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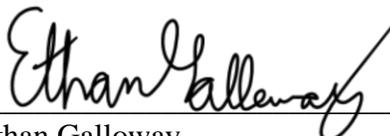
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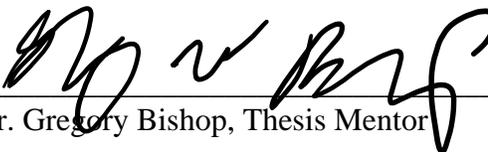
Nitrogen Doping of Electrochemically Activate Carbon Screen-Printed Electrodes

A thesis presented to
the faculty of the Department of Chemistry
East Tennessee State University

In partial fulfillment
of the requirements for the degree
Bachelor of Science in Chemistry

by
Ethan Galloway
April 2022


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ABSTRACT

Nitrogen Doping of Electrochemically Activated Carbon Screen-Printed Electrodes

by

Ethan Galloway

Screen printed electrodes (SPEs), which are prepared by patterning conductive inks or pastes onto an insulating support (e.g., plastic film), are widely employed as sensing and biosensing platforms due to their ease of fabrication and relatively low cost. This is especially applicable to electrodes of this nature prepared with carbon-based inks (SPCEs). To date, the most successful and significant commercial application of SPEs has been as test strips for glucose meters. Despite the maturity of this technology, SPE research remains very active as improvements in sensitivity and selectivity, which often involve modifying the electrode surface, hold the key to advancing their utility in routine applications and extending their benefits to other target analytes. Recent studies in the Bishop research group have demonstrated that nitrogen-doped SPCEs (N-SPCEs) exhibit enhanced electrochemical response towards hydrogen peroxide (H_2O_2), a product of oxidase enzyme (e.g., glucose oxidase, lactate oxidase, etc.) reactions and a common target in biosensing strategies. The presence of nitrogen heteroatoms on the carbon surface facilitates breakage of oxygen-oxygen bonds, a key step in reduction of H_2O_2 . Since previous studies showed only modest incorporation of nitrogen species on SPCEs prepared from commercial ink, these studies aim to investigate the possibility of enhancing N-doping by performing a simple pre-treatment strategy that reportedly increases surface oxygen content of SPCEs prior to N-doping. Since surface oxygen sites have been previously reported to be preferentially modified with nitrogen during N-doping strategies, this seems like a promising technique for improving sensitivity of N-SPCEs for H_2O_2 reduction. To quantify the actuality of these claims, experimental groups were fabricated having undergone no enhancement, pretreatment enhancement only, nitrogen-doping enhancement only, and a combination of the pretreatment and nitrogen-doping enhancements. Here the electrochemical behaviors of pretreated SPCEs, N-SPCEs, and pretreated N-SPCEs for the detection of H_2O_2 by completing comparative cyclic voltammetry (CV) experiments with and without the presence of H_2O_2 and with it present in varying concentrations is compared. It is projected that, if successful, the fabricated electrodes that have undergone both the pretreatment protocol and the nitrogen-doping process will have an increased sensitivity and detection limit towards H_2O_2 .

DEDICATION

This work is dedicated to my family and friends for always supporting me throughout my scholarly career.

ACKNOWLEDGMENTS

I would like to thank Dr. Gregory W. Bishop for allowing me to be a part of his research group and always being supportive of my work and providing me with guidance. I would also like to thank Dr. Catherine McCusker for agreeing to be my secondary thesis reader. Additionally, I would like to thank previous graduate students Emmanuel Peprah-Yamoah and Emmanuel Nkyaagye for help with the success of this research and helping me understand protocols and methodologies in the lab. Finally, I would like to thank the honors college for providing me with the Honors-in-Discipline scholarship.

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LIST OF ABBREVIATIONS

CV – Cyclic Voltammogram

SPE – Screen-Printed Electrode

SPCE – Screen-Printed Carbon Electrode

SPGE – Screen-Printed Graphene Electrode

N-SPCE – Nitrogen Doped Screen-Printed Carbon Electrode

SPCE-PRE – Pretreated Screen-Printed Carbon Electrode

N-SPCE-PRE – Nitrogen Doped and Pretreated Screen-Printed Carbon Electrode

DFT – Density Functional Theory

EP – Electrostatic Potential

PBS – Phosphate Buffered Saline

CHAPTER 1

INTRODUCTION

Electrochemical Sensing

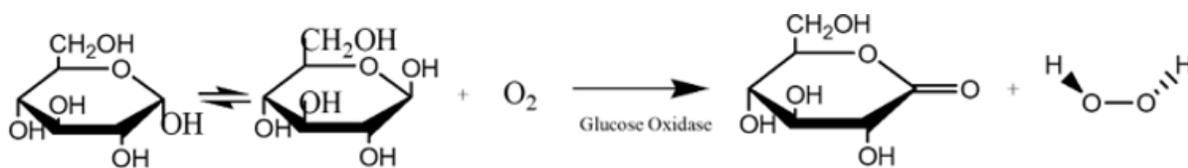
Electrochemical sensors are devices that utilize an electrode as a transducer to produce an electrical signal (e.g., current, voltage) in the presence of an analyte.¹ Electrochemical sensors have some inherent advantages over other types of sensors, like those based on optical methods such as absorbance or fluorescence. Comparatively, electrochemical sensing strategies are usually associated with lower costs, little or no maintenance, and ease of miniaturization due largely to the simplicity of the instrumentation and materials involved in electrochemical measurements.² While electrodes employed in electrochemical sensors can take many forms, screen-printed electrodes (SPEs) have emerged as particularly popular platforms over the past few decades due to their low cost and ease of production.^{3,4}

SPEs are manufactured by printing conductive inks on an insulating support.³ Inks consist of conductive carbon or metal particles, a polymeric binder (cellulose acetate⁵, ceramic-based supports⁶, etc.) and a solvent.⁷ As with other types of electrodes, surface modification procedures can be carried out on SPEs to improve their sensitivity and selectivity for particular analytes.⁸ These strategies are especially important for sensing applications that involve measurements made in complex media, where the possibility of interference is high, and those where the target does not directly participate in a convenient electron-transfer reaction, which are both cases commonly encountered in sensing biomolecules.⁹

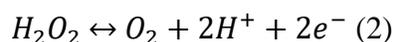
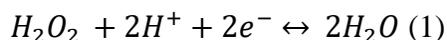
Biosensors are sensing devices that produce a signal based on interaction with certain biological and chemical species.¹⁰ Electrochemical biosensors leverage these chemical or biochemical interactions to generate measurable electrical signals (e.g., current or voltage) that

can be attributed to the biomolecule or metabolite of interest. Such devices may utilize biorecognition agents such as antibodies to isolate a specific analyte from the matrix and/or signal transducing species such as enzymes and diffusible redox-active molecules to produce a measurable signal.¹¹ For example, electrochemical biosensors based on immobilized oxidase enzymes have been developed for species such as glucose (Scheme 1) and lactate.

Glucose sensor technology in many glucometers is based around these enzyme-based electrodes.¹² Hydrogen peroxide is a product of oxidase enzyme reactions (Scheme 1), and these biosensors can work by measuring a current associated with either direct reduction (Equation 1) or oxidation (Equation 2) of H₂O₂.¹³



Scheme 1. Oxidation of Alpha and Beta Glucose by Glucose Oxidase



The technology for the basis of the first glucose sensor was a platinum electrode that utilized an amperometric response to peroxide.¹³ While platinum is still a common electrode material for carrying out oxidation of hydrogen peroxide, its high cost has resulted in much research into alternatives like Prussian blue- and various nanomaterials-modified carbon electrodes.^{9,14} Since species such as oxygen, dopamine, and ascorbic acid can usually be oxidized at anodic working electrode potentials, modification strategies that impart selectivity are necessary for detection of H₂O₂ by oxidation.^{12,15} Detection of H₂O₂ by reduction typically

suffers less from matrix interferences making it the more appealing method for peroxide detection. This issue that then arises with this method is the breakage of the oxygen-oxygen bond via reduction usually requires larger applied potentials to overcome the slow kinetics.⁹ Thus, aims at improving the working electrode's ability to complete this important step hold the key to improving performance of oxidase enzyme-based sensors and to optimize electrochemical H₂O₂ detection for other applications, like oxidative stress. One method that has been increasingly explored to accomplish this is heteroatom (Phosphorus, Nitrogen, etc.) doping, for these atoms all for disturbances in the graphitic structure that can lead to these carbon materials becoming increasingly electrocatalytic.¹⁶ The modification of carbon materials with surface nitrogen-containing groups (i.e., nitrogen doping) has emerged as a simple and promising strategy to facilitate easier breakage of oxygen-oxygen bonds during reduction of molecular oxygen and hydrogen peroxide.

Nitrogen-Doping

Nitrogen doping is the process of incorporating nitrogen into the graphitic structure on the electrode surface.¹⁷ This doping primarily occurs at oxygen-containing sites on the electrode surface.^{18,19,20} Density functional theory (DFT) completed in prior studies has revealed that N-doping leads to better absorption of hydrogen peroxide on the electrode surface.²¹ Nitrogen doped on the electrode surface can be either pyrrolic, pyridinic, and/or graphitic in nature (Figure 1).¹⁷

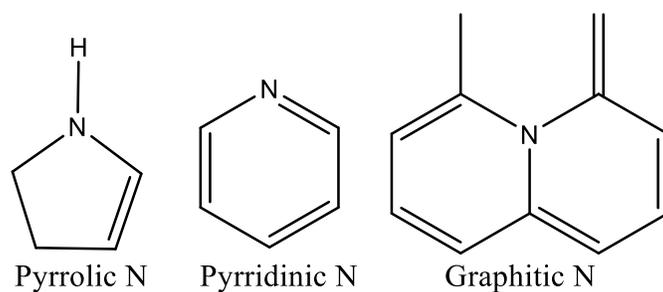


Figure 1: Various Nitrogen Arrangements in Graphitic Structure.

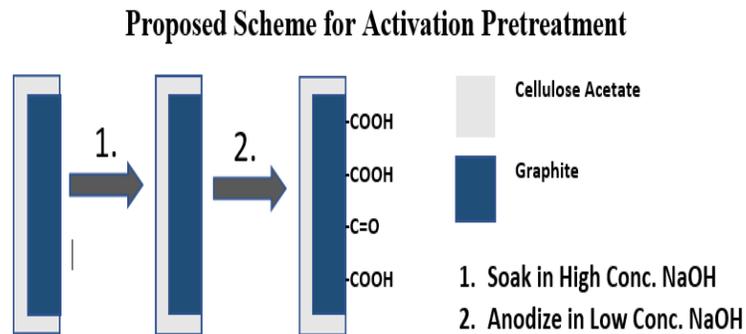
Electrostatic potential (EP) calculations completed in prior studies have shown that pyridinic and pyrrolic nitrogen atoms in doped graphene were the most reactive with peroxide.¹⁷ Common procedures to attain nitrogen doping of carbon-based materials that have been tested in prior studies include nitrogen plasma-based²², ammonia-based²⁰, and urea-based¹⁸ strategies. Ammonia can be utilized to perform a nucleophilic attack upon carbonyl groups to produce amide groups; these amide groups can be converted into pyridinic and pyrrolic nitrogen at high temperatures.^{19,23} In previous studies an ammonia-based strategy for N-doping resulted in a five-fold increase in surface nitrogen content when applied to screen-printed carbon electrodes (SPCEs) prepared from a commercially available ink.²⁴

Since oxygen-containing sites on carbon surfaces have been identified as the primary locations for incorporation of surface nitrogen groups during doping processes, it would seem that enhancing the surface oxygen content of SPCEs could provide benefit to N-doping and, in turn, detection of H₂O₂ by electrochemical reduction using N-SPCEs. Numerous pretreatment protocols have reported an increase in surface oxygen content with these modified electrodes also showing increased electrochemical response to many target analytes.^{15,25,26}

Pretreatments of SPEs

An example previously reported pretreatment strategy for enhancing surface oxygen content of SPCEs reported this method to increase surface oxygen content of the SPE by nearly 10%.²⁵ These pretreatment steps range from anodization procedures²⁶ (electrochemical) to soaking steps (chemical), and some studies reported success with a combination of these protocols¹⁵.

Wei et al. reported a two-step pretreatment protocol that involved soaking SPCEs in 3M NaOH for 1 hr, which was done to remove surface interfering species (e.g., insulating binder from ink, surface contaminants) to better expose the graphite structure. The second step involved applying a potential of 1.2V for 20 s in 0.5M NaOH to promote the formation of more oxygen-containing sites on the electrode surface. The proposed two-part scheme (Scheme 2) showed an improvement in the electrodes' electroactivity towards various biological molecules to which the author attributed to the formation of these oxygen-containing sites.¹⁵



Scheme 2: Proposed Theory of Chemical and Electrochemical Pretreatments¹⁵

Research Objective

Prior surface enhancements for SPCEs by nitrogen doping led to promising results for the detection of peroxide, but the reported sensitivity of these electrodes was low compared to other modified SPEs.²⁴ Since the surface nitrogen content of N-SPCEs was only 1.34% after doping²⁴ and previous literature indicates that incorporation of surface nitrogen groups occurs primarily at oxygen-containing sites, here, we attempt to improve upon previously reported N-SPCEs by subjecting SPCEs to pretreatment that reportedly enhances surface oxygen prior to N-doping.^{18,19} The pretreatment protocol utilized in this study is a previously reported biphasic process consisting of a soaking step to remove surface interferents and an electrochemical step utilizing an anodic potential to promote the formation of oxygen-containing groups.¹⁵ The nitrogen-doping protocol utilized here consists of suspending the electrodes in a heated ammonia solution (2%) for 6 hours.¹⁸ The aim is for these electrodes to have a higher surface nitrogen concentration and both a lower detection limit and higher sensitivity towards hydrogen peroxide.

CHAPTER 2

EXPERIMENTAL

Materials

All chemicals used for these experiments were utilized at their purchased purity. Ammonium hydroxide (30%), sodium hydroxide, urea, potassium chloride, and ferrocene methanol were obtained from Sigma-Aldrich. Phosphate buffered saline (PBS) (M.P. Biomedicals) was dissolved according to manufacturer instruction to prepare PBS solution (pH 7.4). Carbon graphite paste (C2050106P7) and dielectric paste (D2071120P1) were obtained from Gwent Electronic Materials. Nitrogen gas (N₂) was obtained from Airgas. All aqueous solutions were prepared using ultrapure water (18.2 MΩ·cm).

Instrumentation

A 760E CH Instruments electrochemical workstation (Austin, TX) equipped with a CH Instruments picoamp booster and faraday cage was utilized to carry out all electrochemical analysis. A Canon Power Shot (SX 260 HS) camera was used to digitally photograph all electrodes after production beside a reference size guide. Image J software from the National Institute of Health was utilized for geometric analysis of electrodes. Each electrode's working area was free traced with comparison to the visualization of the electrode, and this defined zone's area was determined by the software based on the reference measurement set from the size guide in the photograph. All electrochemical scans were normalized to reflect current density by dividing the current by the geometric area of the electrode.

Fabrication of Screen-Printed Electrodes

Screen-printed carbon electrodes were produced by manually screen-printing carbon graphite pastes onto cellulose acetate film as previously reported.²⁷ Briefly, the electrode and insulating (dielectric) layer stencils were developed on 110 mesh screens. Ink was placed on the screen and a 1.27cm x 3.81cm piece of cellulose acetate was placed under the electrode stencil. The ink was forced through the stencil by sweeping a 75-durometer squeegee over the screen. After printing, electrodes were cured in an oven at 60°C for 30 minutes. After curing, each electrode was carefully placed under the insulating (dielectric) layer stencil of the screen. Dielectric paste was screen-printed over the conductive track connecting the circular working area and the rectangular instrument connection pad in order to define the working electrode area ($\sim 0.0314\text{cm}^2$). After printing the dielectric layer, the electrode was again cured for 30 minutes in an oven at 60°C (Figure 2).

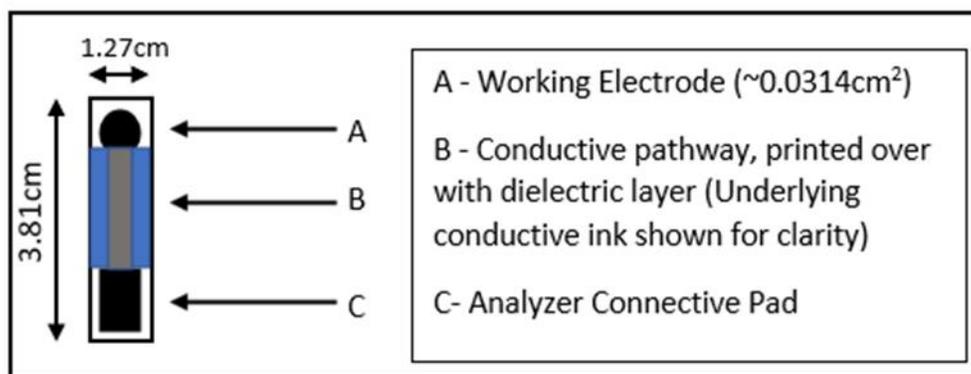


Figure 2: Labeled Diagram of Screen-Printed Electrode Portions.

Surface modifications to electrodes were completed in between the printing step and the dielectric pasting step.

Pretreatments for Surface Modification

The pretreatment methodology initially utilized in this study has been previously reported to be effective at increasing SPE efficacy towards the oxidation and reduction of other small biomolecules such as dopamine. These enhancements were attributed to the removal of surface interferants by a chemical pretreatment and by the formation of oxygen-containing functional groups, such as carboxyls and carbonyls, on the electrode surface assumed to be the results of the electrochemical pretreatment step.¹⁵ Initially electrodes were soaked in 3M sodium hydroxide (NaOH) for one hour. Following this, the electrodes were anodized in 0.5M NaOH at a potential of 1.2 volts for twenty seconds vs. a silver/silver chloride reference electrode. The electrodes were then rinsed with deionized water and air dried.

A second studied pretreatment protocol also proven successful at increasing efficacy of SPEs toward the reduction of H₂O₂ by 140-fold compared to SPCEs due to assumed formation of oxygen-containing groups on the electrode surface was attempted in this study.²⁵ Electrodes that underwent this protocol degraded prior to the dielectric layer being fully printed (Figure 3), and thus, no further analysis could be conducted on these modified electrodes.



Figure 3: Representative Electrode Having Underwent Second Pretreatment Protocol.

Nitrogen Doping for Surface Modifications

A nitrogen doping strategy that had proven successful for the deposition of nitrogen onto SPEs was utilized in this study.^{20,24} Electrodes were suspended in an ammonia solution (2%) as it was sonicated for fifteen minutes. Following, the solution was heated to 80°C and stirred while the electrodes remained suspended in it for six hours. Following doping, electrodes were rinsed with deionized water and cured overnight at 60°C.

CHAPTER 3

RESULTS AND DISCUSSION

Active Surface Area of SPEs

SPEs are printed from inks that have conductive and insulating regions. Characterization of SPEs in terms of their geometric and electroactive areas (i.e., area of the electrode that can participate in electron-transfer reactions) provides valuable information about the quality and integrity of the electrode.⁷ Electroactive surface area was determined from chronocoulometric experiments which measure the charge associated with the transfer of electrons between well-studied electroactive species (FcMeOH) and the electrode over time. The measured charge can be replotted against the square root of time to compose an Anson plot (Figure 4).

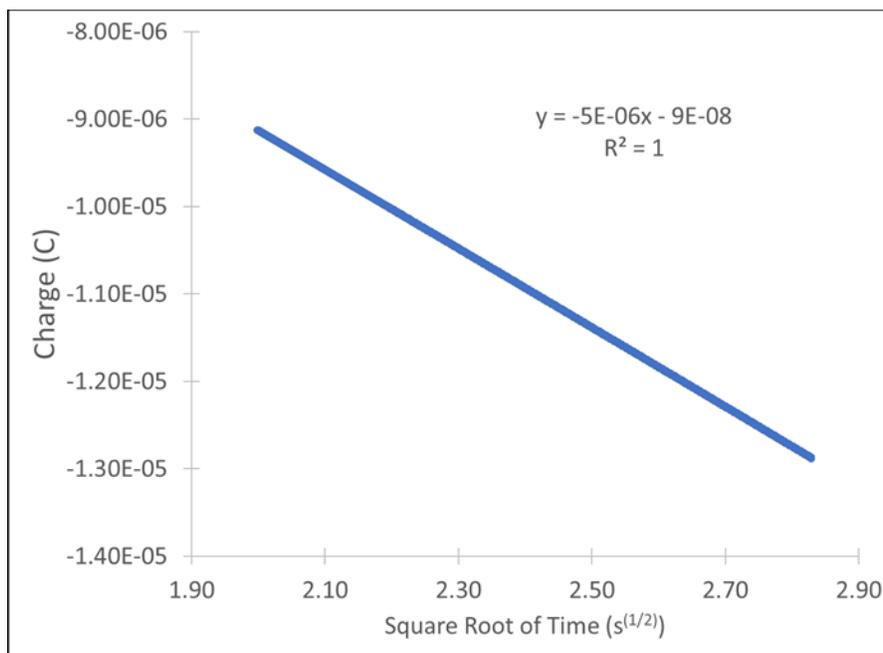


Figure 4: Representative Anson Plot of SPCE in 0.5mM Ferrocene Methanol (FcMeOH) / 0.1M Potassium Chloride (KCl) with an applied potential step from -0.2V to 0.3V.

The Anson equation (Equation 3) was used to take the slope of this plot (Q) and determine the electroactive area (A_e) of the electrode.

$$Q = Q_{dl} + Q_{ads} + 2nFA_eC(Dt/\pi)^{1/2} \quad (3)$$

Equation 1: Anson Equation Where Q_{dl} and Q_{ads} are the charges associated with double-layer charging and Faradaic reactions of adsorbed species, respectively, A_e is electroactive area, t is time, n is the number of electrons involved in the faradaic reaction, F is the Faraday constant, C is concentration of the electroactive species, and D is the diffusion coefficient.⁵

The ratio of electroactive surface area-to-geometric surface area represents the relative portion of conductive material to the whole.⁷ This ratio is a quantity that has also been called the real surface area or roughness factor and has been used to compare performances of different SPCEs. It was found that SPCEs had a ratio of 1.01 ± 0.02 , SPCE-PREs had a ratio of 0.92 ± 0.03 , N-SPCEs had a ratio of 1.30 ± 0.02 , and N-SPCE-PREs had a ratio of 1.13 ± 0.02 . The increase in this value due to nitrogen doping can indicate, to some degree, and increase in surface “roughness” or the incorporation of more utilizable surface defects. The decline shown from the pretreatment method can be indicative of degradation of the ink or formation of surface interfering species that create inactive patches.⁷

Voltametric Behaviors of SPEs

SPEs underwent typical cyclic voltammetry studies to investigate their behavior with a common redox probe (FcMeOH) for further characterization of electrochemical properties (Figure 5).

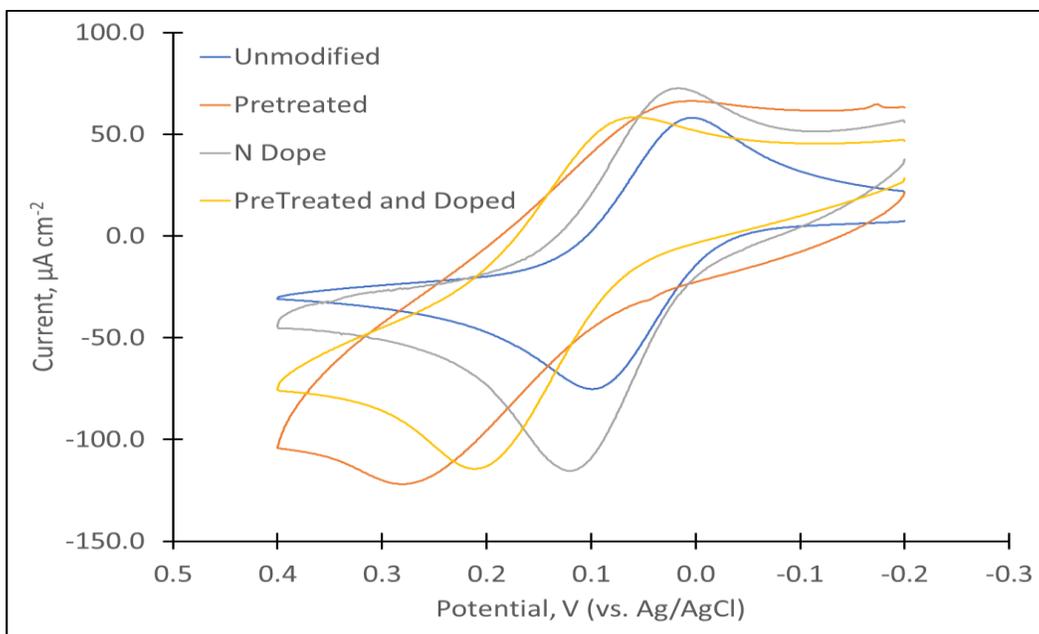


Figure 5: Representative CVs of SPCE (blue), N-SPCE (gray), SPCE-PRE (orange), and N-SPCE-PRE (Yellow) in 0.5 mM ferrocene methanol with 0.1 M potassium chloride. The scan was completed at a potential step of -0.2V to 0.4V (-0.2V initial and 0.4V switch potential step of -0.2V to 0.4V (-0.2V initial and 0.4V switch potentials) with a scan rate of 50mV/s.

Peak separation, anodic and cathodic peak potential, and anodic and cathodic peak current values were calculated based on these CVs (Table 1).

Electrode [n=3]	Cathodic Peak Potential (mV)	Cathodic Peak Current ($\mu\text{A cm}^{-2}$)	Anodic Peak Potential (mV)	Anodic Peak Current ($\mu\text{A cm}^{-2}$)	Peak Separation (mV)
SPCE	-1 \pm 0	50.2 \pm 0.9	105 \pm 5	-59 \pm 1	105 \pm 5
SPCE-PRE	19 \pm 2	20 \pm 10	220 \pm 70	-40 \pm 30	200 \pm 60
N-SPCE	14 \pm 2	70 \pm 6	119 \pm 3	-86 \pm 2	105 \pm 3
N-SPCE-PRE	50 \pm 10	53 \pm 9	200 \pm 10	-70 \pm 2	160 \pm 16

Table 1: Electrochemical Measurements from Cyclic Voltammetry Studies.

Peak separation is indicative of the rate at which species can easily be oxidized and reduced; this value can also give insight into factors effecting this rate such as resistance between the electrodes and/or the solution. Ideal peak separation value for redox probe species undergoing a reversible, one electron transfer is 59 mV.²⁸ However, for SPEs, this value is often larger than this reported value.²⁹ Peak separation values reported for various commercially available SPCEs for ferri/ferrocyanide ($1e^-$ redox couple) in one study ranged from 98mV to 535mV.⁷ Peak potentials are indicative of the amount of current produced when all species molecules at the electrode surface have been oxidized or reduced.³⁰ Analysis of these CVs indicates that all electrode test groups performed within the prior reported range for peak

separation for commercially available SPCEs. It was also revealed by the analysis that nitrogen doping allowed for the electron transfer to occur at approximately the same rate as with no modifications as indicated by a peak separation of ~ 105 mV for both groups. The pretreatment protocol appeared to decrease this rate as indicated by a peak separation of 200 ± 60 mV for SPCE-PREs and 160 ± 16 mV for N-SPCE-PREs. This analysis also shows that the nitrogen-doped electrodes produced a slightly stronger current response compared to the unmodified SPCE with cathodic peak currents of 70 ± 6 $\mu\text{A cm}^{-2}$ and 50.2 ± 0.9 $\mu\text{A cm}^{-2}$, respectively. SPCE-PREs showed an average cathodic peak current of 20 ± 10 $\mu\text{A cm}^{-2}$. These values show that N-SPCEs produced a larger current compared to all other electrode groups, SPCE-PREs produced a smaller current than the unmodified electrodes, SPCEs. SPCE-PREs and N-SPCE-PREs experienced an electrochemical shift on the CVs that could indicate a decrease in the integrity of the conductive ink. Furthermore, analysis of SPCE-PREs yielded large standard deviations amongst metrics revealing their erratic behavior.

Detection of Hydrogen Peroxide

Cyclic voltammetry scans were completed to assess the electrodes' capabilities for reduction of H_2O_2 . The first study was completed in 15mL of PBS that had nitrogen gas bubbled through it for ten minutes to remove the oxygen. The second study was completed in 15 mL of PBS that had been bubbled with nitrogen as well. This solution was spiked with hydrogen peroxide to make a 10 mM solution. During both trials the continuous nitrogen gas was dispersed above the solution to prevent reentry of oxygen into the solution. The analysis during both trials was completed at a scan rate of 50 mV/s between the potentials of 0.4 volts and -0.6 volts. The first studies were subtracted from the second study (after the spike) to determine the current produced by each electrode from the spike (Figure 6). The background run was subtracted at a

potential of -0.3V. Three electrodes from each group were measured. It was observed that SPCEs measured $26 \pm 3 \mu\text{A cm}^{-2}$, SPCE-PREs measured $13 \pm 0 \mu\text{A cm}^{-2}$, N-SPCEs measured $210 \pm 17 \mu\text{A cm}^{-2}$, and N-SPCE-PREs measured $90 \pm 22 \mu\text{A cm}^{-2}$.

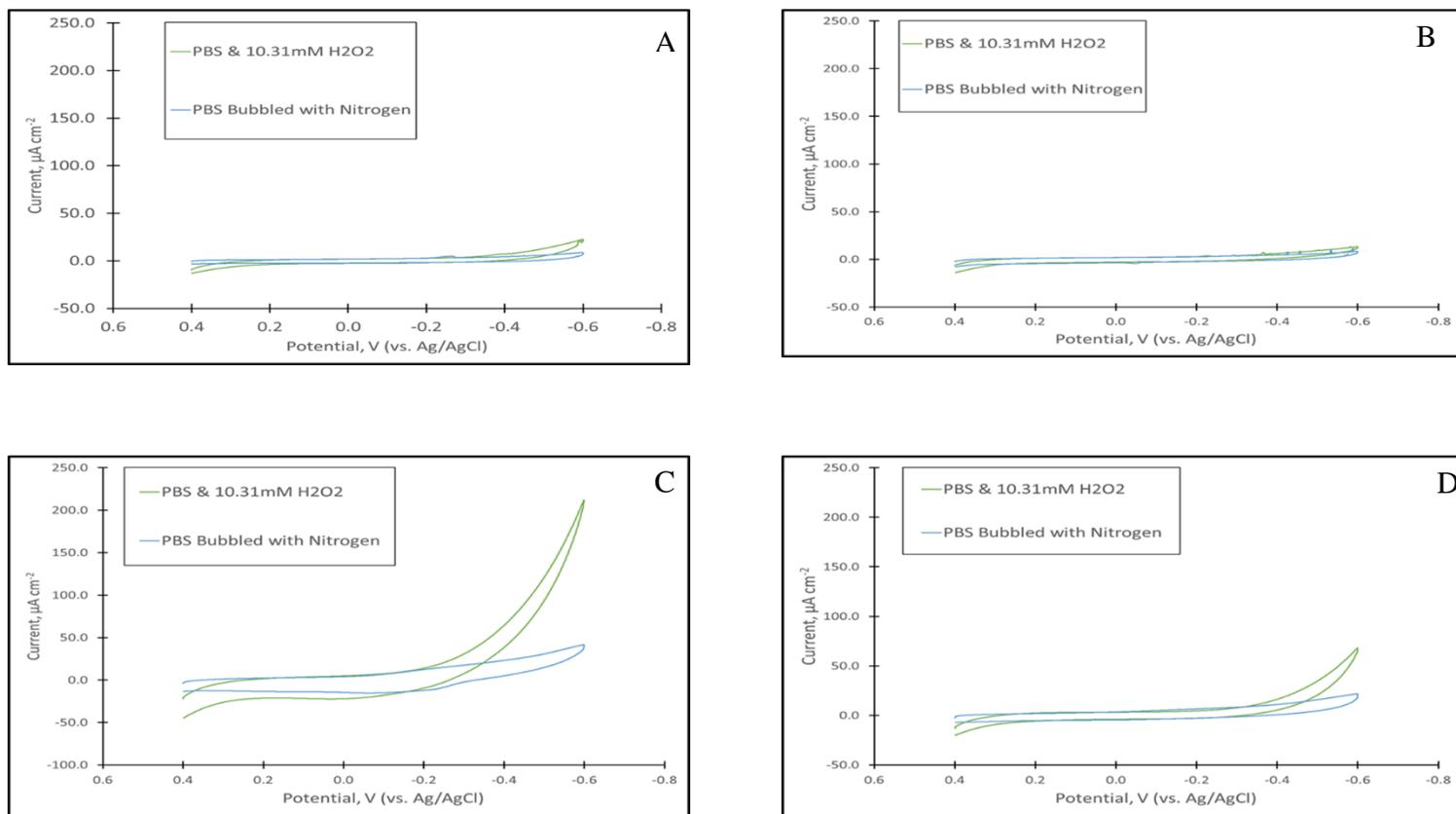


Figure 6: A.) CV Before and After H₂O₂ Spike with SPCE B.) CV Before and After H₂O₂ Spike with SPCE-PRE C.) CV Before and After H₂O₂ Spike with N-SPCE D.) CV Before and After H₂O₂ Spike with N-SPCE-PRE.

These results show that nitrogen doping is effective at improving the electrodes' ability to detect hydrogen peroxide confirming prior reported data²⁴. These studies also show that the SPCE-PREs and N-SPCE-PREs performed poorly towards the detection of hydrogen peroxide as

their observed current after the spike was relatively close to that of the unmodified SPE. N-SPCEs in previous studies were reported to have a low sensitivity, and with these electrodes undergoing pretreatment performing worse in this detection study it is logical to not proceed with amperometric studies to determine sensitivity as it can be assumed to be worse.²⁴

CHAPTER 4

CONCLUSIONS AND FUTURE WORK

Conclusions

In this study, the results of the geometric to electroactive area ratio study indicate that the pre-treatment likely degrades the ink in some way. Based on degradation during fabrication, the binding between the ink and the cellulose acetate was likely altered, but it is also reasonable to assume the pretreatment promoted the formation of some surface interferant species, limiting its conductive ability.⁷ Based on this same analysis and other testing shown in this study, it was concluded that N-doping likely improved the electrochemical behavior of the electrodes. N-doped electrodes also proved to perform better for the detection of H₂O₂, as shown by the lower applied potential required for its reduction and the larger current produced by this reaction.

Future Work

Following this project, other work will be completed to investigate additional modifications to enhancement protocols with both the same ink and with other ink options. These strategies include additional pretreatment strategies that have been proven to enhance the electrodes' ability to be both selective and sensitive towards H₂O₂ reduction. They also include other strategies for nitrogen doping that have been proven successful in similar standards. XPS will be conducted on electrodes that prove successful to further analyze their surface composition to better aid in understanding the linkage between these modifications and their efficacy.

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