Dopamine Detection Using Mercaptopropionic Acid and Cysteamine for Electrodes Surface Modification

A Thesis

by

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ABSTRACT

This research work emphasizes on main objective of dopamine detection using electchemical detection analysis. Dopamine is an electro-chemical neurotransmittor and is an essential part in human body for many descions. İt can also be described as a chemical released by neurons (nerve cells) to send signals to other nerve cells. The interest in dopamine was stimulated due to several physiological and neurological diseases such as Parkinson's disease, schizophrenia, obsessive compulsive disorder and many drug addictions.

Gold electrodes are often not suitable for the dopamine measurements as dopamine creates a non conducting polymer layer on the surface of the electrodes, which leads to the increased amount of electrode passivity with the gradual increase in voltammograms measurement.

This work is presented to contribute in a better understanding on the comparative study of targeted dopamine detection with two surface modifications for Au electrodes with mercaptopropionic acid (MPA) and cysteamine. The results are further chracterized with the impedance spectroscopy (EIS) and cyclic-voltammetry (CV) for providing a comparison of dopamine detection for thermally bonded and ultrasonically welded microfluidic chips respectively.

Moreover, the effects of selecting optimized tubing, bonding techniques, and cleaning methods of the devices with KOH solution played crucial role for improvements in dopamine detection which are observed in results. Also a comparison for the modification with

unmodified chips, and finding the unknown concentration of dopamine solution using flow injection techniques has also been illustrated.

Keywords:

Gold electrodes, Dopamine, Cysteamine, Mercaptopropionic acid (MPA), Thermal Bonding, Ultrasonically Welding, Microfluidics, Impedance Spectroscopy, Cyclic Voltammetry

CHAPTER 1: INTRODUCTION TO ELECTROCHEMISTRY

1.1 Background and Theory

The origin of the link between chemistry and electricity goes back to 1793, when Allesandro Volta discovered, that it may be possible to produce the electricity by keeping two unlike metals on opposite sides, away from each other but keeping a wet paper between them connected. Later on carrying the Volta experiment, it was understood and discovered that oxygen and hydrogen can be separated by applying electric current. This originated the concept of having a two opposite forces which are holding the water molecule together, i.e. positive and negative electric charges. The classification of atoms was proposed by a Chemist Berzelius in 1812, according to that classification, nonmetallic and metallic including hydrogen are charged as negative and positive respectively. This concept was used to prove that in a process of electrolysis, if the applied potential could be greater than that of bonding charges between hydrogen and oxygen, would result in separation of water molecule into ions. **[1]**

For a longer time, an electricity was used to make chemical changes in the component. This was presented first time by Humphrey Davey who created sodium from sodium hydroxide by electrolysis process. After that a Michael Faraday related the process of electrolysis by

the amount of electric potential applied and the formation of the product quantity from the process. **[1]**

1.2 Electrochemistry

A simple way to define electrochemistry is a process which combines both electrical and chemical behavior or effect together and examines the phenomena and its result. An electrochemistry process includes a charge transfer between the electrodes, possibly metal or semiconductor and molecules on the surfaces. The component of electrochemistry process includes an ionic conductor, the electrolyte solution or carrier which need to transfer mass between the cathode and anode. Fig. 1, simply represents electrochemistry phenomena. **[2, 3, 4]**

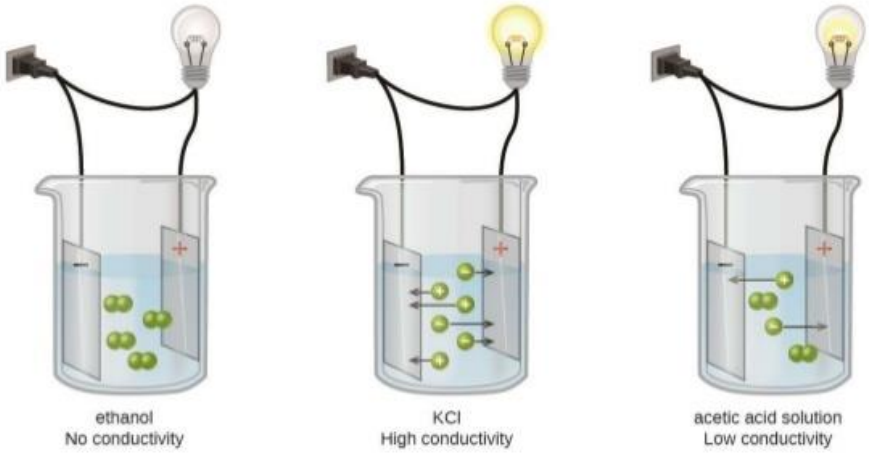

Figure. 1: A simple electrochemistry principle no, high and low conductivity **[2]**

This fields cover, an electrolyte Process: in which chemical properties changes as the current is passed through the chemical solution and Galvanic or Voltaic processes: a production of electrical current due to the chemical reactions happing in the process.

A mode of transfers is: The motions of an electrons are due to the charge transport in the electrodes or holes and the motion of ions i.e. positive or negative are due to charge transport in the electrolyte solution. **[3, 4]**

1.3 Electricity and Chemistry Interface

In this section, the interace between electrical and chemical properties is discussed. There are two electrode with electrical potential and an electrolyte with its chemical properties. The reaction occures at each electrode with the electrolyte is called half cell reaction and intotal two half cell reactions occure as of two electrodes. The reactions accouring at two electrodes are classified as oxidation reactions and Reduction reactions. A reaction is classified as oxidation or reductions depending on the flow of direxion of electron trasfer. Below we will discuss oxidation or reductions reactions: **[4]**

Oxidations:

The oxidation procee is defined as, when the loss of electron happens, which mean the transfer of electron happens in the solution from the specie to the electrodes. A simple reaction below explain the phenomena:

$$R = O + n^e \quad (1)$$

The oxidation reaction are energitec processes, i.e. when the energy of the electrode falls below the energy level of the highest molecule of the compound. **[4]**

Reductions:

The reduction procee is defined as, when the gain of electron happens, which mean the transfer of electron happens in the solution from the electrode to the species. A simple reaction below explain the phenomena:

$$O + n^e = R \qquad (2)$$

The reduction reactions are also energitec processes, i.e. when the energy of the electrode increases above the energy level of the lowest vacant molecule of the compound. **[4]**

Figure. 2, shows the simple Sodium choride (NaCl) oxidation and reduction example below.

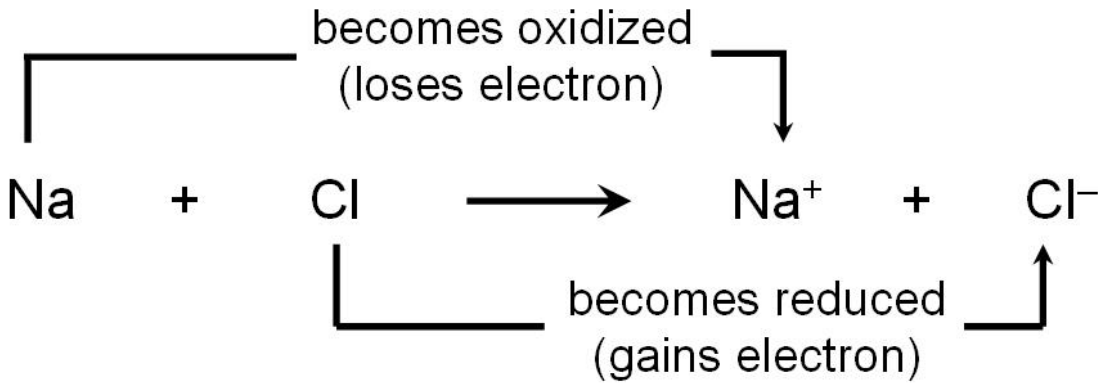

Figure. 2: NaCl gets oxidized and reduced **[5]**

1.4 Modes of Transportations

The displacement of the material or component in any solution due to the different chemical properties or in electrical potential at two distinct points in the solution is discribed as mass transfer. Following are the modes of mass transfer:

1. Diffusion, chemical species movement due to chemical gradient i.e. a difference in concentration.
2. Migration, charged species movement, under the effect of an applied electric field.
3. Convection, consequence of density gradients, happning due to fluid flow that occurs naturally. **[6]**

1.5 Mass Transfer and Electrode Kinetics

According to Faraday's law, a specie which is electically active experiences an electron trasfer reaction results in a current production, which is approximatley proportionally to the amount of reactant.

In a circumstance where this electroactive species is transported exclusively by diffusion to the surface of the electrode, also, no other reactions happened, then the current is identified with the measure of species diffused to the electrode. Generally a faraday's law can be summrized in a simple form as **[7]**:

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right) \qquad (3)$$

m = mass of substance seperated from electrode

Q = total electric charged passed through the substance

F = faraday's constant

M = molar mass of the substance

z = valency number of ions

1.6 Transportation of Charges

The electron reaction that happens at the interface between the chemical solution and the dipped electrode (metal or semiconductor) surface, there is no way to measure the electron transfer rate or reaction between the two interface or an instrument to control the flow between them. This is possible by introducing two electrode metal-electrolyte solution interface. Such system is known as galvanic cell **[1]**

By such interface we can have a better degree of control and measurement of the process. We can play with the reaction by adding an extra control variable switch and observe the process. Similarly, the reactions can be forced, to behave non-spontaneous and the direction can also be controlled. **[1]**

Example:

A small simple electrochemical system can be considered as, a two electrodes, Zinc and Copper are placed in sulfate solution respectively. Both the electrolytes are separated by a thin semi permeable membrane which prevent the mixing but allows ionic transportation.

When the reaction starts, a zinc metal electrode gets oxidized which means electron goes to the solution.

$$Zn = Zn^{2+} + 2e \qquad (4)$$

Similarly, Copper ions in solution gets reduced; deposited on the copper electrode.

$$Cu^{2+} + 2e = Cu \qquad (5)$$

Electrode at which the oxidation reaction occurs is called the anode and electrode at which the reduction reaction occurs is called the cathode. In above example Zinc is anode and Copper acts as cathode. **[4]**

1.7 3-Electrode Setup

There are two electrode mechanism, one is 2 Electrode and other is 3 Electrode system. 2 electrode systems are consisting of working electrode (WE), a counter electrode (CE), shown in figure. 3 **[3]**. Similarly, a 3 electrode system are consisting of working electrode (WE), a counter electrode (CE) and an extra reference electrode (RE). The schematics is shown below in figure. 4 **[3]**:

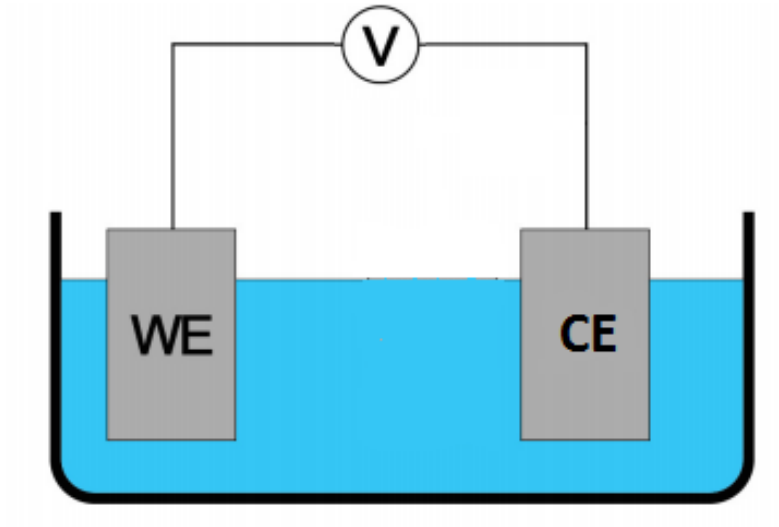

Figure. 3: 2 Electrode setup with working and counter electrode **[3]**

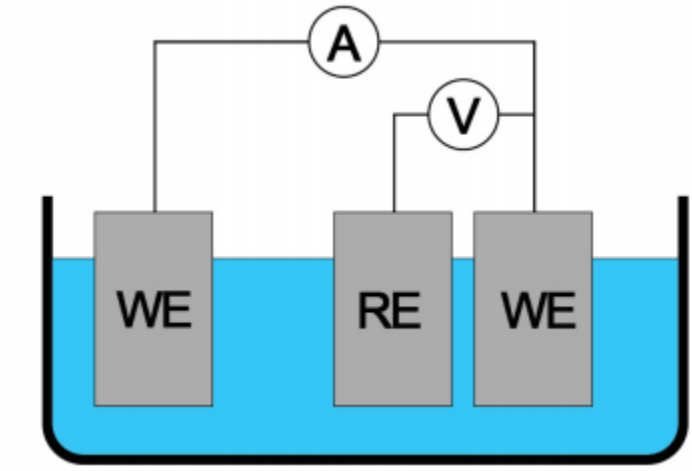

Figure. 4: 3 Electrode setup with working, counter and reference electrode **[3]**

2 electrode systems only measure the potential difference between the electrodes and 3 electrode system can measure the voltage and control them between the working electrode (WE) and reference electrode (RE) and the current flows between CE and WE. **[4]**

1.1 Reference Electrodes (RE):

To measure the precise electrochemical potential which are charge build in or on an electrode, there must exist a proper and well defined mechanism that can be measure easily, that mechanism is known as reference electrode. **[4]**

CHAPTER 2: INTRODUCTION TO DOPAMINE

2.1 Background of dopamine

Dopamine (3-hydroxytyramine; DA) is a catecholamine neurotransmitter available in mammalian brain. Initially it was considered that dopamine has no signaling power but later on in 1958 it was observed that dopamine itself has the signaling ability. Bertle et al, in 1959 proved by their work that DA is available in good quantity at certain positions in brain called basal ganglia. Later in 1965 by Fuxe and in 1971 by Ungerstedt, the pathways, direction and mapping of DA patterning and signaling were displayed and discussed. Weiner and Ganong 1978 presented these pathways as follows: Tuber infundibular pathway, the nigrostriatal pathway, the mesocortical pathway, the mesolimbic pathway.

It has been also found that the location, area and region of pathway plays a crucial role in signaling the brain behavior. (Volkow, Wang et al. 2002; Sotak, Hnasko et al. 2005; Robinson, Rainwater et al. 2007). **[8]**

2.2 Why dopamine

The research in dopamine boosted due to medical application requirement observed in recent decades. The main focus of the research is on neurological diseases and physiological behavior. Some of the diseases are schizophrenia, Parkinson's disease, obsessive compulsive disorder, bipolar disorder, binge eating disorder, and addiction **[4, 9-12]**

The communication inside the brain is performed by a chemical released by the neurons to send signal to other neuron and the dopamine acts as a neurotransmitter in brain. Its one of the major neurotramitter, affecting cognitive, behavioral and motor functions. **[4]**

2.3 Dopamine: Learning, Memory and Motivation

Dopamine is just not about one specific function in human brain. When positively, the dopamine is released a record of that release and function is noted down in a brain which helps to recreate such effect in brain again when needed. While the negative effect, blocks the relase of recorded function which results in not repeating the positive function, hence which effects in overall learning as well.

Researchers belives that such positive and rewarded release of dopanine creates a path and a connection between neurons and if such actions happens for enough time, then it results in a formation of permanet neural pathway which triggers together and helps to recall information overtime. Such effect results in process called as LTP (Long Term Potentiation).

Researchers also beleive that drugs has significant effects on LTP systems. It has been observed for a while that Alcohol has effects on learning memory due to the impact on hippocampus, which is a central part of new memory formation. **[13]**

2.4 Coordination and Structure of neurotransmitter

The communication in between the body and brain is performed by nervous system by conveying signals all over the body in micron of seconds. There are two main types of communication systems of nervous systems.

The central nervous system (CNS)

peripheral nervous system (PNS)

The central nervous system (CNS) contains the coordination between brain and spinal cord while the peripheral nervous system (PNS) contains the nerves that connect the CNS to every other part of the body. **[9][4]**

The composition of neuron is as soma, axon and dendrities. Soma contains the nucleus and organelles in cytosol, axon plays a crucial role to transfer the information and a dendritic tree of the neuron is composed due to the branched projections of dendrites from the sona. **[9, 13 ,4]**

2.5 Electrochemistry and Measurement of Neurotransmitters

Because of electrochemical nature of neurotransmitters, they are divided into three main class. The first class of neurotransmitters are those which have surface reaction on electrode because of they are electrochemically active and undergo redox reaction.

The second class of neurotransmitters are those which do not are electrochemically active, hence cannot be directly detected. Surface modification by enzymatic reaction is done in order to make them electrochemically active. **[4, 14]**

Third class of neurotransmitter are not detected by electrochemical methods, such compounds use microdialysis and subsequent analysis methods. **[4, 14]**

2.6 Techniques for measuring neurotransmitters signals

There are three main techniques which are oftenly used to measure the transmittion signals between neurotransmitters. **[6]**

2.6.1 Electrochemical Detection

Many neurotrasmitter are electrochemically active and those which are not, can also be made electrochemically active hence can be measured via electrochemical detection. **[6]**

2.6.2 Spectroscopic Method

This is technique based on princple in which sample absorbs visible light. Currenly most preffered methods in spectroscopic are positron emission tomography (PET) and functional magnetic resonance imaging (fMRI). **[6]**

2.6.3 Micro dialysis Technique

This technique is based on minimally-invasive sampling method which allow easy measurenment of concentrated liquid, fluid specially related to tissues or neurons. **[6]**

2.7 Physical and Chemical laws for Dopamine Detection

Several laws and principle are involved in dopamine detection. Some of them are listed below, and are not discussed for this work. Such as oxidation, reduction, Faraday's law, The Arrhenius Equation, Butler-Volmer Kinetics, Fick's Laws of Diffusion, Cottrell Equation and many more. **[6]**

CHAPTER 3: MEASUREMENT OF DOPAMINE BY CYCLIC VOLTAMMETRY

3.1 Introduction:

The voltrammetry analysis developed from the branch of electrochemistry was initially discovered by Czech chemist Heyrovsky in 1922. Because of this development, a nobel prize in 1959 was awarded to him due to his great contibution in the field of electrochemistry. At the time of invention, the technology has significent drawbacks and difficulties. Huge development was done in the era of 1960 and 1970. The common principle of all voltammetric techniques includes the potential applied to the electrode and current passing through a electrochemical cell is measured. The applied potention is also varied over the time in order to see the behaviour of current over a time. The reperesentation of these potential, current and time is given as E, I and t in most of the voltammmetric process. **[15]**

3.2 Voltrammetric Technique

There are several techniques of and to perform voltrammetry analysis. The differenc between them exist due the use of potential function on working electrode and the material used as an working electrode. **[16]**

1. Linear Sweep Voltammetry (LSV)

2. Square Wave Voltammetry (SWV)
3. Anodic Stripping Voltammetry (ASV)
4. Normal Pulse Polarography (NPP)
5. Differential Pulse Poralography / Voltammetry (DPP/ DPV)
6. Fast Scan Cyclic Voltammetry
7. Cyclic Voltammetry (CV)

For our research we are concern for Cyclic Voltammetry technique.

3.3 Cyclic Voltammetry

Cyclic voltammetry (CV) is famous for its simplicity for the functionality and for the high detailed information content for potentio-dynamic electrochemical measurement. Cyclic voltammogram trace is obtained when the current at working electrode is plotted graphically against the applied potential for that respective counter electrode. CV analysis gives the best study not only for the electrochemical properties of an analyte but also for the oxidation and reduction patterns and rates for specific specie deposition on electrode in a sample of chemical solution. CV can also be used to determine the diffusion coefficient of an analyte, and the formal reduction potential of an analyte, which can be used as an identification tool. In addition, because concentration is proportional to current in a reversible, Nernstian system, the concentration of an unknown solution can be determined by generating a calibration curve of current vs. concentration.

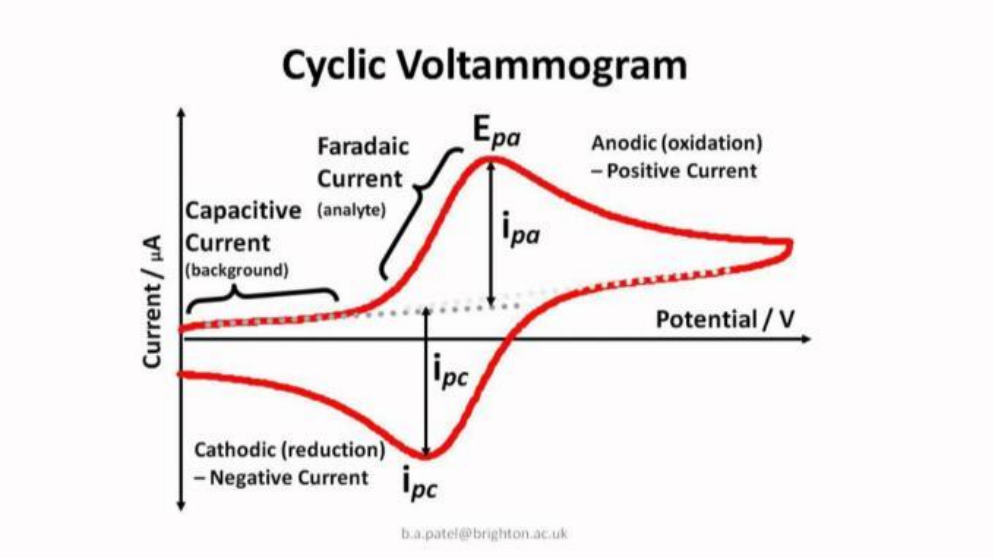

Figure. 5: CV graph with forward and reverse scan **[17]**

The waveform of the voltage applied to a working electrode in CV is triangular shaped (i.e., the forward and reverse scan). Since this voltage varies linearly with time, the scan rate is the slope (V/s). An example of a CV is shown in figure 5. The peak shape of the reductive and reverse oxidative current vs. electrode potential curve (I-E) in figure. 5. It is typical of an electrode reaction in which the rate is governed by diffusion of the electroactive species to a planar electrode surface. **[18-21]**

3.4 EIS (Electro Impendency Spectroscopy)

Besides CV, "Electrochemical Impedance Spectroscopy (EIS)" technique is a reliable way to measure the solution Resistance and Capacitance developed on electrode systems due to deposition of monolayer R(Ohmic) and R(Ohmic)+R(ct) which gives blockage at the electrode surfaces by giving more resistance readings; it can estimate state-of-charge and

capacity. EIS is able to read each component of the Randles model individually; however, analyzing the value at different frequencies and correlating the enormous data quickly. Impedance measuring is a complex phenomenon and it is one of the electrochemical measurements that is being used in number of fields (Biosensor, corrosion measurements and surface coating evaluation, fuel cells and many more.

CHAPTER 4: LITERATURE REVIEW

4.1 Surface modification of Electrodes

One of the major contribution for surface modification of electrodes in an electrochemical analyte solution was demonstrated by Heiskanen **[22]** et.al., in year 2006. Since DA responds ineffectively on gold, six thiols; hydroxy-terminated, having negative charge on them, carboxy-terminated and positively charged were screened for their preventive impact on electrochemically prompted DA poly-merization. It was found that changes with the weakcarboxy corrosive MPA had the best impact on DA electrochemistry and significantly forestalled electrochemi cally incited DA polymerization.

It was observed that mercaptopropionic acid (MPA), possessing weak acid functionality, decreased the rate of dopamine polymerization resulting in least electrode passivation of Au electrode. It was also found that modifications of microchip electrodes with MPA did not only improve dopamine electrochemistry but also significantly increased the storage stability of the transducers. **[22]**

4.2 Bonding Techniques on Chips

Device integration process was discussed, integration of polymer substrate with microfluidic channels with electrodes by using the Ultrasonic and UV bonding technique. To lower the resistance of overall system, optimazation was done on diffrent parameter for both ultrasonic and UV bonding technique i.e. welding energy, bonding temperature, seed layer. Further more the performance of both techniques were analysied by Cyclic voltammetry (CV) and Electro Impedence Spectroscopy (EIS).

In light of resistance estimations and CV characterization, electrodes on UW-bonded chips had essentially better electrochemical execution in contrast with TB chips. CV assessment likewise demonstrated that in a clump of manufactured UW chips, near 100% of electrodes were completely useful, while in a bunch of TB chips fortified utilizing the enhanced parameters, a few chips had absolutely non-utilitarian electrode. In addition, EIS portrayal exhibited that electrode on UW chips had low chip-to-chip variety of both charge exchange resistance and double layer capacitance. **[23]**

4.3 Measurement Techniques

Apart from the CV analysis measurement, an impedance spectroscopic study of the interaction between thiol-modied Au electrodes and Saccharomyces cerevisiae was presented first in year 2008 by Heiskanen **[24]** et.al., in which monolayer coverage was reached after 20-28 h of cultivation, and was observed as 15 percent decrease in the real capacitance of the system by cysteamine-modied Au microelectrodes techniques. It was also

seen that after an addition of S. cereVisiae cells at pH 7.2, the obtained value of R(ct) showed over 560 percent from the value obtained on the same thiol- modied electrode. **[25-29]**

4.4 Our Objective

The main objective of this presented work is to give a better understanding on the comparative study of targeted dopamine detection with two modifications for the surface of Au electrodes i.e., (1) Cysteamine and (2) Mercaptopropionic acid (MPA) for thermally bonded and ultrasonically welded microfluidicchips respectively. The influence of both bonding techniques along with the selection of optimized tubing for the fabricated microfluidic device and cleaning functions with KOH has also been illustrated for better calibrations and results. Additionally, results for comparison of the modification with unmodified chips, and finding the unknown concentration of dopamine solution using flow injection techniques is also presented.

CHAPTER 5: MICROFABRICATION

5.1 Electrode Fabrication

Electrodes were fabricated on an injection molded COC substrate having dimensions of 50 mm diameter and thickness of 2 mm by the following fabrication steps:

First of all, substrate was spin coated with 10um thick layer of positive photoresist AZ (4562 Standard) to be used as a etching mask. Then UV exposure through chrome mask using Mask Aligner was applied and was developed afterwards. Reactive Ion Etching (RIE) was then used with a power of 150W; pressure of 300 mTorr, gas composition of 80 % of Oxygen and 20 % of Nitrogen, to create grooves for embedding metal structures of dimensions (depth: 5 um for ultrasonically welded chips; and 900 nm for thermally bonded chips). The resist was stripped of in an acetone by ultrasonic bath. Resulting substrate was again spin coated with AZ (4562 Standard) positive photoresist and was then exposed in UV and was developed further. E-beam evaporation method was used to deposit first 20 nm Titanium layer for adhesion and support purpose and then finally 200nm thick layer of Gold (Au) was deposited for electrode functionality. Lift- off process in acetone using ultrasonic bath was used to strip off metal coated photoresist. Figure 6 shows the schematic of electrode fabrication.

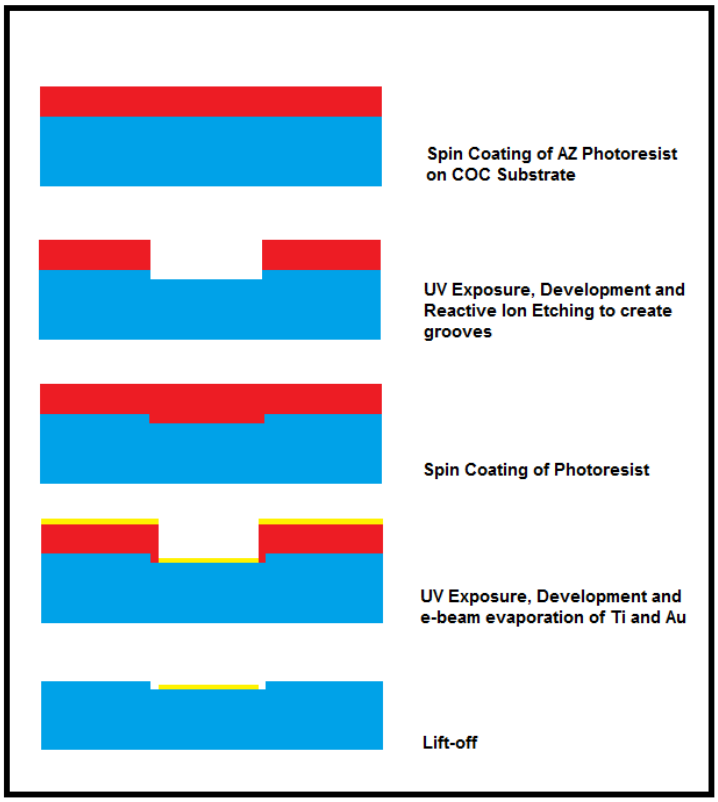

Figure. 6: Process flow of gold electrode fabrication

Below in figure 7 is the completed electrode fabrication on Cyclic olefin copolymer (COC) substrate. A electrode patterns can be seen on the substrate clearly.

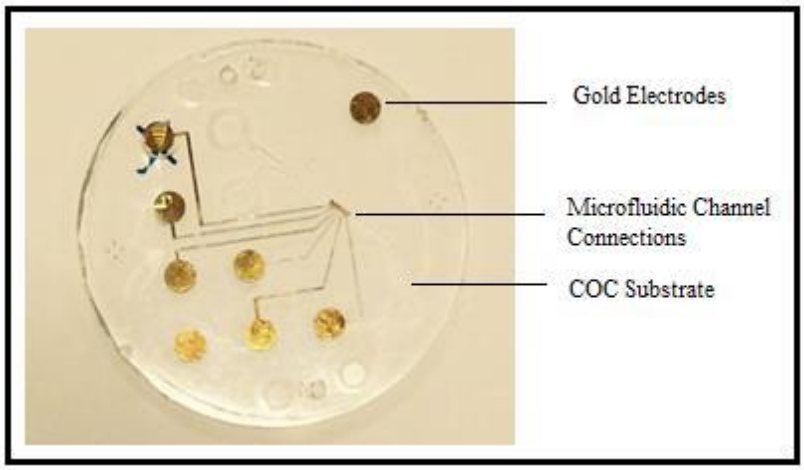

Figure 7. Gold electrode fabricated on COC substrate

5.2 Silicon Mold Fabrication

Silicon Wafer substrate mold was generated to create a Nickle shim out of it using Injection molded technique. The steps to create Si Mold are given as follows: Si wafer substrate was first spin coated with 1.5 um thick layer of AZ MIR (701 Standard) at 4600 rpm and was pre baked at 90 ºC for 60 seconds. UV exposure of 169 mJ / cm.sq using hard contact recipe of mask Aligner. Then it was developed further with TMAH surface puddle for 60 sec to get rid of excessive photo-resist. The resulting substrate was then dry etched first for 5 um and for 5 minutes and substrate surface was further smoothened by using Plasma Asher for 30 minutes at 400 ml / min O_2, and 70 ml / min N_2 at power of 100 W to make it ready for metal deposition for creating shim. figure 8 shows the schematic of Si mold fabrication for nickle shim.

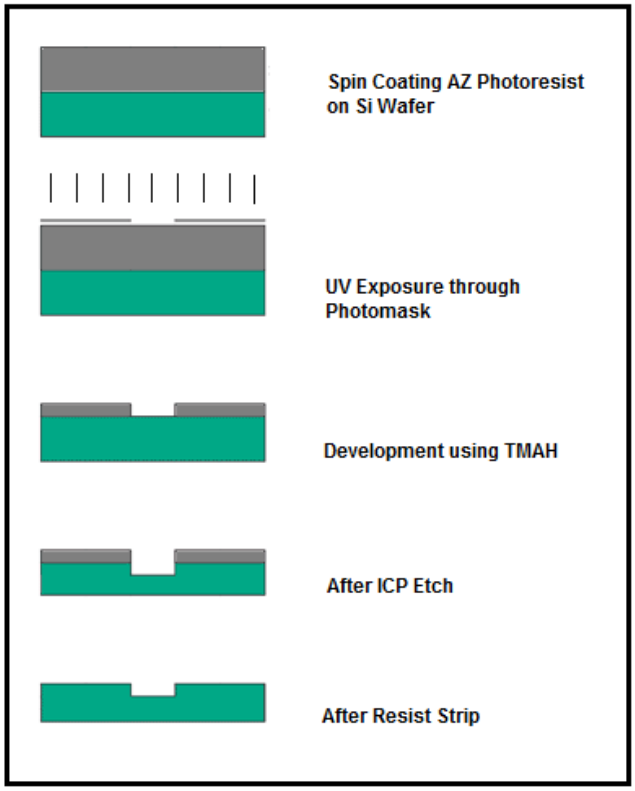

Figure 8. Process flow of photolithography process for silicom mold

5.3 Shim Fabrication

Nickle Shim was made out of Silicon Mold substrate fabricated in above procedure with the steps mentioned as follows:

Seed metallization of Nickle Vanadium (NiV) alloy was carried out at the specifications of 1000 seconds of time, 5 mtorr of pressure, and power of 157 W using sputter system. Electroplating of Nickle was then proceeded for upto 6 hours and 13 mins of deposition procedure to get the required thickness for the Ni shim. Silicon wafer was then removed using wet etching KOH process in fume-hood with 25 wt % of KOH at 80 ºC for 6-8 hours. figure 9 shows Nickle shim fabrication steps.

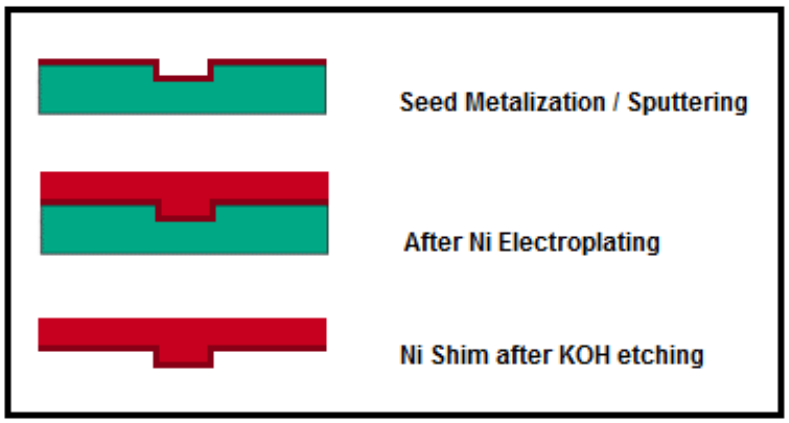

Figure 9. Process flow of nickle shim fabrication

5.4 Device Fabrication by Injection Molding

Nickle shim was then used to fabricate required microfluidic devices of COC substrate using Injection Molding techniques as explained in following steps:

Once the Nickle shim was created and separated from Silicon wafer, it was cut with 1064 nm Laser Micro machining tool using 255mm optics with a laser power of 1.9 W at 10 %. After cutting, Nickle shim was cleaned in water with ultrasonics for 10 minutes and was rinsed and wiped. The main task of polymer injection molding was then carried out in Topas 5013L10 polymer using Injection molding tool for the replication of structures on polymer devices. Figure 10 shows Injection molding steps from Nickle shim.

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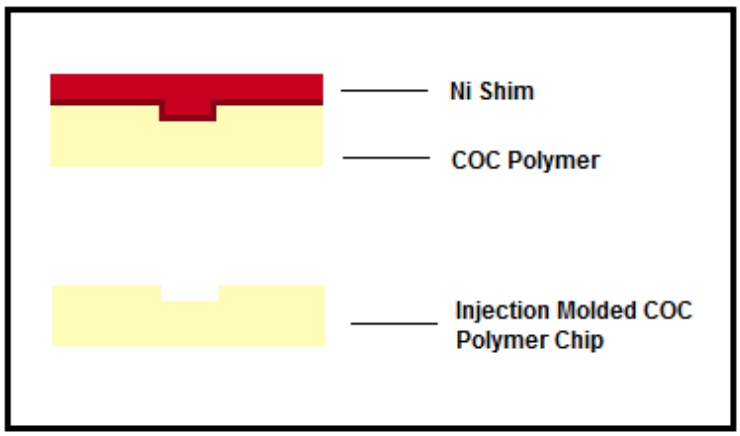

Figure 10. Process flow of injection molded chip

5.5 Bonding Methods of Microfluidic Chips

Two methods for Bonding of Microfluidic chips were used for the devices made above with channels dimensions of 400 um in width and 80 um in height. Those two techniques are detailed below:

5.5.1 Ultrasonic welding

20 KHz Telesonic USP4700 welder tool was used to bond the two chips together to make a full real time device for testing with bonding specifications as 1 atm welding pressure, 0.35 seconds hold time, with energy directors: base 100 um and height 8um.

5.5.2 UV assisted Thermal Bonding

First, UV exposure for 30 seconds using 5000-EC series UV curing Flood Lamp system was given and then the two chips were thermally bonded with the specifications as (1kN, 125ºC for 10 mins) using PW20 hydraulic press tool.

5.6 Complete Fabricated Device

Below is the labelled schematic of the whole bounded working chip. There are in total four working electrode, a counter electrode, reference electrode and microfluidic inlet and outlet as shown in figure 11 and figure 12.

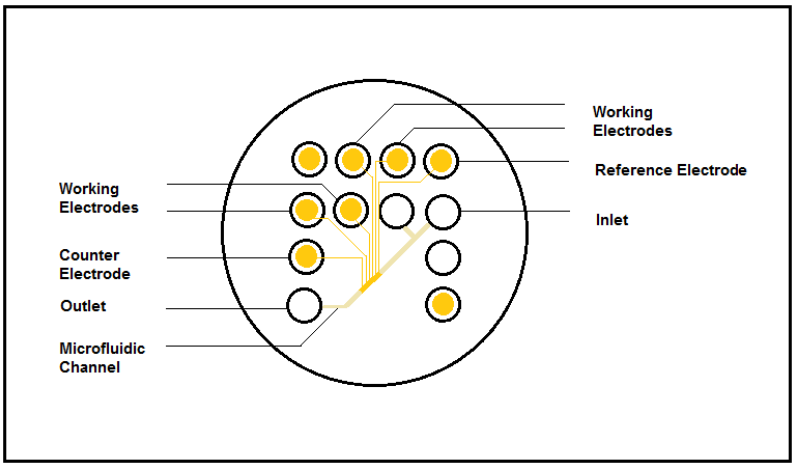

Figure 11. Schametic of complete fabricated chip

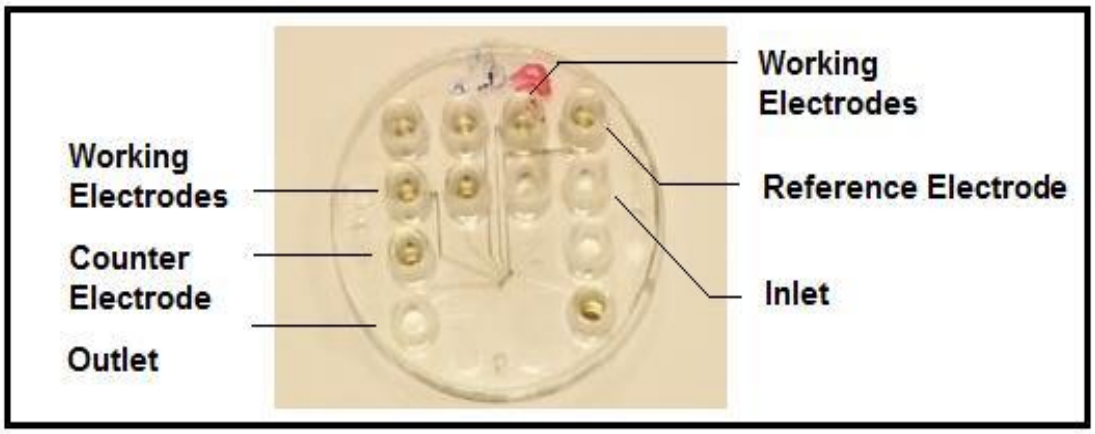

Figure 12. Complete chip after fabrication and bonding

CHAPTER 6: RESULTS AND DISCUSSIONS

6.1 Effect of Cleaning Procedure on Analyte Signal

Two chips which were thermally bonded and ultrasonically welded were first tested before making any cleaning on to them and it was observed that on different scan rates for cyclic voltammetry (CV), the peaks for current were in range from 12 to 14 micro-amperes (uA) respectively. While after cleaning with KOH solution, not only current values were improved but also the sensitivity was observed close to ideal scenario. Figures (13, 14, 15, 16) show the CVs for both chips which were bonded using different methods as mentioned above.

Electrochemical impedance spectroscopy results also demonstrate that cleaning had a clear effect on both typed of bonded chips in a matter of reducing initial overall impedance. Also the effect of KOH cleaning on both devices show less deviation from the ideal behavior as compared to their respect uncleaned states. Figure (17, 18) show these vivid impact of KOH treated surface of electrodes.

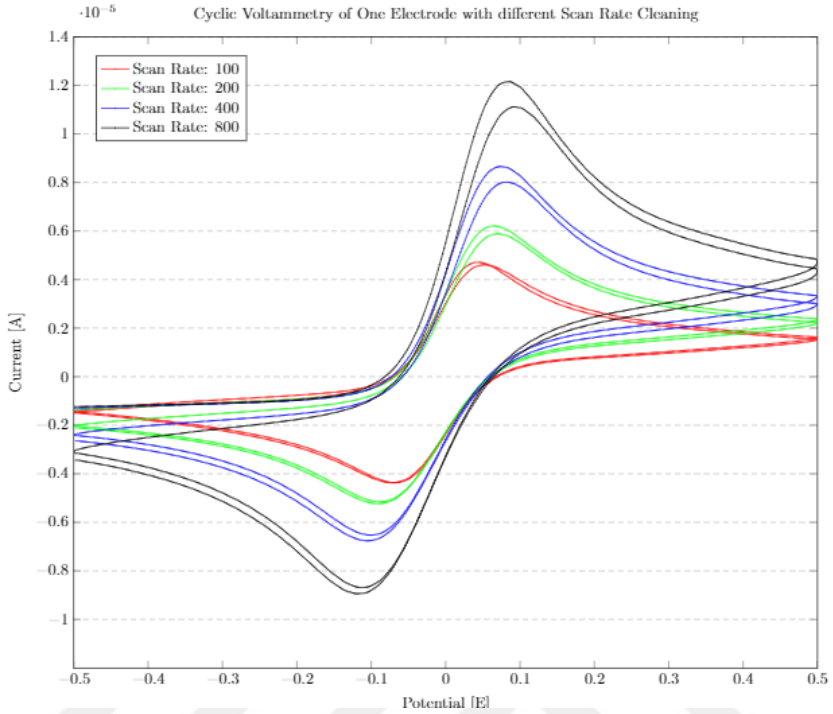

Figure 13. Cyclic Voltammograms at different scan rates for uncleaned thermally bonded chip

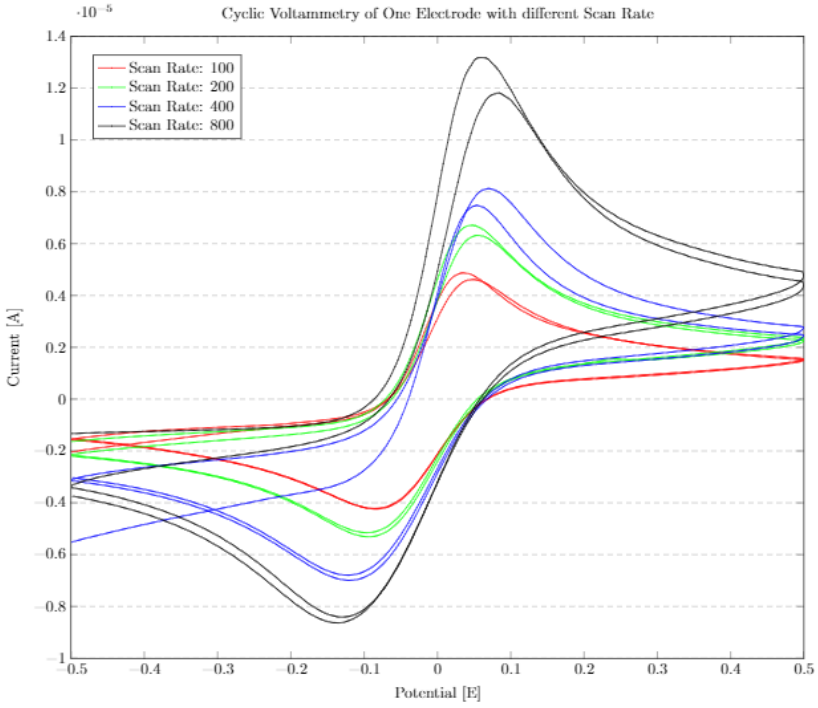

Figure 14. Cyclic Voltammograms at different scan rates for cleaned (with KOH) thermally bonded chip

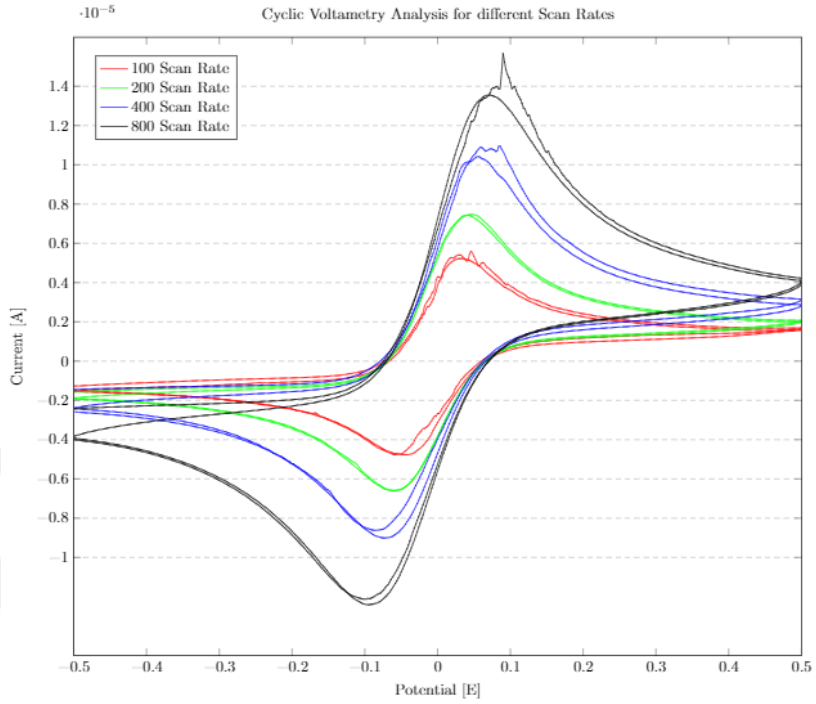

Figure 15. Cyclic Voltammograms at different scan rates for uncleaned ultrasonically welded chip

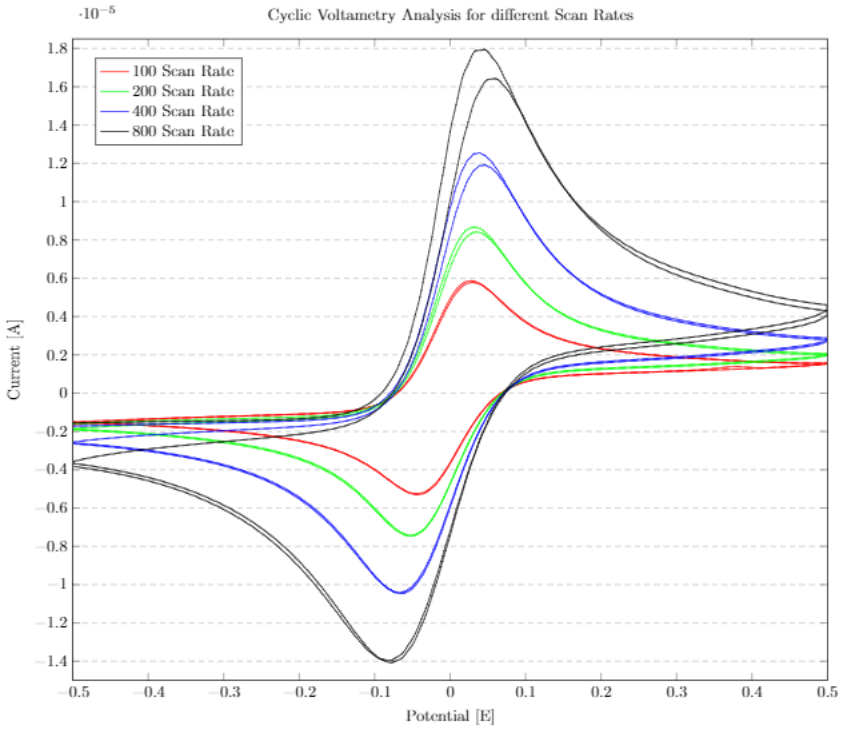

Figure 16. Cyclic Voltammograms at different scan rates for cleaned (with KOH) ultrasonically welded chip.

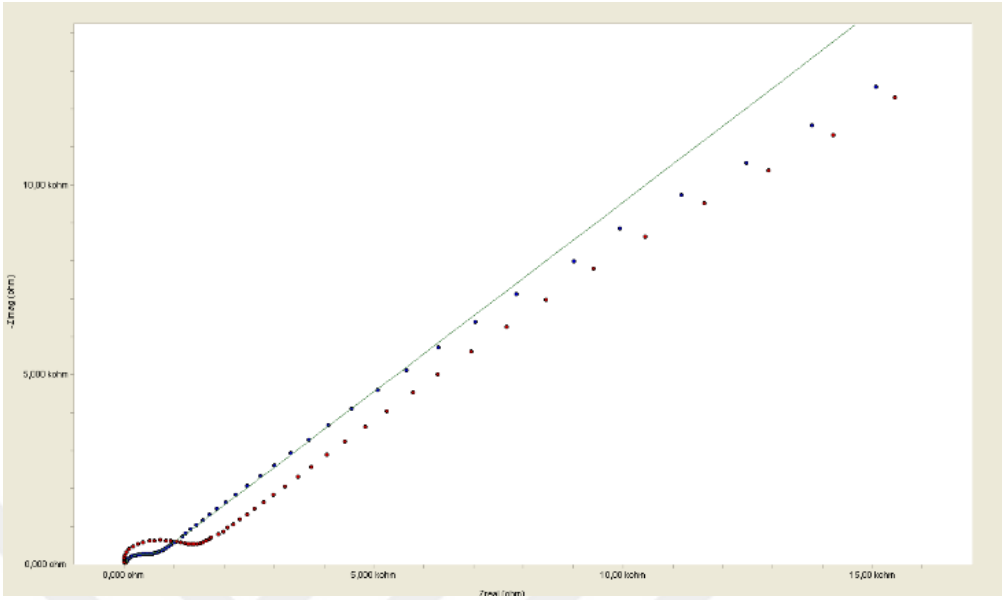

Figure 17. Impedance Spectroscopy for cleaned and uncleaned thermally bonded chip

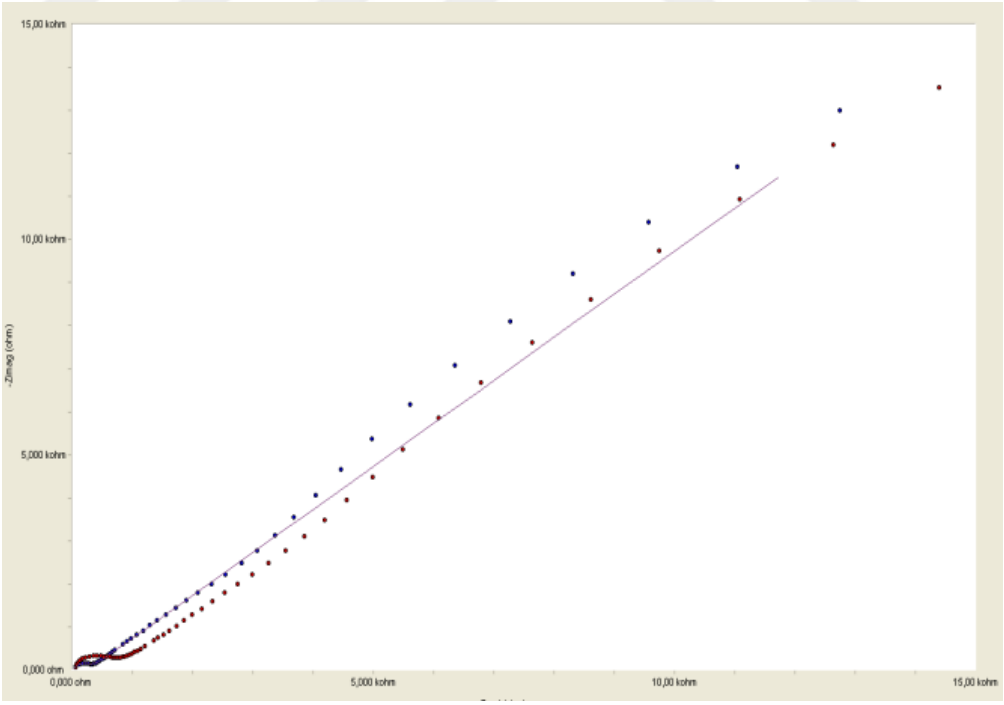

Figure 18. Impedance Spectroscopy for cleaned and uncleaned ultrasonically welded chip

6.2 Influence of Surface Modification on Charge Transfer Properties of Dopamine

Comparative study of unmodified and mercaptopropionic acid (MPA) modified ultrasonically welded chip is demonstrated in figures (19, 20). It is found that mercaptopropionic acid decreased the rate of dopamine polymerization. MPA, possesses a weak acid functionality which had the greatest effect on the dopamine electrochemistry by decreasing electrode passivation, as well as improving reversibility and sensitivity closer to ideality. Besides that, result for thermally bonded chip with cysteamine modification in figure 21 also shows a good deal for less electrode passivation and better reversibility of cyclic voltammograms. EIS results in figure 22 shows comparison of two modifications on electrochemistry of dopamine.

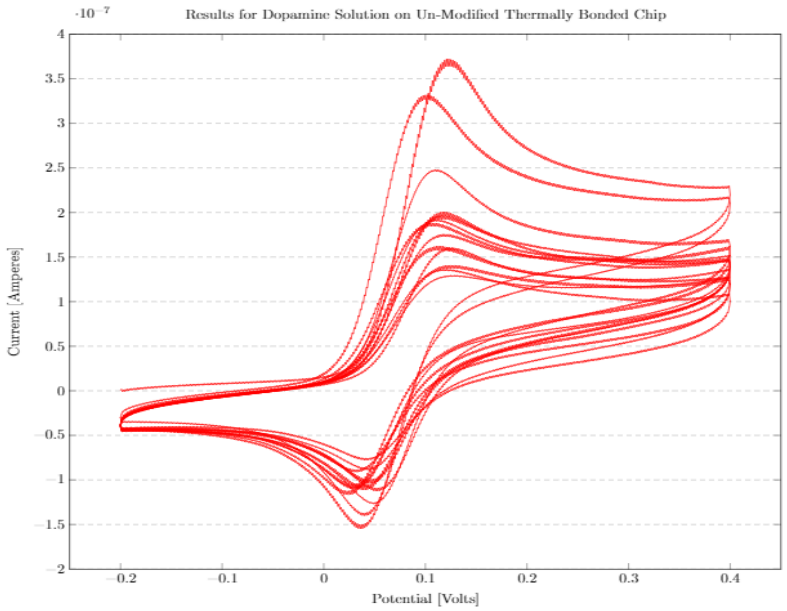

Figure 19. CVs of Dopamine detection on unmodified ultrasonically welded chip

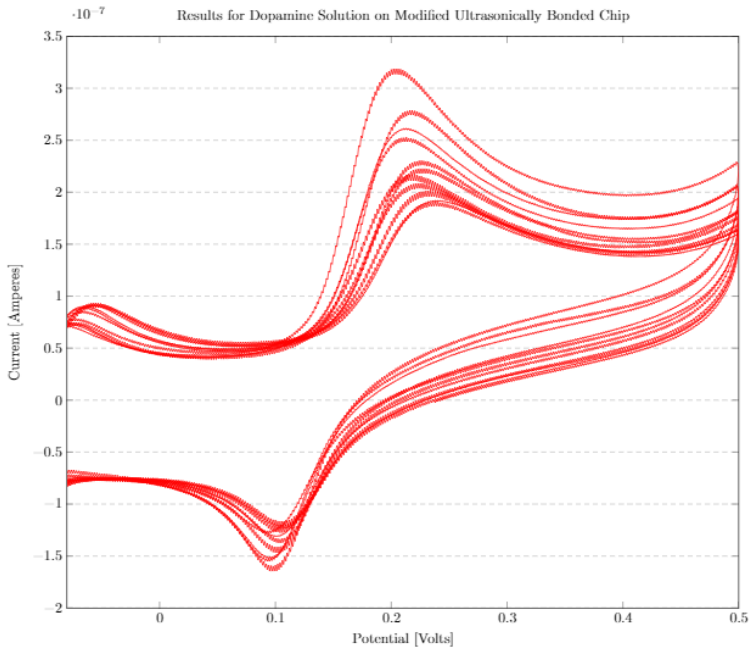

Figure 20. CVs of Dopamine detection on MPA modified ultrasonically welded chip

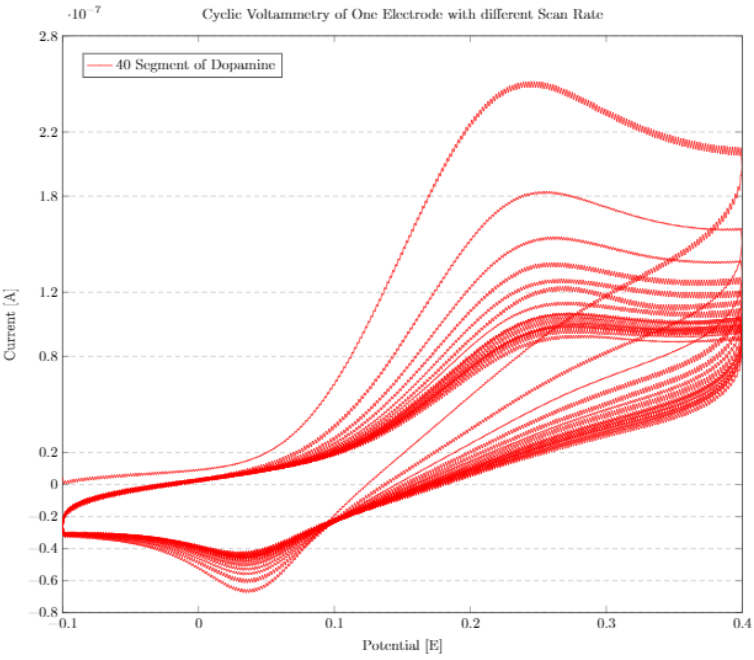

Figure 21. CVs of Dopamine detection on Cys modified thermally bonded chip

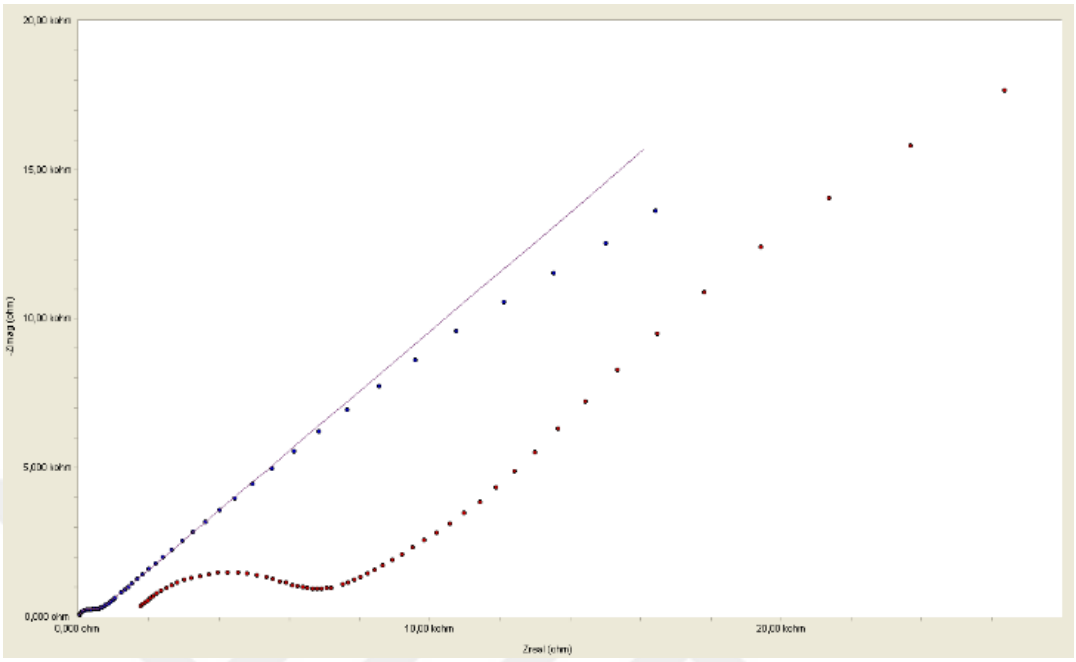

Figure 22. Impedance spectroscopy for dopamine detection on thermally and ultrasonically bonded chip

6.3 Flow Injection Analysis

6.3.1 Effects of Different Tubings

Tubings having different dimensions were tested to select an optimal tubing which can prove to be best suitable for the flow-injection method for the developed microfluidic chip. Three tubings with dimension (500 um Diameter, 15 cm length), (750 um Diameter, 15 cm length) and (500 um Diameter, 30 cm length) as show in figure 23 were examined at 750 flow rate for their respective functionalities. And result in figure 24 shows that the first mentioned tubing not only improved the functionality of flow rate but also provided with the highest current values in flow injection process.

6.3.2 Unknown concentration detection of dopamine and ferrycyanide by known concentration spectra

Figures (25, 26) show the unknown concentration detection for both solutions i.e., ferricyanide and dopamine by using known concentrations of the respective analyte solutions using cyclic amperometry in injection flow analysis. Some known concentrations are first evaluated before checking the unknown concentration of solution in order to detect the value for that required unknown concentration of an analyte.

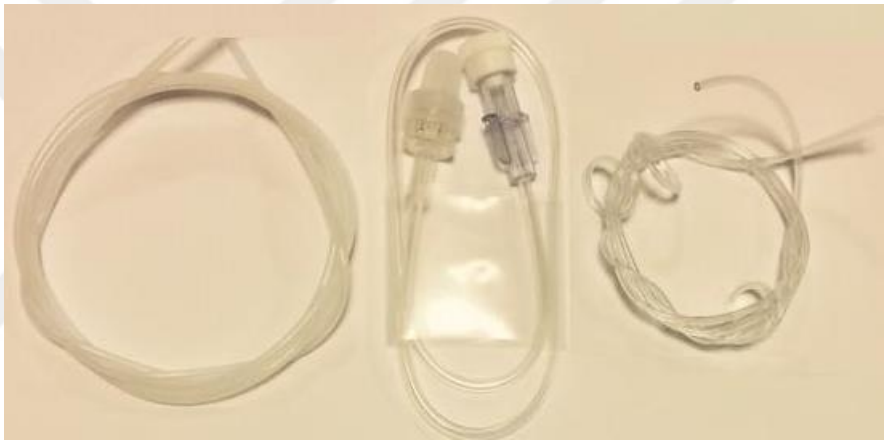

Figure 23. Tubing with different dimensions to find the suitable dimension for the flow-injection method

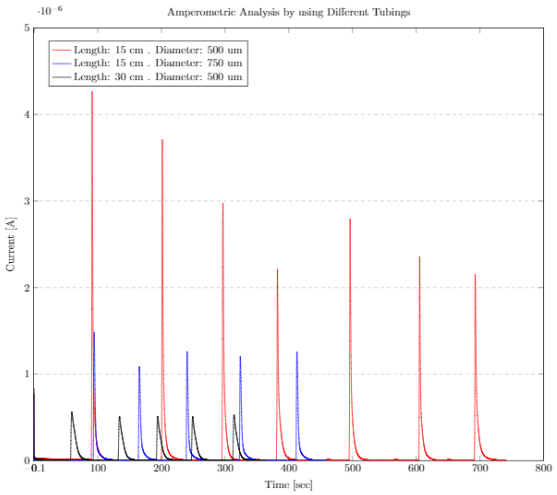

Figure 24. Influence of different Tubings

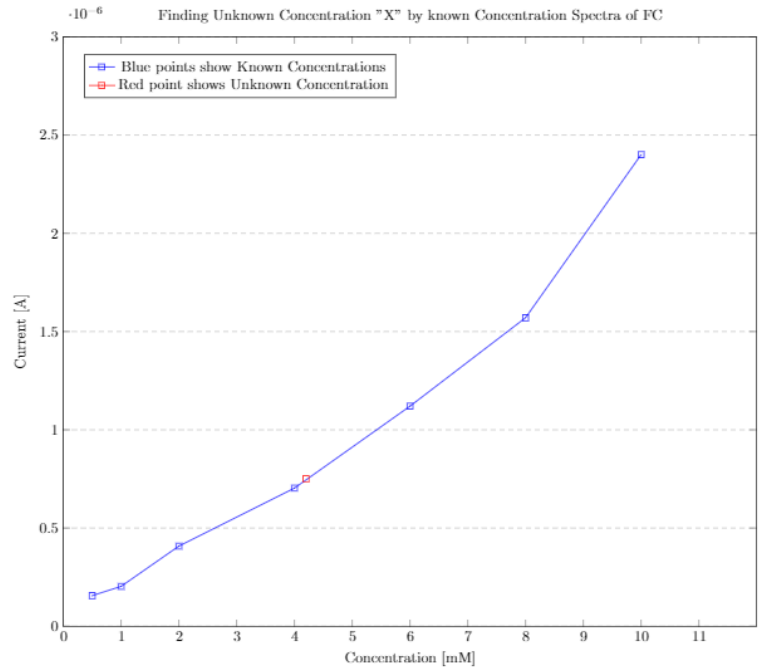

Figure 25. Cyclic amperometry results for detection of unknown concentration of ferricyanide analyte

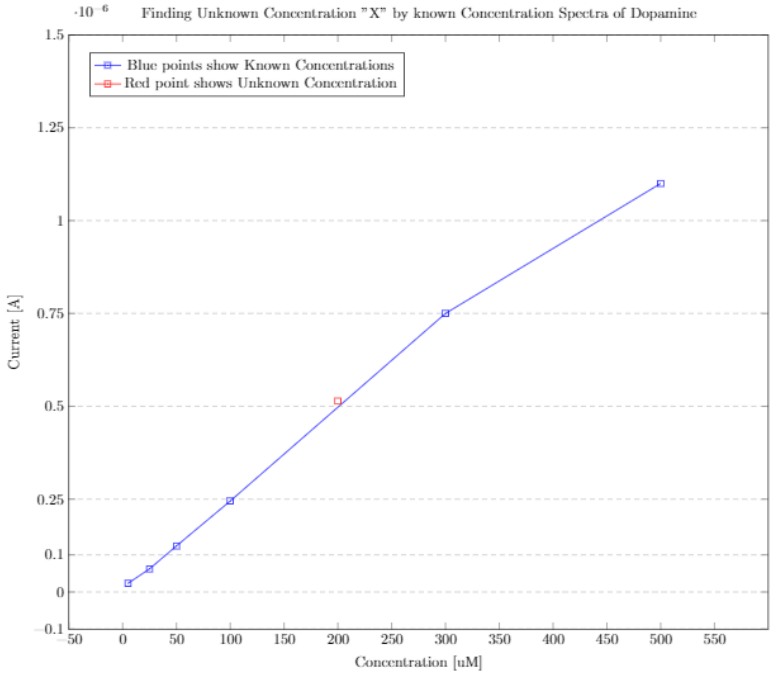

Figure 26. Cyclic amperometry results for detection of unknown concentration of dopamine analyte

7. CONCLUSION

A comprehensive study for different surface modification for electrodes, different bonding techniques and flow injection analysis is presented to detect the best optimal detection of dopamine on electrodes. It is found that modification with mentioned chemicals not only improved the peak current values for dopamine detection but also provided great sensitivity and reversibility of dopamine cyclic voltammograms. Influence of various tubings and cleaning with KOH effects also helped significantly in ameliorating the outcomes.

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