on adsorption or filtration methods that produce a waste stream that can further contribute to the contamination cycle. Using BDD and electrochemical oxidation, a combined current density technique was evaluated using both simulated salt solutions and simulated ion exchange regenerate solutions. Ultimately, the study showed that the two ideal regenerate solutions currently in literature to be further treated with electrochemical oxidation are those based on ammonia, ammonium hydroxide with methanol and the mixed solution of ammonium hydroxide and ammonium chloride. Due to the byproducts produced from these processes, further studies will need to be completed.

Overall, these three studies have shown that existing electrochemical methods can be advanced

to address problems in today's world to benefit the planet and humankind.

# **CHAPTER 6**

# **FUTURE OUTLOOK**

### 6.1 Future Outlook

### 6.1.1 Isatin Detection

The next steps for the detection of isatin with the 3-in-1 BDD sensors include the detection in a real bodily fluid. Since the sensors were only tested in a urine simulant it is important to study the in a real solution to understand if there are other compounds that can influence the response of isatin. Additionally, a process for renewing the surface of the working electrode should be investigated to allow for improved reproducibilities from day to day studies. Ultimately, these sensors would be used following a liquid chromatography system so a trial with a flow through injection system should also be completed.

### 6.1.2 Indium Tin Oxide Characteristics

Since other metals present in environmental samples have the potential to influence the response for manganese on the HA ITO sensor, the next step in this study would be to run a set of calibration curves with differing levels of other metals present. Once a better understanding is obtained for how the manganese response changes with the presence of other metals, a real environmental sample will need to be studied. In addition, if this sensor is to be used to better understand the toxicology of manganese in the human body, studies with a simulated biological fluid will need to be performed before allowing for the detection in a real biological solution.

### 6.1.3 Mineralization of Per- and Polyfluoroalkyl Substances

The next step in the PFAS remediation studies would be to obtain and characterize an industrial ion exchange regenerate solution. These solutions could have co contaminants that can influence the degradation rates of different PFAS chains. They could also be producing different byproducts from those that are simulated. It is also important to begin to look into the byproducts that are being generated in the off gasses of the system. This will be critical to know when scaling this technology for industrial use. It can also be of interest to reverse the combined current density configuration to look at the difference in applying a lower current density before a higher one. This may be beneficial in precursor conversion in industrial solutions.