

TOBB UNIVERSITY OF ECONOMICS AND TECHNOLOGY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

**DEVELOPMENT OF SYNTHETIC NERVE ENDINGS FOR
AXO-AXONAL TRANSPORT AND TESTING AS ACETYLCHOLINE ION
PUMP**



MASTER THESIS
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APRIL 2017

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Nazrin ABDULLAYEVA

ABSTRACT

Master of Science

DEVELOPMENT OF SYNTHETIC NERVE ENDINGS FOR AXO-AXONAL TRANSPORT AND TESTING AS ACETYLCHOLINE ION PUMP

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Currently, more than 450 million people are globally suffering from some types of neurological diseases that can hardly be treated. These diseases are caused by distorted electrical and neurochemical signaling in the nervous system. The awareness of this worldwide problem is not brought in yet and definitive treatment has not been introduced so far. Most of therapies associated with neurological disorders are based on medical treatment such as medical therapy or electric stimulation. However, results are temporary and ineffective. The major effect obtained so far, was to conceal the disease and this was just not enough. In our study, by taking into consideration this problem we are presenting a biomimetic system that duplicates the function of a neural cell and helps to reinstitute the defective electrochemical transport of nervous system. Nerve impulses are communicated across synapses by diffusible molecules called neurotransmitters, of which one is acetylcholine. Acetylcholine molecules are contained in the axon foot inside vesicles. After the release of acetylcholine into the synaptic cleft, it binds to the cholinergic receptors located on the postsynaptic neuron and mediate

excitation or inhibition on postsynaptic cells and thus causing the transportation of neural signal. The system developed by our group resembles a two electrode structure with PEDOT:PSS deposited on them and a tiny 2 mm overoxidized region that cuts off electrical conductivity thus allowing only ionic transport. By using an easy and effective method of depositing conjugated polymers (PEDOT:PSS) on flexible substrates, a new design for organic bioelectronic devices has been developed. FTIR and Raman measurements have demonstrated that electrochemical overoxidation region which separates the PEDOT:PSS electrodes and allows ionic conduction has been achieved successfully. The influence of both electrical and ionic conductivities on organic electronic ion pump (OEIP) performances has been studied. The highest equilibrium current density, which corresponds to 4.81×10^{17} number of ions of acetylcholine was about $41 \mu\text{A cm}^{-2}$ observed for the OEIP with the electrical conductivities of 54 Scm^{-1} . The OEIP performances were not changed much beyond this threshold electrical conductivity. Once Nafion™ has been applied for enhancing the ionic conductivity, the equilibrium current density increased about ten times and reached up to $408 \mu\text{Acm}^{-2}$. Therefore, it has been demonstrated that the OEIP performance mainly scales with the ionic conductivity. A straightforward method of producing organic bioelectronics is proposed here giving rise to their effortless mass production in the near future.

Keywords: Ion pump; Electrically conductive polymers; PEDOT:PSS; Ionomers

ÖZET

Yüksek Lisans Tezi

AKSO-AKSONAL İLETİM İÇİN SENTETİK SINIR UÇLARI GELİŞTİRİLMESİ VE ASETİLKOLİN İYON POMPASI OLARAK TEST EDİLMESİ

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Günümüzde 450 milyondan fazla insan, tedavi edilemeyen nörolojik hastalıklardan küresel olarak muzdarip. Bu hastalıklar, sinir sisteminde bozulmuş elektriksel ve nörokimyasal sinyallerden kaynaklanır. Dünya çapında bu sorunun farkındalığı henüz kazandırılmadı ve bugüne kadar kesin bir tedavi yöntemi bulunamadı. Nörolojik bozukluklarla ilişkili tedavilerin çoğu tıbbi terapi veya elektrik stimülasyonu gibi tedavi yöntemleridir. Bu tedavi yöntemlerinden elde edilen sonuçlar ise maalesef geçici süreliğine etkilidir. Çalışmamızda, bu problemi göz önüne alarak, bir sinir hücresinin işlevini çoğaltan ve sinir sisteminin kusurlu elektrokimyasal iletiminin tamir edilmesine yardımcı olan bir biyomimetik sistemi sunmaktayız. Sinir uyarıları, sinapslar boyunca sinir iletilen olarak adlandırılan asetilkolin molekülleri tarafından iletilir. Asetilkolin molekülleri, veziküllerin akson ayağında bulunur. Asetilkolin'in sinaptik yarığa salınmasından sonra, postsinaptik nöron üzerinde bulunan kolinerjik reseptörlere

bağlanır ve postsinaptik hücreler üzerinde uyarılma veya inhibisyona aracılık eder ve bu şekilde sinir sinyalinin taşınmasına neden olur.

Grubumuz tarafından geliştirilen sistem, üzerinde PEDOT:PSS bulunan iki elektrot ve yalıtılmış, sadece iyonik taşınmaya izin veren 2 mm'lik aşırı okside bölgeye sahiptir . Esnek yüzeyler üzerinde konjuge polimerlerin (PEDOT:PSS) kaplanmasının kolay ve etkili bir yöntemi kullanılarak, organik biyoelektronik cihazlar için yeni bir tasarım geliştirilmiştir. FTIR ve Raman ölçümleri, PEDOT:PSS elektrotlarını ayıran ve iyonik iletme izin veren elektrokimyasal aşırı oksidasyon bölgesinin başarıyla elde edildiğini göstermiştir. Asetilkolin iyonlarının 4.81×10^{17} kadarına tekabül eden en yüksek akım yoğunluğunun 54 Scm^{-1} elektriksel iletkenliği olarak gözlemlenen yaklaşık $41 \mu\text{Acm}^{-2}$ idi. Organik elektronik iyon pompası performansları bu denge iletkenlik değerinin çok ötesinde değişmedi. Nafion TM, iyonik iletkenliği arttırmak için uygulandığında ise, denge akım yoğunluğu yaklaşık on kat artmış ve $408 \mu\text{Acm}^{-2}$ 'ye ulaşmıştır. Bu nedenle, OEIP performansının esas olarak iyonik iletkenlik ile ölçüklendiği gösterilmiştir. Yakın gelecekte zahmetsizce seri üretim yapmalarını sağlamak için, organik biyoelektronik üretimi basit bir yöntem önerilmiştir.

Anahtar Kelimeler: İyon pompası, Elektrisel iletken polimerler, PEDOT:PSS, İyonomerler

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ABBREVIATIONS

OEIP	: Organic Electronic Ion Pump
PEDOT:PSS	: Poly(3,4-ethylenedioxythiophene)Polystyrenesulfonate
PET	: Poly(ethylene terephthalate)
PVC	: Polyvinyl chloride
WHO	: World Health Organization
AChCl	: Acetylcholine Chloride
KCl	: Potassium Chloride
CaCl₂	: Calcium Chloride
UV	: Ultraviolet
IPA	: Isopropyl Alcohol
EG	: Ethylene Glycol
NMP	: N-methyl-2-pyrrolidone
DMSO	: Dimethylsulfoxide
LiClO₄	: Lithium perchlorate
IR	: Infrared
FTIR	: Fourier Transform Infrared
AFM	: Atomic Force Microscope
RMS	: Root Mean Square
NaClO	: Sodium Hypochlorite

LIST OF SYMBOLS

The symbols used in this study are presented below along with their explanations.

Symbols	Explanation
σ	Protonic Conductivity
ρ	Resistivity
l	Path Length Between Electrodes
A	Cross sectional area available for protonic transport
Z'	Real part of impedance response
W	Width of Sample
T	Thickness of Sample

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1. INTRODUCTION

1.1 Aim of the study

Taking into account the continuously developing neurological diseases and disorders, the following study aims to develop a certain way of curing it by using bioelectrical applications. By transferring the working principle of neuronal transport via neurotransmitter motion to laboratory scale, our self-developed system mimicks the same process by using a simple ion pump structure. We are also aiming to obtain maximum current and ion transfer with lowest applied driving force.

1.2 Motivation of the Study

Nerve cells are building blocks of our nervous system. Although they are classified as cells, their operation mechanism vastly differs from that of others. Nerve cells or in other words neurons are able to share information in-between by using electrochemical signals. This intracellular communication process is a chemical-electrical-chemical process that works due to the motion of ions. This inner communication induces our thoughts, motions, reactions and reflexes. The communicating part of the information-delivering cell is called presynaptic neuron and of the information, receiving cell is postsynaptic neuron. Although the communication is uninterrupted, the interesting fact is that these two cells never touch and this is why the messaging is called electro-chemical. The basic principle that lies behind that is the bunch of sequential chemical processes that involves motion of tiny macromolecules called neurotransmitters. Neurotransmitters diffuse across the synaptic cleft, a tiny gap between presynaptic and postsynaptic neuron, get linked to receptors on postsynaptic neuron and allows the headway of the information. When the transfer of neurotransmitters through synaptic cleft is disturbed or interrupted, this gives rise to some neurological disorders.[1] Diseases such as Alzheimer, epilepsy and

other physical disorders arise from the lack of specific neurotransmitter and their proper transport is what we are willing to obtain. According to statistical numbers reported by World Health Organization (WHO), in 2005 neurological disorders constituted 12% of total deaths globally. These values keep on constantly increasing and since neurological malfunctioning are such big threats to our world at the moment, a prevailing method of curing has to be developed. [1] Our study focuses on developing an effective solution to abnormalities in neural functioning, by designing a simple but potent structure that mimics the electro-chemical communication system similar to that of neurons. Here the main mission is to rehabilitate the transport of neurotransmitters through synaptic cleft and to further neural activity. Due to the recent advancements in the area of electrochemical flexible devices, the proposed structure for mimicking the electrochemical communication of neural cells was decided to be applied on conjugated polymers. Taking into account the fact that even conjugated polymers do not provide a very high conductivity, several precautions have been taken in order to provide proper current values.

1.3 Conductive Polymers and Ionomers

It is a known thing that polymers like plastics or rubbers have resistance to electrical conductivity and act as either dielectric materials or insulators. However, with the invention of polyacetylene, the very first conductive polymer, this idea has changed. From now on conductive polymers are receiving a great significance and interest in scientific and technological fields. Especially in the area of bioelectronics and polymer-based electronics the huge demand for these materials grows daily. The properties that make conductive polymers so attractive is that their electrical conductivity can be tailored with various doping levels. At the same time, these materials are highly flexible and thermally stable allowing their utilization in everyday applications. In some very popular fields like LEDs or supercapacitors, conductive polymers make a significant difference in performance over conductive metal oxides. The working principle of electrical charge flow in conductive polymers is generated as a result of electrical potential. Negatively charged electrons are driven towards the positive pole and generate current while passing from one atom to another. However, in

comparison to metal electrons, the electrons of polymers are not usually delocalized and their motion is much harder. While investigating the structure of most conductive polymers an alternating single-double bond pattern can be seen in Figure 1.1, which represents a conjugated backbone. [2] Here the double bonds known as pi bonds, strengthen connection between atoms by allowing the electron flow as a result of formation of delocalized orbitals. In this situation, the mobility of electrons can be enhanced via doping process in which number of electrons in polymer can be altered.

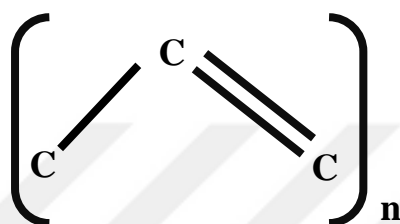


Figure 1.1 General structure representing conjugated conductive polymers

In addition to conductive polymers, there is one other class of polymers known as ionomers. An ionomer is a type of polymer containing ionic groups in its structure. In comparison to polyelectrolytes, which contain a large concentration of ionic groups, ionomers contain both normal repeating units and low concentration of ions on its backbone. In ionomer structures, nonpolar chains are gathered together while the polar ionic units have attraction in between. In case of presence of ionic groups in the backbone of polymer, some of its properties change seriously. Especially changes in viscosity, elastic modulus and glass transition temperatures are quite significant under heat application. [3]

1.4 PEDOT:PSS in Bioelectronics

The bioelectrochemical applications of conjugated polymers have increased the demand for their utilization in several progressive fields such as biosensors [4,5], actuators [6,7], transistors and flexible electronics. A special interest was addressed to poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), a transparent, conductive polymer, which is suitable for utilization in flexible electronic devices for their high ductility and fair conductivity. The molecular structure of PEDOT:PSS can be clearly observed from Figure 1.2. PEDOT itself is a highly conductive blue colored material, which in combination with an intrinsically conductive PSS provides good electrical and ionic conductive properties. PSS which is a sulfonated polystyrene contains a deprotonated group and carries a negative charge.

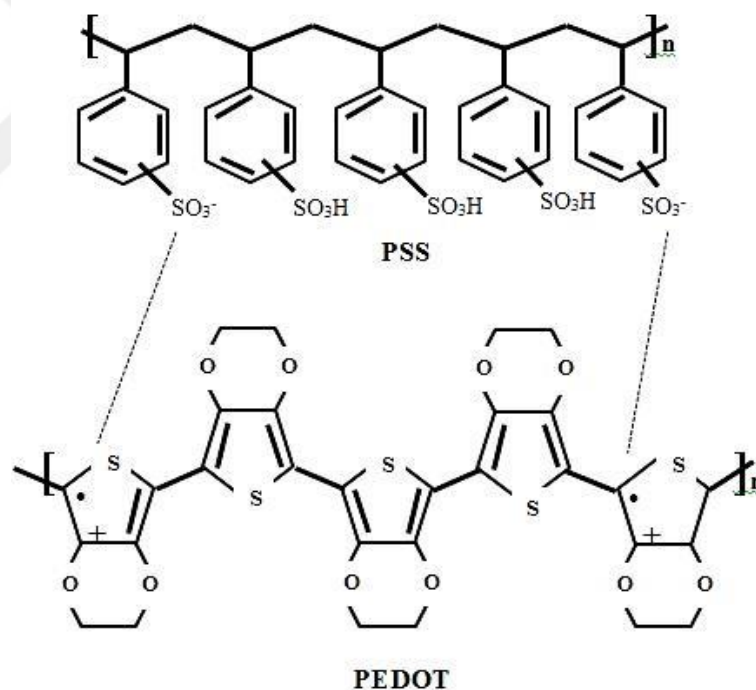


Figure 1.2 PEDOT:PSS structure with one deprotonated sulfone group

Thanks to their high conductivity and ductility, their utilization in electronic devices has grown vastly. Additionally, in one of the studies conducted in this area it was proven that PEDOT:PSS provides a suitable environment for cell culture as well. All together these properties of PEDOT:PSS made this material

and indispensable part of bioelectronics which is why several methods have been proposed in order to properly incorporate PEDOT:PSS into bioelectrochemical systems. The main reason of PEDOT:PSS drawing so much attention is because it combines both ionic and electrical conductivity where PEDOT part serves for electrical conductivity of conjugated polymer while PSS offers ionic transport. System consists of selectively deposited PEDOT:PSS electrodes on poly(ethylene terephthalate) (PET) substrates with a tiny overoxidized region which serves as electrically insulating but ionically conductive part. [8].

1.5 Tailoring PEDOT:PSS Conductivity

A large amount of investigations and researches are done in the field of PEDOT:PSS conductivity enhancement for the past few years. With the improvement in its conductivity, application area of PEDOT:PSS has developed equally. Although PEDOT:PSS itself has much better physical and electrical properties in comparison to other conductive polymers it still shows weaker and lower properties than metals and metal oxides. The enhancement of the conductivity of this conjugated polymer is reported to be done by organic compounds known as secondary dopants. Most of these organic compounds are ionic liquids, solvents containing polar groups, salts etc. The time of exposure of PEDOT:PSS to conductivity reinforcing additive is as important as the type of selected additive. Most of these additives effect the PEDOT:PSS structure by eliminating the PSS layer that provides ionic transport rather than electrical conductivity to the polymer composition. The most effective and highly powerful additives are N-methylpyrrolidone (NMP), dimethylsulfoxide (DMSO), sorbitol, ethylene glycol (EG), methanol etc. Of course, solvent treatment is not the only method. Metal dopants such as lithium perchlorate (LiClO_4) also succeed in conductivity enhancement.[9,10] According to most of studies performed in this area the significant increase values of PEDOT:PSS electrical conductivity are given in Table 1.1.

Table 1.1 The effect of solvent additives to the conductivity of PEDOT:PSS

Solvent	Conductivity (S/cm)
Dimethyl sulfoxide (DMSO)	364
N-methyl-2-pyrrolidone (NMP)	236
Ethanol	384
Ethylene glycol (EG)	240
Lithium perchlorate (LiClO ₄)	437

1.6 Flexible Electronic Substrates and Their Patterning Techniques

Flexible substrates also constitute a big part of electronic application in nowadays technology. Often named as flexible electronics, these devices are developed in order to assemble electronic systems on their surfaces and facilitate their utilization. Some of these substrates are well-known polyimide, polyether ether ketone (PEEK), polyester, polyethyleneteraphthalate (PET) type polymers. These substrates are applicable in several areas where flexibility, easy production and space saving are the main concern. In addition, some of these substrates like PET are completely biocompatible and can be used in bioelectronic devices for human body. Most of recent studies done in this field utilized PET as substrate for bioelectrical circuits. The deposition of PEDOT:PSS on flexible substrates is suggested by various methods in literature. Processes like screen-printing, resist mask printing, UV lithography have been among the methods developed for PEDOT:PSS deposition on these substrates. Most of these methods are highly advanced and suitable for complex patterns. For instance, UV lithography also known as photolithography uses light to transfer the geometric configuration from the mask to photoresist on substrate. After a sequence of chemical treatment steps the remaining pattern enables the deposition of desired ink in relevant shapes. Screen-printing is another deposition technique, which has a simple application method. System consists of a mesh used to transfer ink on substrate. A squeegee, blade-like structure, moves along the screen, as shown in Figure 1.3, in order to fill the empty parts of mesh with ink and transfer the image to the substrate

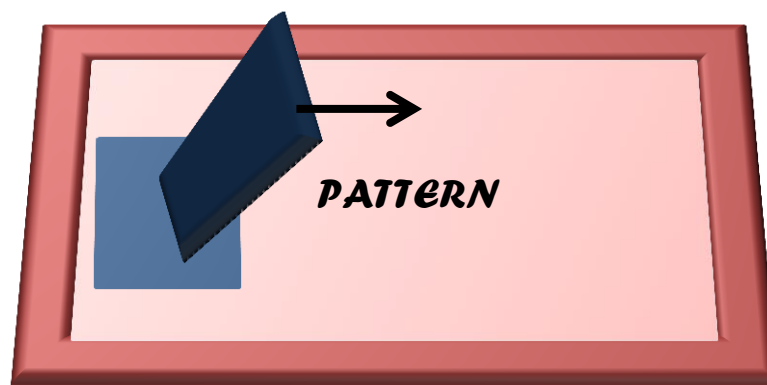


Figure 1.3 Schematic representation of screen-printing technique

Of course, many innovative and less effortful methods have been developed in comparison with UV lithography and screen-printing. One of these methods is line patterning method that we have used in our system for selective PEDOT:PSS deposition. [11-12]

Line patterning method, developed by MacDiarmid et al., is the most simple and economically available method of substrate patterning. The method consists of formation of negative of desired pattern via toner ink and depositing that ink on substrate by using printer. Method is simple as the formation of pattern is easily done by using computer-aided software programs. After pattern has been deposited, polymer solution can be injected on the empty parts of it via simple dropcast method. When the polymer solution dried on the surface completely, substrate may be sonicated in either toluene or acetone for approximately 10 seconds in order to get rid of toner ink. However, even in these developed methods several drawbacks such as tuning the photoresist thickness, time of exposition and development, reproducibility constantly occur. In some cases multiple steps of patterning processes hinder the massive production of these devices. Although this field of study is quite advanced, there are still some restrictions related to the performance of organic electronic devices for their low release rates, high voltage demands and limitations in design parameters. Therefore the preparation procedure of organic electronic ion pump (OEIP) from PEDOT:PSS for electronic control of ionic groups usually exchanged in neuronal cells is further improved in our laboratory.

In this study a straightforward but cost effective and time saving method called line patterning is used to selectively deposit PEDOT:PSS conjugated polymer on PET substrate at desired shapes required better ion pump performances. The reason of using line patterning method instead of other more utilized and recognized methods is that it is time saving and easy. The method is based on formation of a hydrophobic region leaving the desired shaped gap empty for further treatment. The toner ink forms homogeneous borders allowing the dropcasted ink to take the required shape. Several studies in the area of organic electronic devices have been done. Some of them are mainly based on the construction of OEIP, a delivery system designed to transfer ions from one subsystem to another via electrophoretic motion, thus mimicking the synaptic transfer in neural cells [12]. Schematic representation of OEIP is given in Figure 1.4.

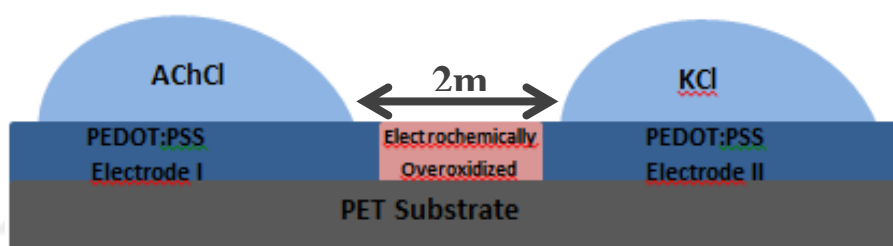


Figure 1.4 Cross sectional image of electrodes I & II on PET substrate with liquid electrolyte of acetylcholine chloride and potassium chloride

The very first study performed in this area consisted of a 4 electrode system (A, B, C, D) from PEDOT:PSS of which 2 (A & D) serve as ion reservoirs and other (B & C) are serving as ion transfer borders. The middle region, which is chemically overoxidized, is 2mm wide and allows ion transport only. Conductivity measurements on system were done by filling the AB side of PEDOT:PSS electrode with KCl and CD side with CaCl_2 solution. Under the application of constant voltage, the ion transport through overoxidized region was measured. 1V potential difference was applied between A & B and C & D electrode groups that served as reservoirs for continuous K^+ ions. Overoxidized region that resembles the synaptic cleft between two neuron endings provides ion transport only thus needs to be fully isolated from any electrical transport.

10V of potential is applied between electrodes B and C electrodes for this reason.

Another study performed in this field was focused on optimizing the previous configuration of OEIP by decreasing the number of PEDOT:PSS electrodes from 4 to 3 and narrowing the channel of ion transport. In that study instead of KCl solution, acetylcholine chloride (AChCl) solution was used. The purpose of this solution switch is because acetylcholine is the actual neurotransmitter. It is a macromolecule that is released because of $\text{Na}^+ - \text{K}^+$ ion exchange that generates action potential. The generating potential opens the Ca^{2+} channels through which calcium ions enter the neuron and release the ACh^+ macromolecules from their sacs. Released acetylcholine ions electrophoretically transfer through synaptic cleft and reach the next neuron thus causing an electrochemical signalling. The new configuration came up with many advantages, such as the increase in current and ability to transfer macromolecules through a tiny channel. However, this was still not good enough since the system operated at 10V.

As we know, 10V is an extremely high potential difference, which cannot generate in human organism. That's why our aim was to provide a configuration with better conditions under which ionic transport can occur under low applied potentials. Pristine PEDOT:PSS itself has a low conductivity that ranges between 0.38 - 2 S/cm. In some applications under low applied voltages, this conductivity is fair but not good to generate enough current. That's why several other methods have been developed to increase the electrical and proton conductivity of PEDOT:PSS. It is even proven that proton conductivity of PEDOT:PSS is a more important parameter that should be considered while characterizing OEIP. Although no certain study focusing on proton conductivity of conjugated polymer has been investigated so far, it was decided to consider this in our study.

To sum up, main difference of our system from the ones used in previous studies is in some slight alterations done with the number and sizes of electrodes. Additionally, the whole process of OEIP formation was self made, while other studies were using prepared PEDOT:PSS deposited PET substrates from Orgacon™. In order to achieve a homogeneous film throughout the substrate glycerol was suggested as an additive to PEDOT:PSS solution. Corona treatment of substrate also provided a stronger ink deposition. The durability of these films

to aqueous environments was also tested by keeping them in water for 24 hours. At the end of the test the overall structure remained unchanged with no rupture or damage on PEDOT:PSS film.



2. EXPERIMENTAL PROCEDURE

2.1 Materials

As the substrate of OEIP, polyethylene terephthalate (PET) and polyvinyl chloride (PVC) were selected as the most suitable ones for their being flexible, biocompatible and electrically insulating. The performance comparison was done between two of them in order to decide which one suits the operation conditions the best. PEDOT:PSS in granule form, ethylene glycol (EG), hydrochloric acid were purchased from Sigma Aldrich. Glycerol (Sigma Aldrich) was selected as an additive to PEDOT:PSS solution for promoting the better adhesion on PET substrate. Potassium chloride (KCl), calcium chloride (CaCl_2) and acetylcholine chloride (AChCl) necessary for the potentiostatic experiments were purchased from Sigma Aldrich as well. As the line patterning material standard printer toner was used. It is selected as the most appropriate material for tuning the surface wettability providing a hydrophobic region for holding off PEDOT:PSS solution. Isopropyl alcohol (IPA) and acetone were purchased from Sigma Aldrich and used as received.

2.2 Line Patterning and PEDOT:PSS Deposition

Before contouring the desired shapes on the substrate, they passed through one more step called air plasma treatment. Air plasma treatment or in other words corona treatment is a special technique used for surface modification by using corona discharge plasma. Under the application of high voltage, plasma is generated through the tip of device changing the surface energy of substrate providing an enhanced bonding during deposition. Without corona treatment, PEDOT:PSS solution could not cling strong enough on surface that's why it was one of the most important steps in OEIP formation. Moreover, the durability of PEDOT:PSS to water also decreases without corona treatment. The treated PET

and PVC substrates ready to use were patterned with the printer toner forming the hydrophobic regions and allowing a determinate space for the ink to be injected [6,13]. The deposition of PEDOT:PSS (0.25 % w/w) solution on substrates was done by standard drop cast method on the area of 1.0 cm². Due to the presence of hydrophobic phase on substrate, PEDOT:PSS solution diffuses to the available regions only taking the desired shape of pattern. The solution was dried on hot plate for 30 minutes at 50 °C and 2 hours at 100 °C as given in Figure 2.1.

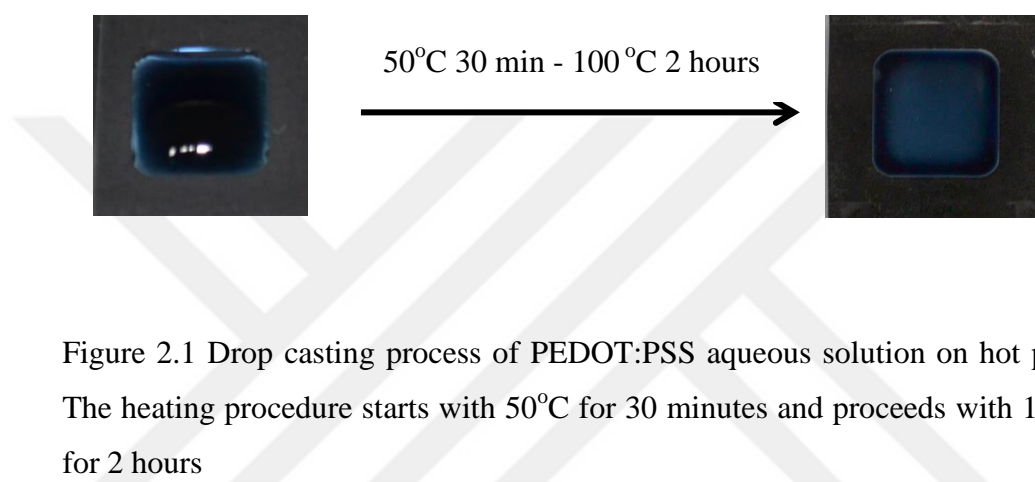


Figure 2.1 Drop casting process of PEDOT:PSS aqueous solution on hot plate. The heating procedure starts with 50°C for 30 minutes and proceeds with 100°C for 2 hours

After overall deposition actualizes the electrochemical overoxidation step proceeds [14]. At this point, PET was selected as the substrate with better mechanical properties as PVC during the deposition step could not endure 100 °C and melted down. Additional solution was to dry PEDOT:PSS solution under IR red lamp. However, this also ended up in poor PEDOT:PSS clinging on substrate surface.

2.3 PEDOT:PSS Overoxidation

Overoxidation of PEDOT:PSS is an essential step in OEIP design. This step permanently cuts off the electrical conductivity of PEDOT phase making that part of system conductive to ions only. The region serves as a good ionic conductor leading to an easy transport of positively charged ions [7,14]. Under the effect of voltage, ions located on one side of electrochemically overoxidized region are transported through it to the opposite side.

PEDOT:PSS overoxidation was done by two methods: chemical and electrochemical method. For chemical overoxidation diluted sodium hypochlorite (0.01% NaClO) solution was dropped on the predetermined 2 mm region of PEDOT:PSS electrodes. This overoxidation step was difficult to control as the longer NaClO solution was kept on PEDOT:PSS the more it etched it from the surface. This was an undesired condition, as an undamaged PSS region should be left in order to provide ion transport. That is why electrochemical overoxidation method was proposed which is assumed safer, faster and easily controlled in comparison to chemical overoxidation achieved by sodium hypochlorite (Figure 2.2) [15-17].



Figure 2.2 Overoxidation step of PEDOT:PSS electrodes. A pre-determined 2 mm region is electrochemically overoxidized with 20% KCl solution via applied voltage

Samples were electrochemically overoxidized with a stainless steel wire as a counter electrode where approximately 15 V was applied between the KCl electrolyte solution and counter electrode. Since the overoxidation is done in a determinate region electrolyte solution is dropped directly to that part of PEDOT:PSS setting the boundaries with insulating polymers [15,17].

2.4 Potentiostatic Measurements

After constructing the OEIP properly, electrolyte solutions (KCl vs CaCl₂ & AChCl vs. KCl both 0.1M) were dropped on pre-determined opposing regions. Two trials were performed in these experiments. First trial included KCl and CaCl₂ in order to test if the system works properly. This was not only tested by current values but also additional pH changes were recorded during experiment. Secondly, AChCl vs. KCl was tested again on the similar OEIP structure. pH recording was also performed at this stage. Under the effect of constant voltage positive ions (K⁺ and ACh⁺) passed through overoxidized region to the opposite electrode. As sourcemeter Solartron 1260 & 1278A was used to apply constant voltage and data were collected via CorrWare computer aided program (Figure 2.3). Several potentials such as 1, 2, 5 and 10 V were applied for the electrodes I and II and current vs. time graphs were analyzed. Counter electrode was connected to K⁺ and working electrode was connected ACh⁺ side and as a result positive ions were driven through electrochemically overoxidized region.

2.5 Fourier Transform Infrared (FTIR) and Raman Spectroscopy

It was assumed that the electrochemical overoxidation of PEDOT:PSS as a result lead to cutting off the electrical conductivity of overall conjugated polymer which would end up in significant changes in its chemical structure [17]. In order to reassure that overoxidation actually took place several spectroscopic methods were used. First analyses were performed by the Fourier Transform Infrared (FTIR) measurements (Perkin Elmer Spectrum 100). The principle of FTIR is based on measuring how good substance absorbs light at each wavelength and gives out the response in spectrum form. Based on the peak intensity and wavenumber the change in structure or possible interaction is concluded. Another characterization technique for the electrochemical overoxidized region of PEDOT:PSS was the Raman spectroscopy (Renishaw, Invia) which was expected to show the main peak shifts prior to and after electrochemical overoxidation steps [18]. Similar to FTIR, Raman also operates on the principle of light absorbance. However, Raman is a more specific

spectroscopic technique by which the molecule can be identified. Raman measurements were performed with 532 nm Ar-ion laser.

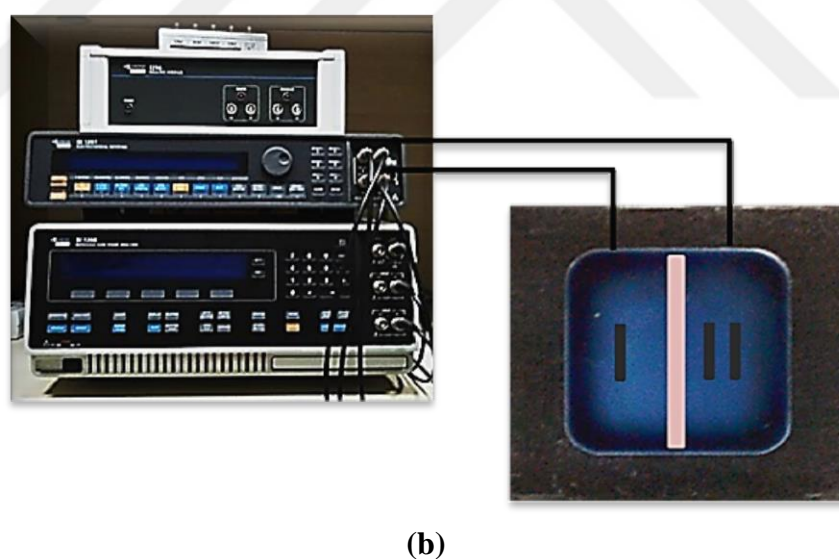
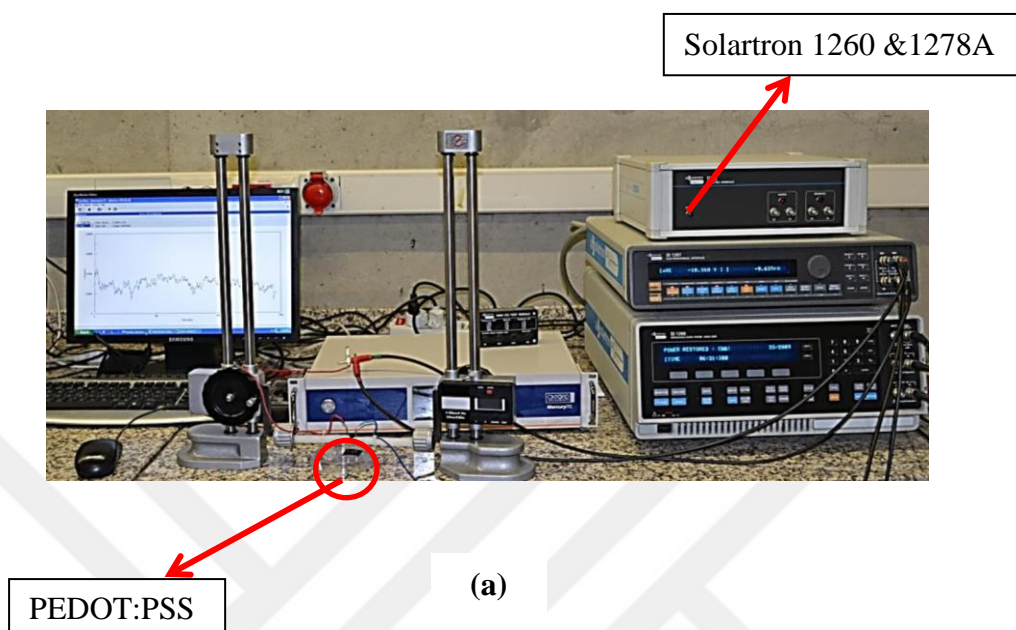


Figure 2.3 (a) Potentiostatic measurement set-up with Solartron 1260&1278A connected to CorrWare program (b) A closer image of sourcemeter connected to OEIP system. Working electrode is connected to ACh^+ (or K^+ in case of $CaCl_2$ experiment) side since similar poles repel each other

2.6 AFM and Contact Angle Measurements

Together with structural changes of PEDOT:PSS after overoxidation, some specific changes in its physical properties were also expected. In order to understand this two more spectroscopic tests were performed. One of them is Atomic Force Microscope (AFM), a device where a tiny 10 nm tip scans a defined area and translates signals to give out the final image of surface. This method is highly popular and has three main operation modes, which are contact mode, non-contact mode and tapping mode. For our AFM measurements, Asylum MFP-3D was used on tapping mode. Another measurement for surface change identification was selected as contact angle measurement performed on OneAttension contact angle device. Its working principle is based on recording the image of water (or any other desired fluid) droplet touching the substrate surface and measuring its angle of contact with surface. The computer aided program gives out the immediate result.

2.7 Conductivity Enhancement

Once the standard potentiostatic tests have been performed, several methods were developed in order to strengthen the electrical and proton conductivity of PEDOT:PSS. As the first method, EG, NMP, methanol vapor and LiClO_4 treatment methods were selected. Dropwise added EG on PEDOT:PSS electrodes were kept at different time intervals of 2, 6, 12 and 24 hours. After EG treatment, samples were annealed at 100°C for 1 hour under vacuum in order to get rid of excess EG left on surface. Similar to EG treatment, NMP and methanol treatment was also tried. Samples were kept in NMP and Methanol separately for 2, 6 and 24 hours. Post-annealing was also applied on these substrates. A different type of conductivity enhancement was done by using LiClO_4 solid into PEDOT:PSS solution. After stirring the solution overnight mixture was dropcasted on OEIP structure. An additional technique to conductivity enhancement was selected as acid treatment. The pH of pristine PEDOT:PSS solution was measured and found to be 0.38 S/cm. It was assumed that the decrease in pH value of solution would increase its conductivity. That is why the pH value of solution was arranged with hydrochloric acid to pH=1.5

and pH=0.9. Electrical conductivities of OEIPs after above mentioned treatments were measured by using 4-point probe resistivity measurement device equipped with Keithley 2400 IV Sourcemeter (Figure 2.4). The working principle of 4-point probe is based on a fixed applied current between 2 out probes and voltage that is measured between other 2 inner probes. The obtained resistivity value must be converted to resistance with following formula. Thus, the $1/R_s$ gives us conductivity value.

$$R_s = \rho/t = 4.53 V/I \quad (2.1)$$

Although enhancing the electrical conductivity was good enough to improve the current performance of OEIP one other alternative was also suggested.



Figure 2.4 Four-point probe conductivity measurement connected to Keithley 2400 IV Sourcemeter

Taking into the fact that Acetylcholine molecules transfer through the overoxidized region by exchanging charges with PSS group of conjugated polymer, addition of an extra ion-conductive layer was suggested. Nafion™ aqueous solution (5% v/v) was dropcasted on electrochemically overoxidized region of OEIP and dried under IR lamp until a homogeneous film forms. The effect of additional Nafion™ layer on OEIP performance was measured with conductivity cell and standard conductivity measurements via Solartron 1260 & 1278A. Conductivity cell contains 4-electrodes to which the material to be tested is attached. The main advantage of 4-electrode system is that the resistance is measured based on charge transport only. All other resistances such as interfacial or charge transfer are not included in these measurements.

The system is connected to a computer equipped with Solartron Instruments; a specific Nyquist plot response appears after the test (Figure 2.5 & 2.6). The Nyquist plot gives us the information about impedance value thanks to which we can perform the conductivity calculation. Of course, the dimension of sample inserted in conductivity cell is also known for further evaluations. All samples were cut at approximately 1.2cm x 2.4cm dimensions. Thickness of each material was determined with a micrometer before the conductivity measurement. After filling a water bath with distilled water conductivity cell, to which PEDOT:PSS deposited PET substrate sample was inserted, was plunged in. The device gives out the Nyquist plot with axes Z'' vs. Z' . The point at which curve intercepts x-axis is recorded as a real part of the impedance response that corresponds to the membrane resistance. By inserting all the necessary values to the equation 2.2, proton conductivity of PEDOT:PSS and NafionTM deposited PEDOT:PSS substrates were calculated.



Figure 2.5 Conductivity cell set-up system connected to Solartron 1260&1278A. OEIP system inserted into conductivity cell is plunged into deionized water bath for measurement

$$\sigma = \frac{l}{Z' A} \quad (2.2)$$

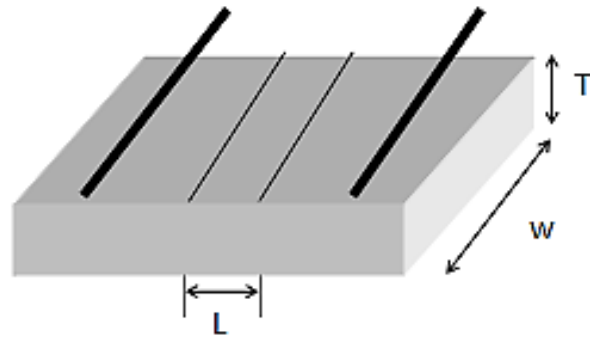


Figure 2.6 Inside structure of conductivity cell. L represents the distance between two side electrodes; W and T are the width and thickness of samples.





3. RESULTS AND DISCUSSION

3.1 PEDOT:PSS Deposition and Substrate Selection

The comparison between PVC and PET substrates was done according to their behavior at high temperatures and the degree of PEDOT:PSS clinging. Both substrates were cleaned with acetone, isopropanol (IPA) and distilled water before being patterned. PET was selected as the substrate with best performance and overall analysis of both of materials are given in Table 3.1

Table 3.1 Performance of different substrates on OEIP production step. PET and PVC were compared for their heat durability and ink clinging degree

SUBSTRATE MATERIAL	AMBIENT CONDITIONS	RESULTS
PET	PEDOT:PSS + Glycerol mixture deposited On PET substrate dried at 50°C for 30 min. and 100 °C for 3 hours	Successfully deposited. High quality, homogeneous film
PVC	PEDOT:PSS + Glycerol mixture deposited On PVC substrate dried under IR lamp for 5 hours	Film detached from Surface. Unsuccessful

The deposition of PEDOT:PSS on flexible PET substrate at pre-determined shapes was done by line patterning method followed by drop casting [18]. An important parameter playing a crucial role at this step is corona treatment that provides an enhanced adhering of conjugated polymer on substrate by modifying the surface energy. The images of corona treated versus corona non-treated PEDOT:PSS deposited on PET substrate are given in Figure 3.1 The

difference in adhesion is clearly seen between two images. As a result defect free well-adhered samples were successively achieved after surface treatment by corona. Overoxidation in this study was successfully achieved electrochemically.



Figure 3.1 Difference between corona treated vs. non-treated PET substrates

3.2 Characterization of OEIP

Spectra obtained from FTIR measurements were analyzed and significant differences were observed due to the electrochemical overoxidation. It is obvious from the Figure 3.2 that prior to overoxidation there is no peak on pure PEDOT:PSS spectra while a prominent peak occurs after overoxidation. The peak occurring close to 1720 cm^{-1} corresponds to C=O stretching, while double-head peaks in 1175 cm^{-1} wavenumber range attributes to sulfonate group (S=O) stretching. These peaks in FT-IR spectra explain the lowering of the electrical conductivities of PEDOT:PSS to about 0.06 S cm^{-1} . According to previous studies done in this area, this change corresponds to the formation of carbonyl groups on thiophene rings that cuts off the conjugation in chain [18,19]. Remaining chemical structure then becomes electrically insulator, but ionically conductive due to the polystyrene sulfonate groups (PSS).

Raman spectra of pristine and electrochemically overoxidized PEDOT:PSS are given in Figure 3.3 There is a visible peak shift at approximately wavenumber of 1430 cm^{-1} which corresponds to symmetric C=C stretching of thiophene ring [19-22]. After the electrochemical overoxidation step, this peak shifts slightly towards 1450 cm^{-1} proving the oxidized state of the PEDOT:PSS. In the previous studies, this type of change in wavenumber and peak intensity increase was correlated to the transformation of resonance structure of

thiophene backbone. Enhanced peaks at 1500 and 1570 cm^{-1} are also reported as asymmetric stretching vibrations of thiophene ring of PEDOT:PSS in the middle and at the end of chains.

A significant change in surface topography of PEDOT:PSS was expected after the electrochemical overoxidation. AFM Imaging was selected as the most proper method for determining the surface roughness values. The root mean square (RMS) surface roughness, R_q , of pristine PEDOT:PSS at 500 nm scaling in AFM were reported in Table 3.2 and shown in Figure 3.4. Pristine PEDOT:PSS films appear to be highly homogeneous with extremely low roughness values. Due to the electrochemical overoxidation surface was resulted with high roughness overall. Together with AFM results, the change in surface morphology was proven by performing contact angle measurements [22]. A pristine, overoxidized and ethylene glycol treated PEDOT:PSS by using simple contact angle method were tested and eventually the change in surface energy was interpreted. According to contact angle measurements, hydrophilicity of surface highly increases after electrochemical overoxidation step. This may correspond to the decrease in surface energy after electrochemical overoxidizing PEDOT:PSS. Therefore, overoxidized region becomes more hydrophilic with the lower surface energy enhancing the aqueous ionic transport from electrode I to II.

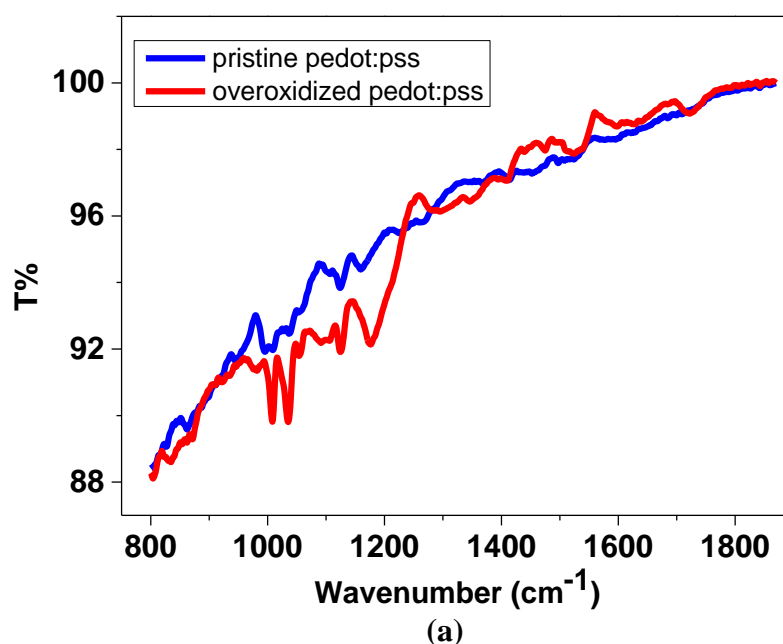


Figure 3.2 (a) FT-IR spectra of pure and overoxidized PEDOT:PSS.

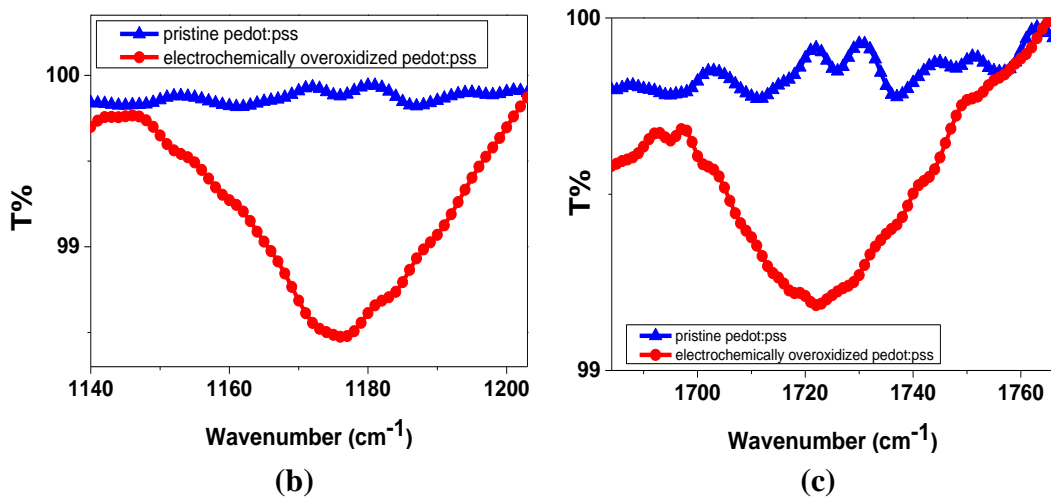


Figure 3.2 continues The most significant peak shifts represent (b) S=O stretching at 1175 cm^{-1} and (c) 1720 cm^{-1} C=O stretching

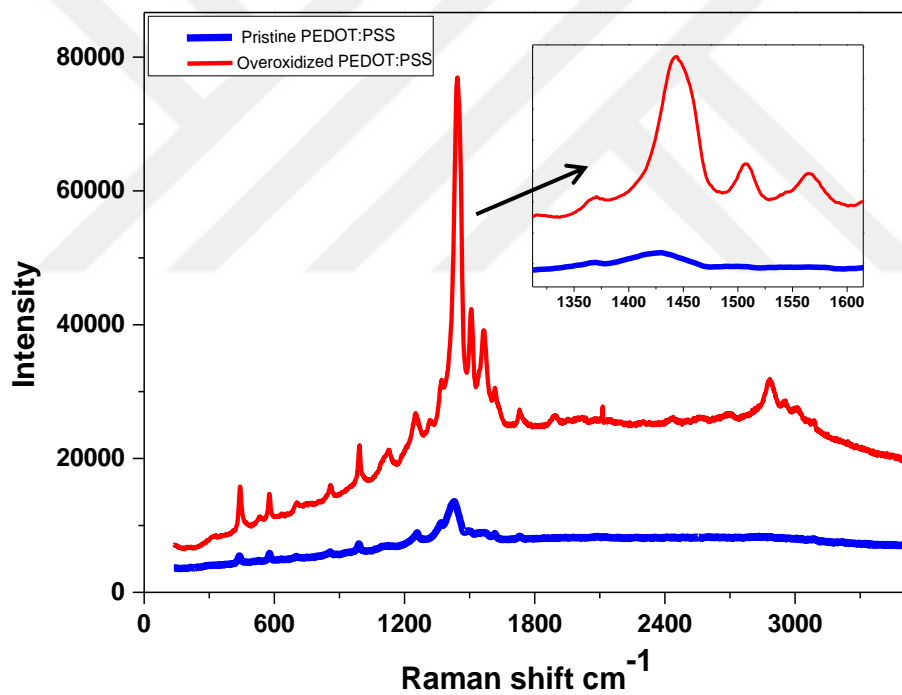


Figure 3.3 Raman spectra for pristine and overoxidized PEDOT:PSS. Peaks at 1430 cm^{-1} corresponds to characteristic C=C stretching of thiophene ring, which shifts and intensifies after overoxidation step.

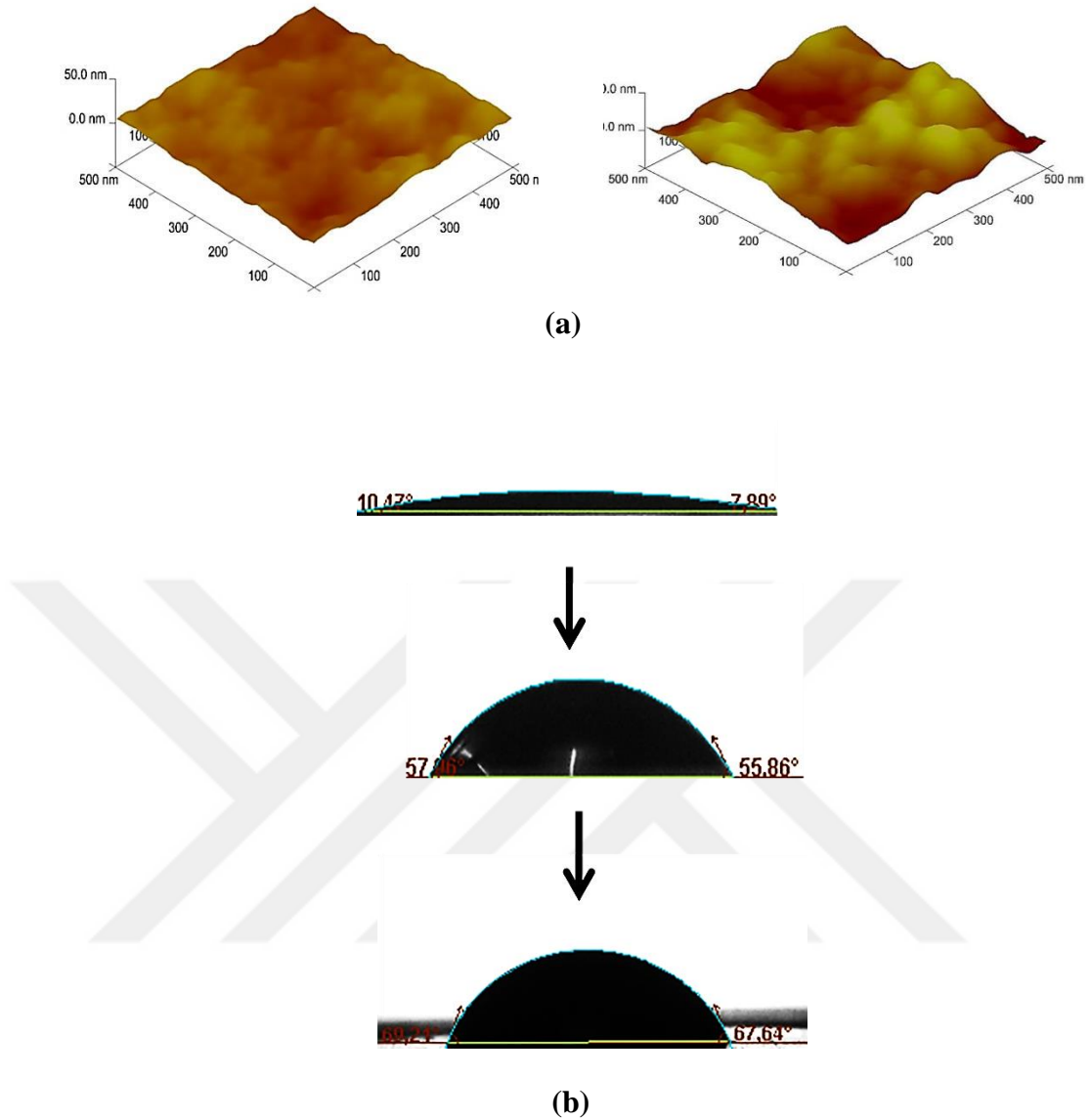


Figure 3.4 (a) 3D AFM images of pristine and overoxidized PEDOT:PSS substrates. After overoxidation the abraded the surface its roughness has increased vastly. (b) Contact angle measurements for electrochemically overoxidized, pristine and EG treated PEDOT:PSS substrates respectively

Table 3.2 Surface roughness and contact angle values for pristine, overoxidized and EG treated PEDOT:PSS. A significant change in surface roughness and contact angle is observed between electrochemically overoxidized and pristine PEDOT:PSS values which is due to change in surface energy.

Material	Av. Contact Angle (Degree)	Surface Roughness (nm)
Overoxidized PEDOT:PSS	9.10	43.5
Pristine PEDOT:PSS	56.53	5.34
Ethylene Glycol Treated PEDOT:PSS	68.39	3.73

3.3 Potentiostatic Measurements and Conductivity Enhancement

Several conductivity measurements were done on PEDOT:PSS electrodes. Most of them involved the presence of ACh⁺ ions as the main aim was to provide the transport of neurotransmitter through the overoxidized region. However, at first steps in order to test the system KCl vs. CaCl₂ tests were performed (Figure 3.5). Afterwards, to understand the effect of additives on electrical conductivity of system similar potentiostatic measurements were repeated in Solartron 1260&1278A. In order to understand clearly the transfer of molecules through the overoxidized region current density values are not enough. pH and number of transported ion measurements were also performed for this reason (Table 3.3). By applying constant voltage for 1800 seconds, the transfer of K⁺ ions through overoxidized region is expected to change the pH of CaCl₂ solution. At the end of the experiment, solution on side II of OEIP structure is tested with pH strips. Same experiment was also performed on systems containing ACh⁺ vs. K⁺.

Table 3.3 Change in pH value of CaCl₂ solution under various applied potential values. The more molecules transport through the overoxidized region to the opposite side the more pH value changes

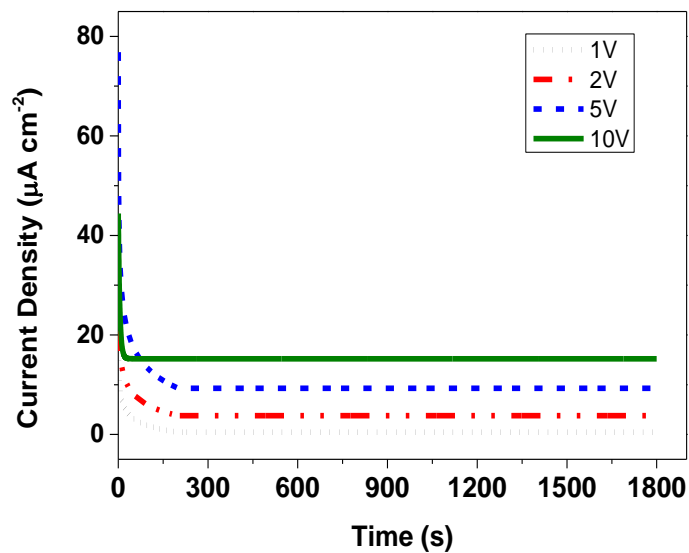
Applied Potential (V)	pH change
1	From 7 to 4
2	From 7 to 3
5	From 7 to 2
10	From 7 to 2

Additionally, to understand the number of ions transported to the opposite side of overoxidized region several calculations have to be done. In order to do that first we need to obtain charge values from the current density data. As we know, current (Ampere) is the flow rate of charge (Coulomb). Here current can also be interpreted as the amount of charges passing through a certain point in a second. Thus, in order to obtain charge from current values the integration of current data has to be done. This is performed by a well-known “Cumulative trapezoidal numerical integration” CUMTRAPZ function in MATLAB2013 computer aided software. As a result, matlab performs an integration of all current values with respect to time and gives out the charge values. However, our ultimate purpose is to obtain number of transported ions and to do this a simple calculation is performed.

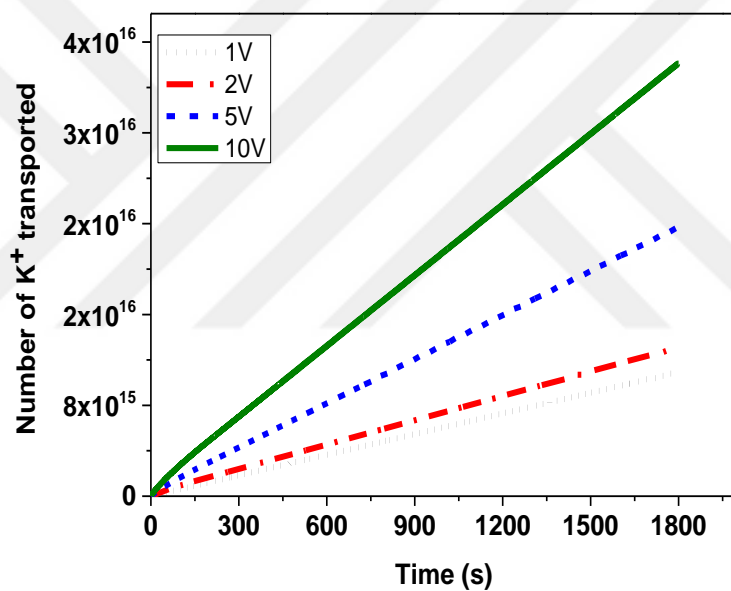
$$\text{Number of transported ions} = \frac{1 \text{ mole} \times \text{Charge C}}{96500 \text{ C}} \times 6.02 \times 10^{23} \quad (3.1)$$

By instering the value of charge into the formula, the number of transported ions can be calculated. Calculations were performed on Microsoft Excel 2010 and MATLAB 2013 softwares. In previous studies performed in the area of the conductivity enhancement of PEDOT:PSS, several additives and/or thermal annealing processes have been well investigated [24-28]. Ethylene glycol (EG) in this study was utilized for the conductivity enhancement experiments as other additives failed in conductivity enhancement. The period of OEIP exposure to

either NMP or methanol did not change the conductivity value or cause any other significant increase. Similarly, addition of LiClO_4 to the PEDOT:PSS solution ended up in poor surface adhesion. As a result of heating after dropcasting, LiClO_4 particles came out on the surface in form of white film. No valuable conductivity change was observed in this method as well. The reason of failure of these additives in our conductivity strengthening trials was related to the type of PEDOT:PSS we used. In comparison to other studies where high conductivity grade PEDOT:PSS viscous solutions were used, in our study PEDOT:PSS bead-like particles were dissolved in water and mixed with glycerol. Thus, this may have probably changed the composition and properties of conjugated polymers. However, a considerable change in conductivity was observed in EG treatment. Moreover, it was observed that the time of exposure of PEDOT:PSS films to EG had a prominent effect as well. While a 2 hour exposure increased the conductivity value by approximately 5 folds, a 6 hour treatment has changed the conductance values by almost 21 folds. Thus, exposing the electrodes I and II to EG solution, the conductivities of the electrodes were expected to increase, while the electrochemically overoxidized part was left unaffected. The explanation of increasing the electrical conductivity of PEDOT:PSS electrodes lies under the fact that EG abolishes the PSS phase that accounts for ionic transfer thus leaving the polymer film with remaining electrical conduction [17]. This way, ions could be driven faster towards the overoxidized region speeding up the overall transfer [30-32]. The conductivities of EG treated, pristine and electrochemically overoxidized PEDOT:PSS were measured with 4-point probe resistivity measurement method. After applying a sweep voltage between -1 and +1V via Keithley 2400 IV Sourcemeeter current vs. voltage data sets were obtained and as a result resistivity values could be evaluated. The effect of EG treatment time on the conductivities of PEDOT:PSS electrodes was also tested. For this purpose, PEDOT:PSS electrodes were exposed to EG for 2, 6, 12 and 24 hours for tailoring the electrical conductivities of them. A significant increase from 0.38 S/cm to 8 S/cm was noticed under the exposure of 6 hours while no noticeable change was observed after 2 hours of ethylene glycol treatment. However, the conductivity increase stabilized after 6 hours of treatment along further 24 h.

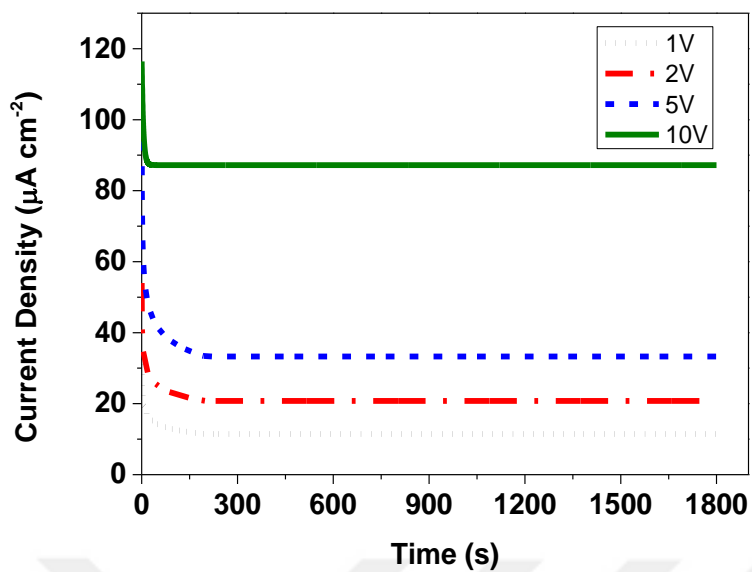


(a)

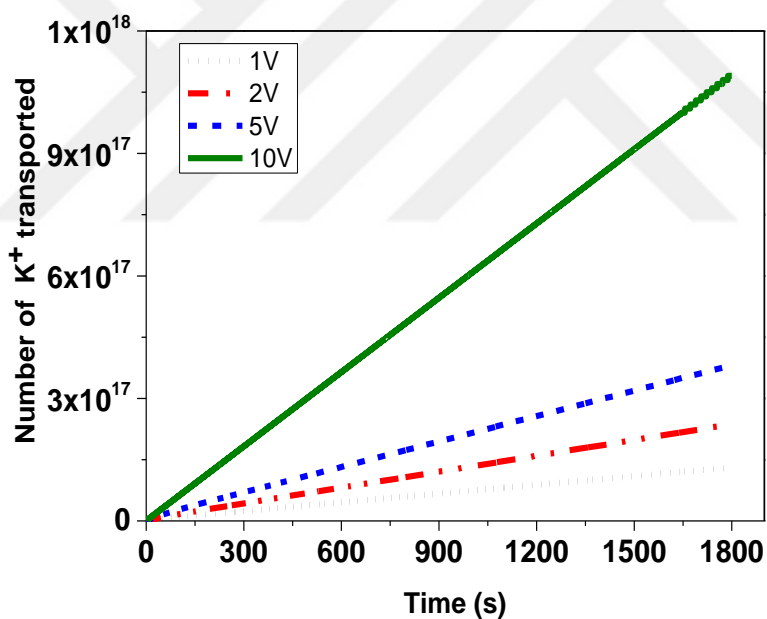


(b)

Figure 3.5 Current vs. time graphs for (a) pristine and (c) EG treated PEDOT:PSS with KCl solution on side I and CaCl₂ solution on side II of electrodes; Number of transported K⁺ ions for (b) pristine and (d) EG treated PEDOT:PSS



(c)



(d)

Figure 3.5 continues Current vs. time graphs for (a) pristine and (c) EG treated PEDOT:PSS with KCl solution on side I and CaCl₂ solution on side II of electrodes; Number of transported K⁺ ions for (b) pristine and (d) EG treated PEDOT:PSS

Another additional method for conductivity enhancement of PEDOT:PSS was selected as pH drop with the hydrochloric acid treatment. Whilst the pristine PEDOT:PSS solution have a pH value of nearly 4.5, by decreasing this value to 1.5 and lower to 0.9 a significant increase is also seen in the conductivity values which can be summarized in Table 3.4. As previously mentioned, the performance of OEIP was tested at various applied potentials between two electrodes. Therefore, the system was tested at 1V, 2V, 5V and 10V and current vs. time graphs were obtained (Figure 3.6). Application of OEIP is aimed for utilization it in bioelectrochemical devices. For this reason, its ability to transfer of macromolecules such as neurotransmitters gives us a better understanding of performance of OEIP later in vivo experiments. Under varying voltage values the amount of current and charge passing through the overoxidized region was measured. Acetylcholine transport has been monitored by the equilibrium current density, which indicates the rate for drifting of the acetylcholine ions from electrode I to electrode II values at several potentials (Figure 3.6).

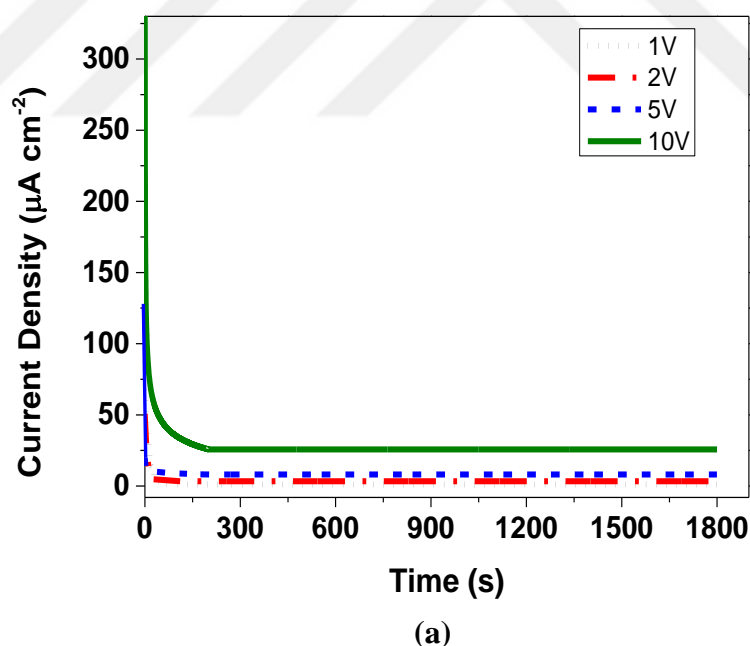
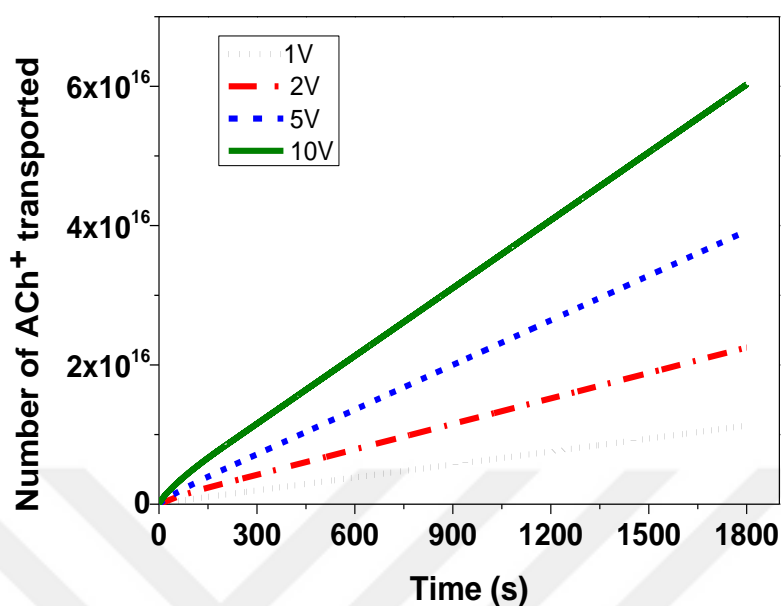
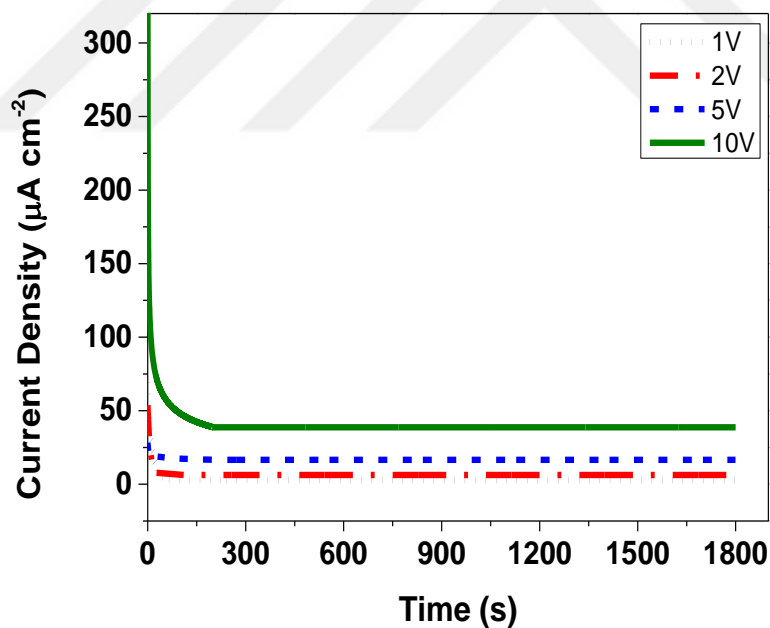


Figure 3.6 Current vs. time measurements at different applied voltages between two electrodes containing AChCl and KCl solutions oppositely for **(a)** pristine **(c)** 2 hours EG treated **(e)** 6 hours EG treated **(g)** pH=1.5 and HCl acid treated **(i)** pH=0.9 and HCl acid treated **(k)** electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes; Number of transported ACh⁺ ions at different applied voltages for **(b)** pristine **(d)** 2 hours EG treated **(f)** 6 hours EG

treated **(h)** pH=1.5 and HCl acid treated **(j)** pH=0.9 and HCl acid treated **(l)** electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes



(b)



(c)

Figure 3.6 Current vs. time measurements at different applied voltages between two electrodes containing AChCl and KCl solutions oppositely for **(a)** pristine **(c)** 2 hours EG treated **(e)** 6 hours EG treated **(g)** pH=1.5 and HCl acid treated **(i)** pH=0.9 and HCl acid treated **(k)** electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes; Number of transported ACh⁺ ions at

different applied voltages for (b) pristine (d) 2 hours EG treated (f) 6 hours EG treated (h) pH=1.5 and HCl acid treated (j) pH=0.9 and HCl acid treated (l) electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes

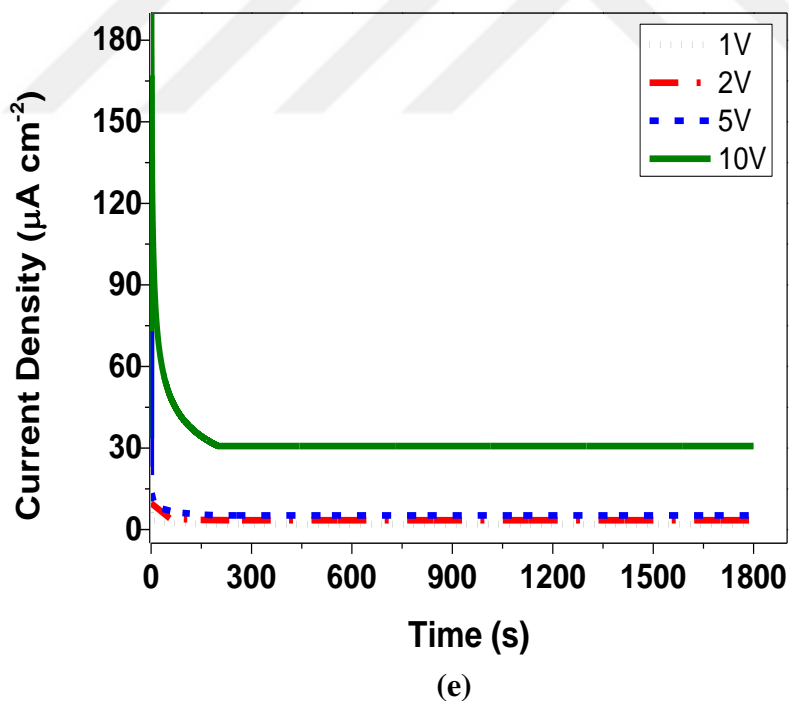
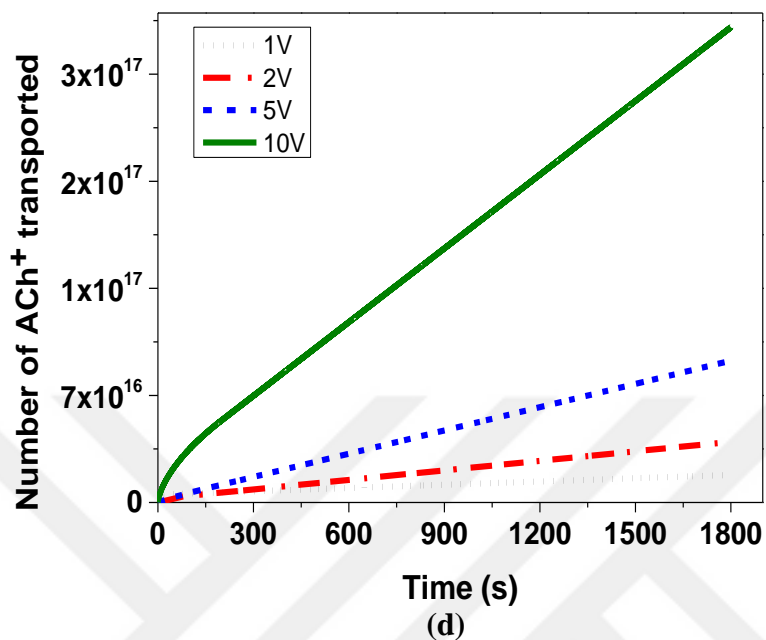


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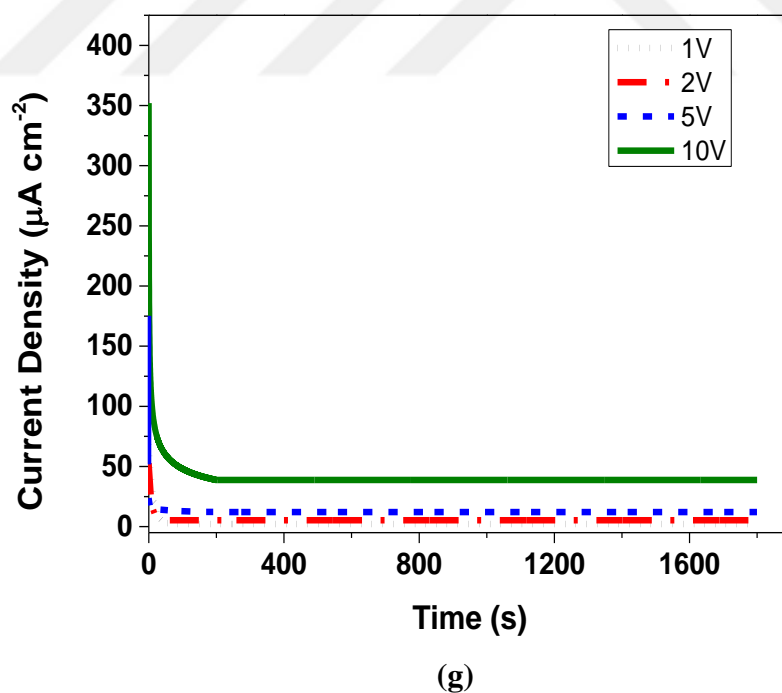
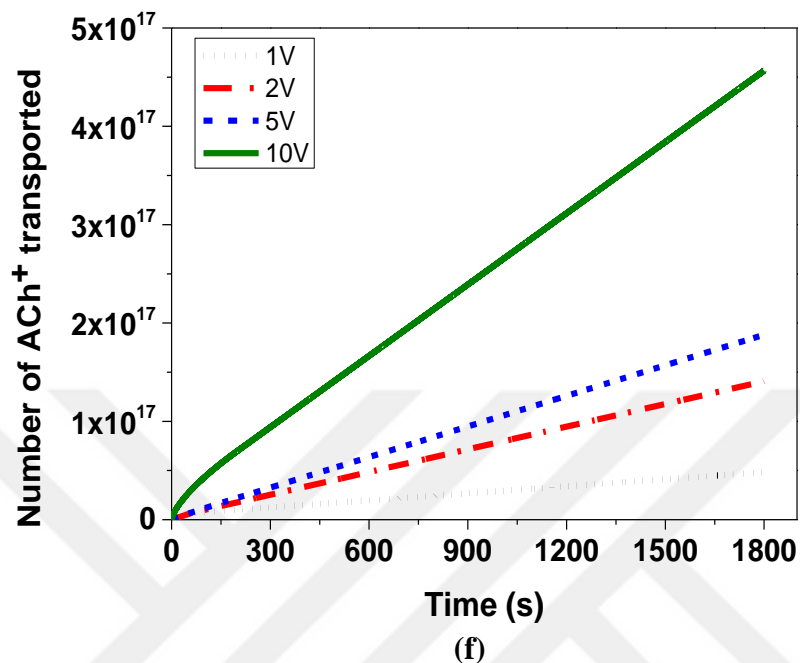


Figure 3.6 Current vs. time measurements at different applied voltages between two electrodes containing AChCl and KCl solutions oppositely for (a) pristine (c) 2 hours EG treated (e) 6 hours EG treated (g) pH=1.5 and HCl acid treated (i) pH=0.9 and HCl acid treated (k) electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes

Nafion™ treated PEDOT:PSS electrodes; Number of transported ACh⁺ ions at different applied voltages for (b) pristine (d) 2 hours EG treated (f) 6 hours EG treated (h) pH=1.5 and HCl acid treated (j) pH=0.9 and HCl acid treated (l) electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes

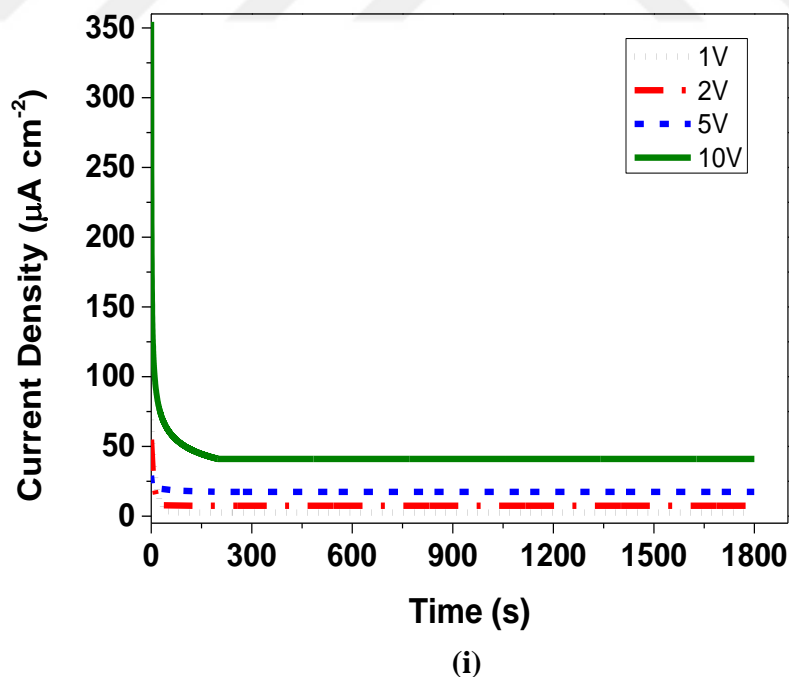
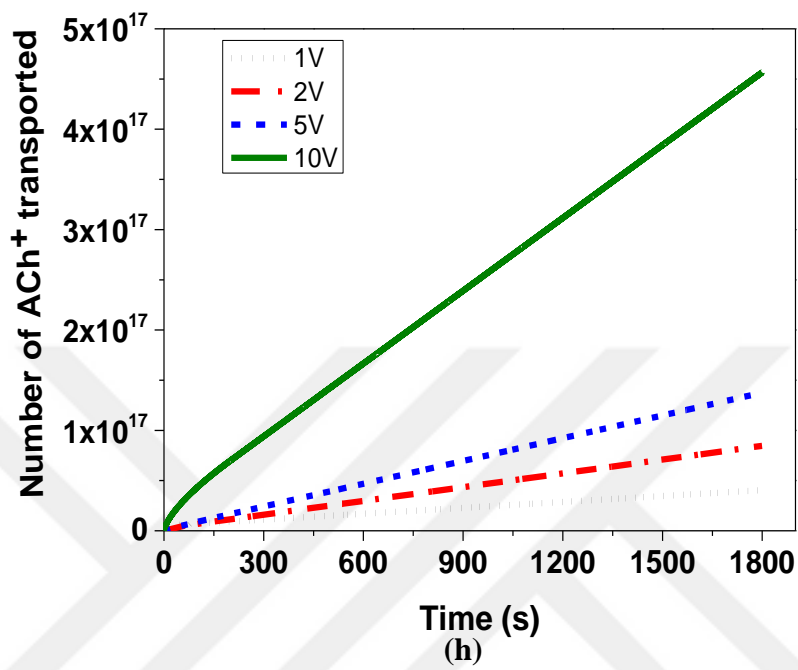
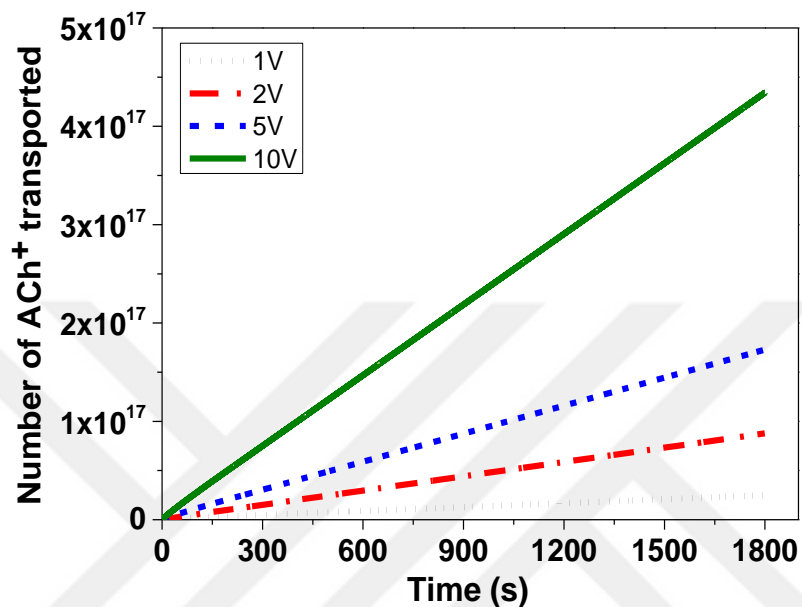
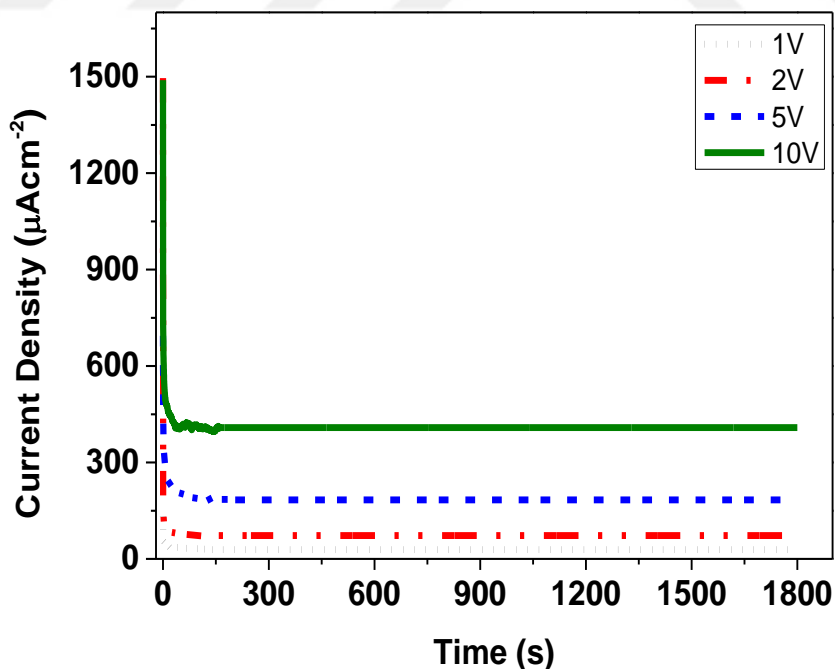


Figure 3.6 Current vs. time measurements at different applied voltages between two electrodes containing AChCl and KCl solutions oppositely for (a) pristine (c) 2 hours EG treated (e) 6 hours EG treated (g) pH=1.5 and HCl acid treated (i)

pH=0.9 and HCl acid treated **(k)** electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes; Number of transported ACh⁺ ions at different applied voltages for **(b)** pristine **(d)** 2 hours EG treated **(f)** 6 hours EG treated **(h)** pH=1.5 and HCl acid treated **(j)** pH=0.9 and HCl acid treated **(l)** electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes



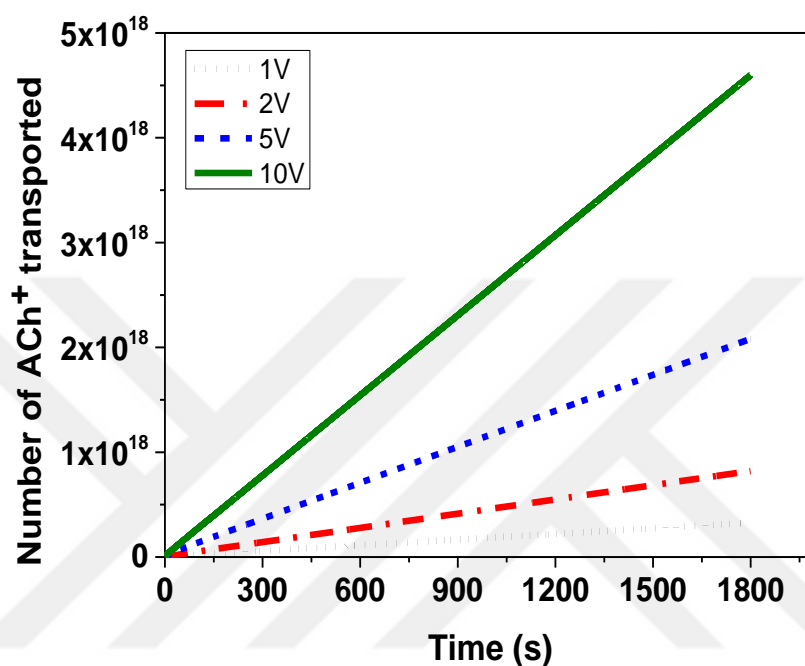
(j)



(k)

Figure 3.6 Current vs. time measurements at different applied voltages between two electrodes containing AChCl and KCl solutions oppositely for **(a)** pristine **(c)** 2 hours EG treated **(e)** 6 hours EG treated **(g)** pH=1.5 and HCl acid treated **(i)**

pH=0.9 and HCl acid treated **(k)** electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes; Number of transported ACh⁺ ions at different applied voltages for **(b)** pristine **(d)** 2 hours EG treated **(f)** 6 hours EG treated **(h)** pH=1.5 and HCl acid treated **(j)** pH=0.9 and HCl acid treated **(l)** electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes



(l)

Figure 3.6 Current vs. time measurements at different applied voltages between two electrodes containing AChCl and KCl solutions oppositely for **(a)** pristine **(c)** 2 hours EG treated **(e)** 6 hours EG treated **(g)** pH=1.5 and HCl acid treated **(i)** pH=0.9 and HCl acid treated **(k)** electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes; Number of transported ACh⁺ ions at different applied voltages for **(b)** pristine **(d)** 2 hours EG treated **(f)** 6 hours EG treated **(h)** pH=1.5 and HCl acid treated **(j)** pH=0.9 and HCl acid treated **(l)** electrochemically overoxidized region Nafion™ treated PEDOT:PSS electrodes

At the highest potential of 10V, nearly $25\mu\text{A cm}^{-2}$ equilibrium current density has been observed. As previously mentioned, the influence of EG on PEDOT:PSS is towards enhancing its electrical conductivity. This provides us with a better transfer of acetylcholine ions through electrodes I and II, thus accumulating larger amount of ions to be transferred through electrochemically

overoxidized region. Therefore, we have observed that the equilibrium current density increased from 25 to 38 $\mu\text{A cm}^{-2}$ when the electrical conductivities varied from 0.38 to 8 S/cm. An additional approach to conductivity increase of PEDOT:PSS electrodes was acid treatment. By using hydrochloric acid pH value of pristine PEDOT:PSS solution was dropped to 1.5 and then 0.9 which significantly increased the conductivity to 34 and 54 S/cm (Table 3.4), respectively. Corresponding equilibrium current densities were then observed as about 39 and 41 $\mu\text{A cm}^{-2}$, respectively. As a conclusion, it has been demonstrated that the equilibrium current densities of OEIP reach a threshold value when the electrical conductivities of the electrodes become 8 S cm^{-1} beyond which the equilibrium current densities remained almost constant at nearly 40 $\mu\text{A cm}^{-2}$.

Table 3.4 Change in conductivity values for pristine, overoxidized and EG treated PEDOT:PSS.

Material	Conductivity (S/cm)
Overoxidized PEDOT:PSS	0.063
Pristine PEDOT:PSS	0.38
Ethylene Glycol Treated PEDOT:PSS	8.0
Hydrochloric Acid Treated PEDOT:PSS (pH=1.5)	34
Hydrochloric Acid Treated PEDOT:PSS (pH=0.9)	54

The final treatment of OEIP was applied to the PEDOT:PSS electrodes with the equilibrium current density performance. This treatment method is based on enhancing the ionic transport of oxidized region of OEIP structure. Nafion™ is a well-known ionic conductor and has been studied extensively specifically for fuel cells and flow batteries [30-32]. In order to observe the influence of the

ionic conductivity on the OEIP performance, Nafion™ aqueous solution was added to the oxidized region drop wise and kept for drying till a homogeneous film forms. As can be seen in Figure 3.7, the equilibrium current density at all four voltage values have increased enormously leading us to the conclusion that the effect of ionic conductivity is larger than assumed. The equilibrium current density of OEIP was increased nearly 10 times and reached up to $408 \mu\text{A cm}^{-2}$ indicating very fast acetylcholine transport from the electrode I to II. The effect of Nafion™ as an ionic conductor to the OEIP structure can be interpreted as enhancement in proton conductivity of the electrochemically overoxidized region. As seen in Table 3.5 the proton conductivities of the electrochemically overoxidized region is highly increased from 0.0035 to 0.13 S/cm. Therefore it has been stated that the influence of ionic conductivity of the electrochemically overoxidized region on OEIP performance is much greater than that of electrical conductivities of the electrodes (Figure 3.8).

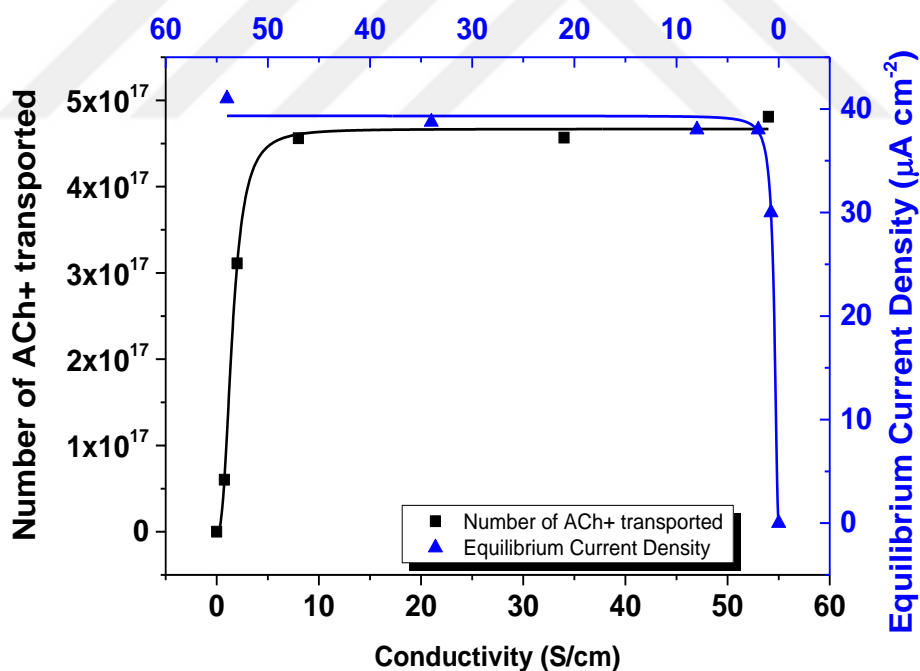


Figure 3.7 Influence of electrical conductivity of electrodes on the number of acetylcholine transported.

Table 3.5 Enhancement in proton conductivity of electrochemically overoxidized region of OEIP.

Type of Electrochemically Overoxidized Region	Proton Conductivity (S/cm)
Nafion™ Deposited	0.13
Pristine PEDOT:PSS	0.0035

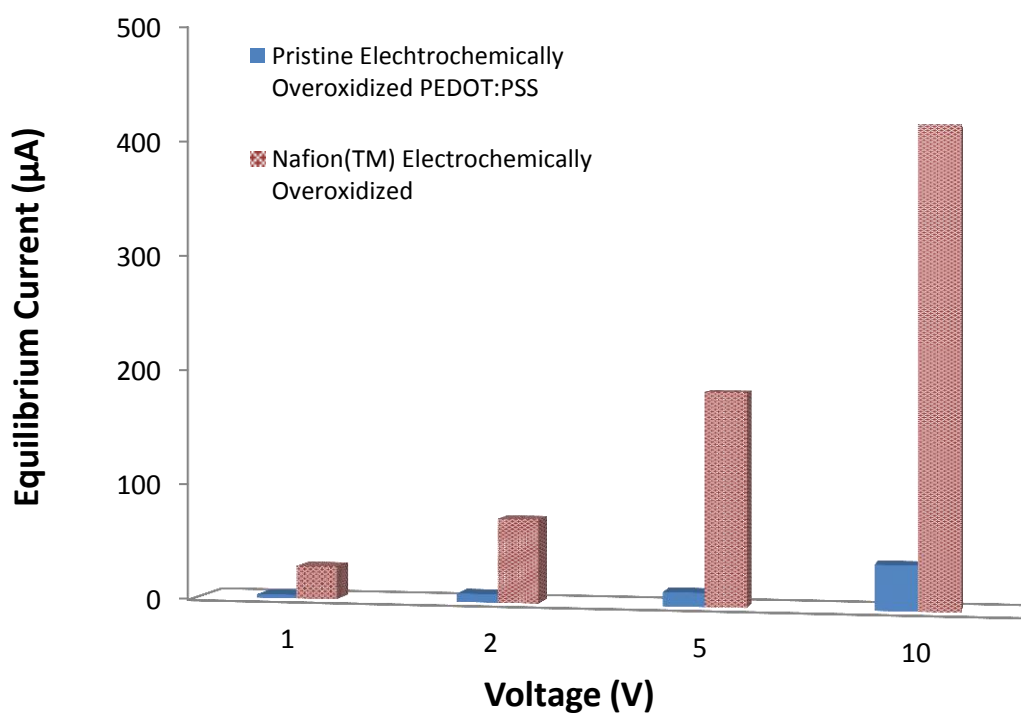


Figure 3.8 Equilibrium current density values for OEIP with Pristine and Nafion™ treated over oxidized regions

4. CONCLUSIONS

Flexible bioelectronic ion pump based on electrically and ionically conductive polymers was fabricated using line patterning method and enhancement in their electrical and ionic properties were performed. A brand new perspective to the production of bioelectronics was proposed and several novel methods have been applied for performance enhancement. The characterization and optimization of overall properties of the OEIP system were done by using FTIR, Raman, Contact Angle, AFM, Four-point probe and other devices. Due to several surface modification techniques, the dropcasted conjugated polymer solution was better adhered on the surface resulting in higher current values and ionic transfer. In order to increase the conductivity of OEIP, several additives were utilized and ethylene glycol was selected as the most effective one. Additionally acid treatments have been applied on the system, as well. The most prominent increase was observed by decreasing the pH value of PEDOT:PSS solution by using pure HCl acid. It was also investigated that proton conductivity had a stronger impact on OEIP performance than that of electrical conductivity leading to another development in the system. The addition of NafionTM solution on the electrochemically overoxidized region assisted the ion transport. This was affirmed with an almost 10 fold increase in current values between pristine and treated OEIP system.

Moreover, the thickness of NafionTM layer also was influential in current values. The thicker was the deposited NafionTM layer the higher were the current values and number of transported ions respectively. The availability and simplicity of the production method makes OEIP quite an applicable bioelectronic device. This promising progress in organic electronic field gave lead to upcoming advancements in this technological field.

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RESUME

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