Mixed conducting membranes for continuous ion transport

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Abstract

Brain cancer is difficult to treat due to the blood brain barrier, which blocks most drug molecules from passing from the blood into the brain. A common way of circumventing this barrier is using convection enhanced delivery, where a catheter is inserted through a hole in the skull and drug solution is administered into the tumour by applying a low pressure. This method suffers from reflux and the local pressure increase inside the brain may cause severe side effects for the patient. The organic electronic-ionic ion pump is an attractive alternative to this method due to its dry delivery, which means that no solvent is transported along with the drug.

A problem with the ion pump in drug delivery applications is that the amount of ions delivered due to an applied potential is severely hampered by the formation of the electrical double layer, which terminates any ionic drift current within seconds. The aim of this thesis was to investigate a novel membrane type and whether electromigration of ions, due to an applied potential, is significantly larger than diffusion.

Multistep amperometry was used to compare the steady state current of the membranes, which was assumed to be a mix of electronic and ionic current. Ion transport experiments was conducted to compare diffusion and electromigration of two different ions: methylene blue and Na^+. Electromigration was found not to be significantly larger than diffusion with this experimental setup.

Acknowledgements

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Contents

1 Introduction

Organic mixed ionic-electronic conductors (OMIEC) are electrical semiconductors that have the added benefit of being able to transport ions. They are usually polymers with weak intermolecular interactions and highly disordered morphology which makes their actual structure difficult to probe. This class of materials started out as a candidate for new electrode materials but has since branched out into organic electrochemical transistors [1], actuators [2], light-emitting electrochemical cells [3] and ion pumps [4].

Since the human body uses ions for internal communication and actuation, being able to control ion flow with the help of an electric current is showing great potential for medical applications. For example action potentials travel through neurons with the help of biological ion pumps that move Na^+ and K^+ through membrane walls. This is the basic signaling mechanism of the nervous system. Mimicking nature's ion pumps with man-made devices is problematic since both electronic and ionic transport have to be controlled simultaneously. The coupling between these two forms of transport, how they influence each other, varies depending on the material used and its specific transport mechanisms.

The aim of this work is to develop an OMIEC membrane for an ion pump, with the goal of achieving significant electromigration of ions. Electromigration is used as a term for all ionic transport that happens due to the presence of an applied potential: electrophoresis, redox reactions and non-faradaic currents. The ion pump would be used to deliver charged drug molecules into brain tumours. The charged drug molecule would be transported from a source reservoir, through the membrane, into a target reservoir. This is the basic setup of an ion pump. The main obstacle to overcome for this application is the electric double layer that forms and screens the electric field, preventing an ionic drift current. This impedes the ability of the ion pump to deliver therapeutic amounts of drug to the target in a controlled manner. A membrane made from the right ratio of electronically and ionically conducting materials is proposed to be able to transport a significant amount of ions due to electromigration, while the electrical double layer is fully formed.

2 Background

2.1 Organic Mixed Ionic-Electronic Conductors

OMIECs can be divided into several different categories. Does it intrinsically contain ionic charge or not? Does the transport of charge occur homogeneously or heterogeneously throughout the material? A non-uniform charge distribution is important for many interesting qualities of the OMIECs and this can occur either by the presence of a polymer with repeating charged units and accompanying balancing charges, or by the presence of a polar polymer. The charge transport might be homogeneous, where both electronic and ionic transport occur in the same part of the material or the material has different intertwined phases of different composition where electronic transport dominates in one phase and ionic transport in another, i.e. a heterogeneous transport [5]. The most studied type of OMIEC is the intrinsically charged heterogeneous variety which is also the one used in this work. The mechanisms behind charge transport in these types of materials are presented in the following paragraphs.

Polymers, or plastics, usually perform as insulators, that is they do not conduct electronic current. This was the general state of affairs until the 1970's when the first π-conjugated conductive organic polymer was discovered [6]. This breakthrough was due to the π-conjugated polymer present in the material. A π-conjugated system is characterised by aligned p-orbitals on adjacent carbon atoms, the interaction of the delocalised electrons and the resulting π-bond. An easy example of this kind of molecule would be a carbon chain with alternating single and double bonds, see Figure 2.1. Single bonds are usually made of σ-bonds and double bonds consists of a σ-bond and a π-bond. Due to its delocalised nature, the π-bond is weaker than the σ-bond. If multiple p-orbitals from neighboring atoms are aligned, the delocalisation can extend over multiple atoms, see Figure 2.2. The electron is delocalised over a certain length of the chain, which is referred to as the conjugation length. The conjugation length may be the whole length of the carbon chain, or due to defects or twists in the chain, the π-bond is disrupted and the molecule could be split into two or more conjugated segments. The electron can delocalise within a conjugated segment and the movement between segments are facilitated by hopping, which is a thermally activated process and therefore limited to a likely range of distances and energy states. In order for an electron to traverse effectively through a material composed of

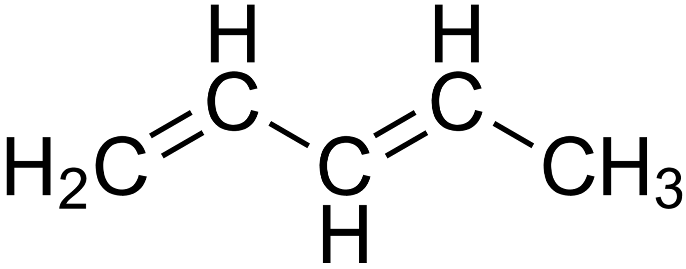


Figure 2.1: The conjugated molecule 1,3-pentadien.

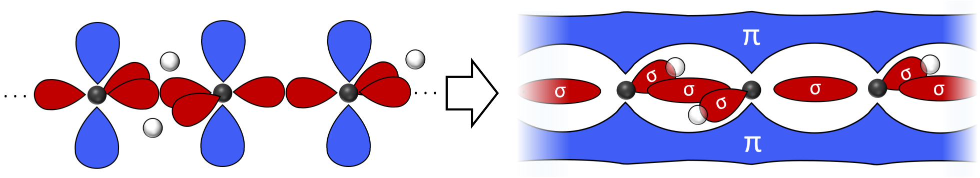


Figure 2.2: The blue p-orbitals in a conjugated polymer forms a delocalised π-bond. The red sp_2 bonds form localised σ-bonds. Picture from reference [7].

both conductive and non-conductive pathways, there must be a high enough concentration of hopping sites to ensure that at least one unbroken pathway exists. The concentration needed for this to be the case is referred to as the percolation threshold.

Since the initial interest of the scientific community was the electronic transport properties of organic materials, mechanisms for ion transport are not as well understood [8]. If there is an uneven distribution of charge in a material on the nanoscale, either due to the polarity of the backbone or repeating charged units, ions may temporarily bind to these sites and hop between them. In dry OMIECs, ion transport is due to this kind of ion hopping accompanied by movement and stretching of the mesh of the material [9]. If the OMIEC comes into contact with water, the material swells. This introduces water channels in the material which allows for easier ion hopping between fixed charges [10]. The ion can also diffuse together with an ion of opposite charge through the water channel. Together the ions does not have a net charge and is therefore unaffected by the fixed charges [11], see Figure 2.3.

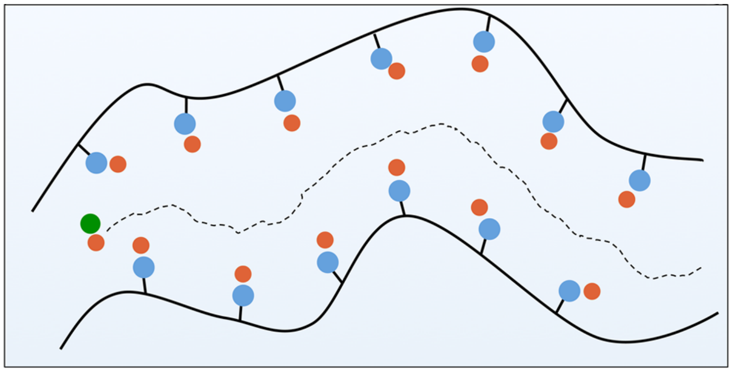


Figure 2.3: The positive red ions are attracted to the fixed negative blue charges in the material. Ion transport occurs due to hopping between fixed charges or free transport in the channel if a counterbalancing ion, portrayed in green, renders the ion pair charge neutral and is therefore unaffected by the fixed charges. Picture modified from reference [11].

The coupling between electronic and ionic transport has a large impact on charge transport; usually the microstructure that improves electronic transport diminishes ionic transport and vice versa. For example, swelling an OMIEC with water will increase ion transport due to more water channels but it will also decrease electronic transport due to the increased average hopping distance. The expansion due to the swelling might also break the contact between the conjugated polymers which removes the possibility of hopping entirely.

2.2 OMIECs in drug delivery applications

Because of their mixed conducting properties, OMIECs are considered well suited for controlling ion flow with the help of an electric field. This property has made OMIECs useful for different drug delivery applications. Actuation of OMIEC materials have been achieved by applying a voltage that transports ions and accompanying water molecules from one side to the other. Alternating this bending motion by applying an alternating voltage has been used in a micropump structure to push drug solution [12].

A redox-mediated drug release mechanism has also been explored. Charged drug molecules are infused into the OMIEC, which binds them to the fixed charges in the material. If the drug molecules are, for example, positively charged, injecting a hole current into the material will screen the fixed charges and allow the drug molecules to diffuse into the target at the desired time [13].

The application investigated in this work is the organic electronic ion pump (OEIP). The simplest form of an ion pump is two liquid-filled reservoirs separated by a semi-permeable membrane, which is sandwiched between two electrodes. Ions are transported from the source reservoir, through the membrane and into the target reservoir by an applied potential. No solvent is transported, only the ions and their hydration layers move through the membrane. This so-called dry transport makes the OEIP unique. Other benefits of the ion pump are high precision spatial delivery, exact control of dosage and easily resupplied devices [14].

2.3 Organic electronic ion pump applications

The first implantable OEIP used for therapeutic purposes in a living, awake, and freely moving animal was reported in 2015 by Jonsson et al. [15]. They demonstrated delivery of the inhibitory neurotransmitter Gamma-Aminobutyric Acid (GABA) in order to treat neuropathic pain in rats. They then applied OEIPs to the treatment of epilepsy. Epilepsy refers to symptoms caused by uncontrolled bursts of electrical activity in the brain. By combining an OEIP delivering GABA with an electrode that sensed when bursts of activity occured, Jonsson et al. were able to quench an induced epileptic seizure in a brain slice model. The device was the size of a single cell and could provide highly localised sensing and drug delivery capabilities [16].

Another epilepsy treating ion pump has been developed by Proctor et al. They developed a syringe-like neural probe with a microfluidic channel, capable of pumping GABA through an OMIEC membrane when a sensing electrode registered a seizure [17].

OEIPs have also been used to study plant physiology. Bernacka-Wojcik et al. reported using an OEIP to deliver the hormone abscisic acid (ABA) into plant leaves. This hormone regulates the stress response of the plant and by examining leaf pores closing, they could reveal previously unreported kinetics of ABA-induced signal propagation in leaves [18].

A novel application of OEIPs is cancer tumour treatment. Cancer is caused by uncontrolled proliferation of abnormal cells and is the second most common cause of death globally [19]. In England and Wales, only 19% of brain cancer patients survive for five years or more [20]. Due to the sensitive environment around a brain tumour, surgery is not always possible. Furthermore, the clinical effect of surgery is still controversial and the most common type of brain cancer cannot be treated with surgery alone [21]. For this reason, different forms of drug administration have been investigated.

Flooding the whole body with cytotoxic drugs, as is done in systemic chemotherapy, is an ineffective way of treating brain tumours because of the blood-brain barrier. This semi-permeable border inhibits the diffusion of foreign molecules, including cancer drugs, into the brain from the blood stream. This method suffers from high off-site toxicity since a therapeutic concentration of drug in the brain is impossible without severe repercussions in the rest of the body [22].

In an effort to circumvent the blood-brain barrier, convection enhanced delivery has been developed. A catheter is guided through a hole in the skull, directly to the tumour site and a drug solution is injected by applying a low pressure. This minimises off-target toxicity and is a reliable way to achieve a therapeutic concentration of drug in the brain tumour [23]. Issues with this method involve reflux of the solution through the insertion channel, and the local pressure increase in the brain due to the extra amount of fluid in the tumour area [24]. The latter may cause symptoms that vary from nausea and dizziness to memory loss and seizures [25].

2.4 The aim of this thesis

The aim of this thesis is to develop a membrane that could exhibit continuous ion transport due to electromigration when put in an ion pump setup. By integrating the membrane in a catheter, connecting it to a microfluidic system and inserting it into the skull, as was done for epilepsy treatment by Proctor et al. [17], the blood-brain barrier can be circumvented. Furthermore, the dry drug transport of the OEIP circumvents the side effects associated with convection enhanced delivery. Due to the formation of the electrical double layer, ion migration due to an electric field within the membrane in a OEIP exponentially decays over time and usually becomes negligible within a few seconds. This makes it difficult to achieve a therapeutic concentration of charged drug molecules. Developing an OEIP capable of continuously transporting a significant amount of ions via electromigration is a step towards solving this problem. Such a device will be investigated in this work by creating a novel OMIEC membrane and applying it within an ion pump configuration.

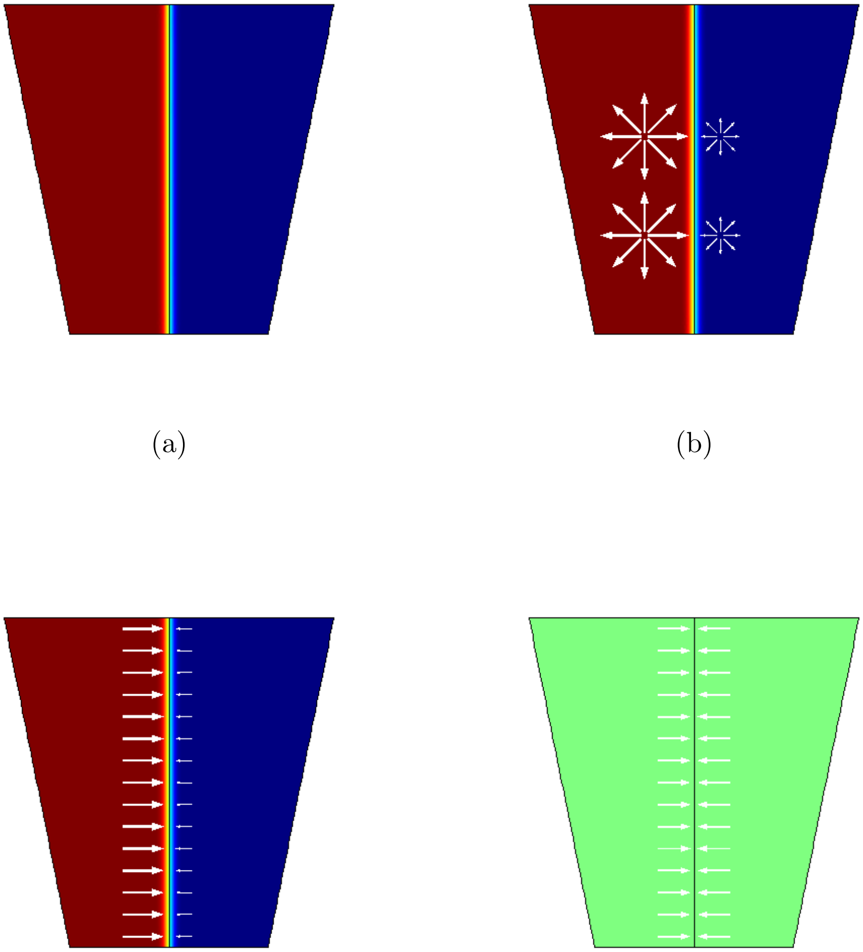
3 Theory

3.1 Charge transport in OEIPs

If two connected liquid-filled reservoirs have different ion concentrations, there will be a net flux of ions between them. This is due to diffusion. Every particle with a temperature above 0 K has some motion associated with it, which is random in direction due to frequent collisions with other particles. It is this random thermal motion that gives rise to diffusion, which causes particles to move from areas of high concentration to areas of low concentration. How random motion produces uniformity is illustrated in the example in Figure 3.1. This phenomenon is relevant for the ion pump, since we have two reservoirs with different ion concentrations. As long as there is a concentration difference there will be a net flux of molecules from the reservoir of high concentration. This will have to be accounted for in the design of the experiments.

Another important mechanism in OEIPs is particle drift due to an external electric field, and the termination of this current due to the formation of the electrical double layer. Electrons and ions will both move under the influence of an electric field which is supplied by the charged electrodes. For example, a positively charged electrode will attract both electrons and negatively charged ions. Unlike electrons, the ions cannot enter the electrodes and will surround them instead. The electrodes adsorb the ions closest to the surface, which creates two layers of opposite charge, one within the electrode and one on the outside. This so-called electrical double layer screens the electric field and diminishes the drift current. The non-adsorbed ions floating around the electrode are referred to as the diffuse layer. These ions also take part in screening the field but are more free in their movement. When the charge of the ions adsorbed to the electrode and the ions in the diffuse layer equal the charge on the electrode, the electric field is fully screened and the current is terminated.

For the application investigated in this thesis, the applied potential is limited by unwanted electrochemical reactions of which the easiest to identify is water splitting. If the electric field due to the applied potential is strong enough to separate hydrogen from oxygen in water molecules, hydrogen gas and oxygen gas are produced. Water splitting and other unwanted electrochemical reactions degrade the experimental setup and prevent reliable and reproducible transport experiments. In optimal conditions for water split-



(a) (b)

(c) (d)

Figure 3.1: The mechanism behind diffusion. a) Assume that we have two liquids, one with a high concentration of particles, pictured in red, and one with a low concentration, pictured in blue. b) The amount of particles moving in a certain direction due to random thermal motion is indicated by the size of the arrows. c) A net flux of particles across the interface from the high concentration reservoir into the low concentration reservoir. d) Eventually the concentration will be equal on both sides, with the net flux being zero across the interface. Pictures from reference [26].

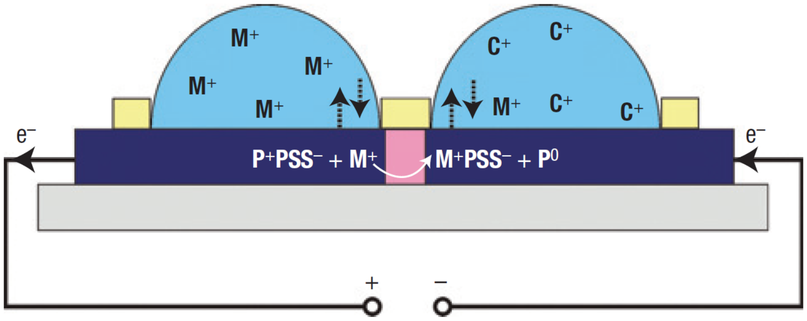


Figure 3.2: The ion pump designed by Isaksson et al. On top of the grey substrate, two dark blue PEDOT:PSS electrodes are separated by a channel of overoxidised PEDOT:PSS, depicted in pink. The light blue source electrolyte contains the ion to be transported, M^+, and the other electrolyte contains another positive ion, C^+. The electrolytes are kept in place by the photoresist SU-8, depicted in yellow. A voltage may be applied across the PEDOT:PSS electrodes, which causes the reaction described in the text.

ting, a potential of 1.23 V is theoretically enough for gas bubbles to form [27].

3.2 The ion pump

In 2007, an ion pump was presented by Isaksson et al. [4] that was based on PEDOT:PSS electrodes. A simplified version of the ion pump will be presented. The microfabricated ion pump consists of two PEDOT:PSS electrodes that are separated by a channel of overoxidised PEDOT:PSS. Overoxidised PEDOT:PSS is an electronically insulating material that conducts ions. Electrolyte solutions are deposited on top of the PEDOT:PSS electrodes, see Figure 3.2. The source electrode is covered with a source electrolyte containing the ion to be transported, M^+, and the target electrode is covered with a target electrolyte containing another kind of positive ion, C^+. The M^+ concentration in the source electrolyte is large, which causes the ions to diffuse into the source electrode and bind to the PSS polymer. By biasing the ion pump as shown in Figure 3.2, the following reaction occurs:

$$\mathrm{PEDOT^+PSS^-} + \mathrm{M^+} + \mathrm{e^-} \rightleftharpoons \mathrm{PEDOT^0} + \mathrm{PSS^-\,M^+}.$$

For the left hand reaction, PEDOT is oxidised in the source electrode resulting in a free electron and the release of the M^+ ion from the PSS^-. The M^+ ion migrates across the overoxidised channel and into the target electrode, either by diffusion or by electromigration. In the target electrode on the right hand side the PEDOT is reduced, allowing M^+ to enter the electrode and bind to a PSS^- unit. The M^+ ions move from the target electrode to the target electrolyte by ion exchange with the C^+ ions.

The ion pump used in this thesis consists of two reservoirs surrounding two gold mesh electrodes that sandwiches a membrane, see Figure 3.3. With an applied potential, the electrical double layer will screen the electric field within the membrane. We hypothesize that with no applied potential, a diffusion current will be present across the membrane, and with an applied potential, both a diffusion and a significant electromigration current will be present.

The hypothesis is motivated by unpublished data by Dr. Christopher Proctor. By varying the amount of PSS in PEDOT:PSS membranes, it was discovered that membranes with a low amount of PSS exhibited a constant current over time, similar to electronic conductors, while a high amount of PSS showed an exponentially decaying current, which is the hallmark of an ionic conductor where the electrical double layer screens the electric field. Furthermore, an intermediary amount of PSS produced a membrane with a peculiar transient. The current initially decays exponentially but reaches a constant non-zero value, see Figure 3.4. This current shows properties of both electronic and ionic conduction and it is assumed that part of the steady-state current is composed of a continuous ionic current. This mixed conducting regime was achieved by adjusting the ratio of electronically and ionically conducting materials in the membrane. This work will aim to achieve a similar regime with a different combination of materials, namely the mixed conductor PEDOT:PSS and the ion conductor PEGDA.

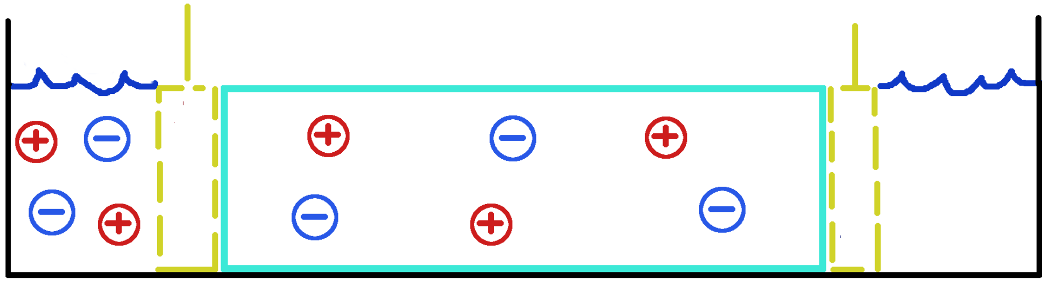


Figure 3.3: An ion pump based on two gold mesh electrodes, depicted in yellow, in contact with a mixed conducting membrane, depicted in light blue. The source reservoir to the left is filled with an electrolyte containing the ion to be transported, and the target reservoir is filled with DI water.

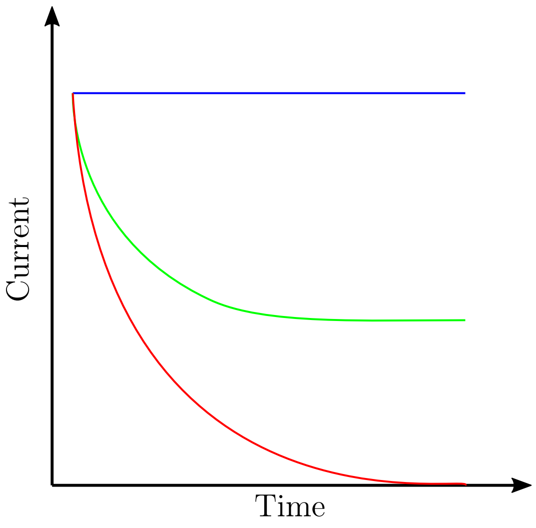


Figure 3.4: Current over time schematic for different conducting regimes. The electronic conducting regime is depicted in blue, the mixed conducting regime is depicted in green and the ionic conducting regime is depicted in red.

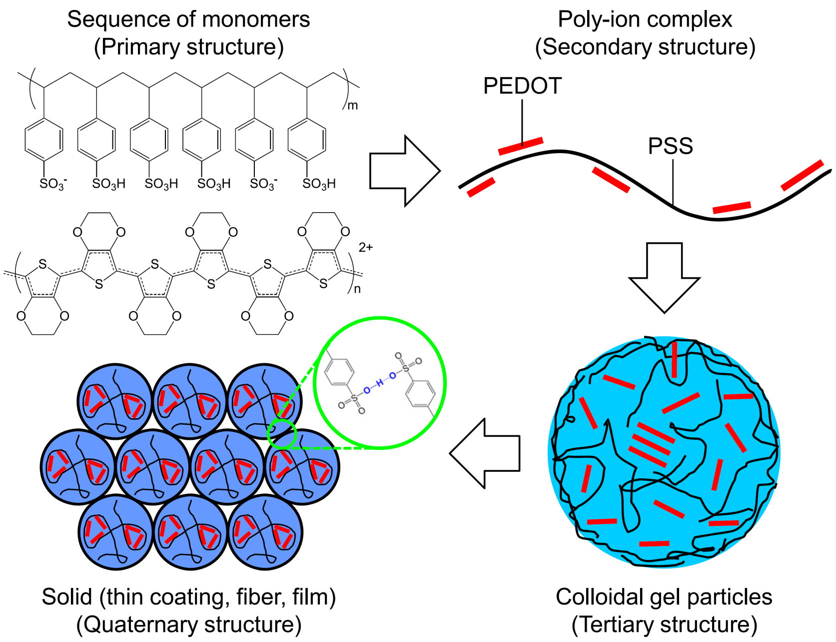


Figure 4.1: The morphology of PEDOT:PSS. The primary structure consists of the separated PEDOT and PSS monomers. The secondary structure shows the short PEDOT chains bound to a longer PSS chain. The tertiary structure depicts a PEDOT:PSS grain which consists of a high PEDOT concentration in the centre surrounded by an even blend of PEDOT and PSS, with an outer shell of PSS. A PEDOT:PSS membrane is composed of multiple grains, which is shown in the quaternary structure. Picture from reference [28].

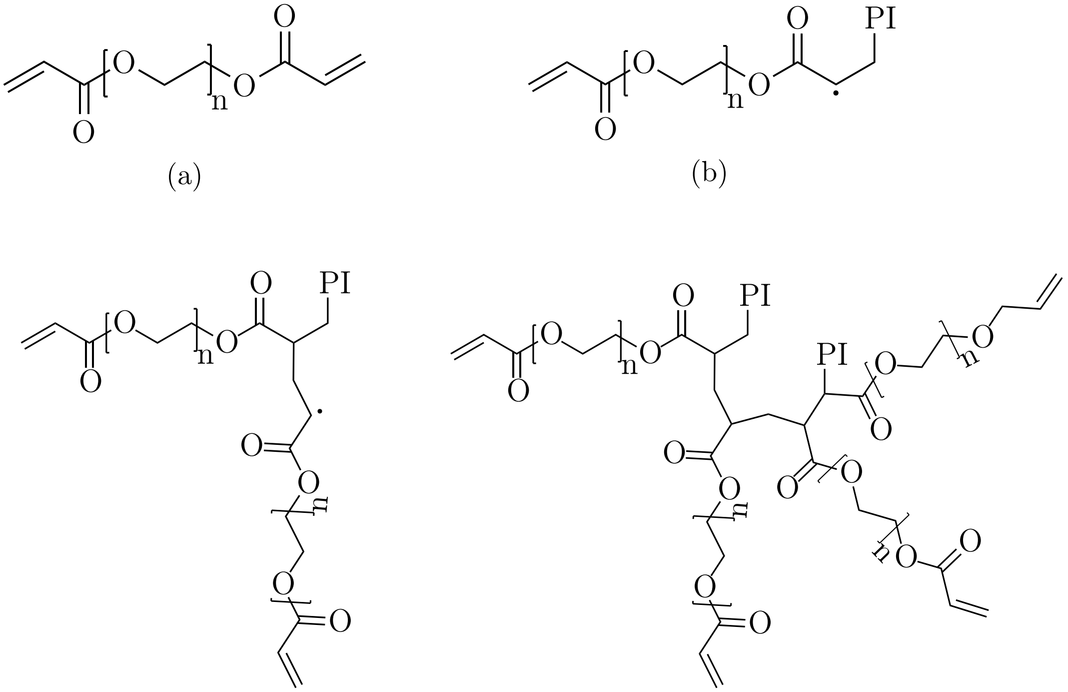
4 Materials and Methods

4.1 Membrane materials

Poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate, abbreviated as PEDOT:PSS, is a commonly used OMIEC that intrinsically contains ionic charge and transports ions and holes in different phases of the material. By doping the conjugated polymer PEDOT with the polyelectrolyte PSS, a water soluble material with a relatively high conductivity is created. The positively charged holes on the PEDOT chain that are responsible for electronic transport are balanced by the negatively charged subunits of PSS. Ion transport is thought to occur mainly in PSS rich phases of the material, where the ions hop between the subunits of PSS. The morphology of PEDOT:PSS is well known and is presented in Figure 4.1.

Polyethylene glycol (PEG) is an organic hydrophilic polymer, which when synthesized into polyethylene glycol diacrylate (PEGDA), can be crosslinked into a hydrogel. A hydrogel is a network of hydrophilic polymers and is usually ionically, but not electronically, conducting. The acrylate group at each side of the PEGDA molecule contains a double bond which can be broken and used to crosslink multiple PEGDA molecules together. This is achieved by introducing a photoinitiator (PI), which is a molecule that produces free radicals when exposed to UV light. A free radical is a molecule with an unpaired electron and is therefore highly reactive. When a free radical encounters a PEGDA molecule, it removes an electron from the weak π-bond in the acrylate unit and forms a bond of its own, attaching itself to the PEGDA molecule. This combined molecule has an unpaired electron left over from the broken π-bond, which makes it a free radical as well. Therefore, it can break a π-bond on another PEGDA molecule, continuing the crosslinking process, see Figure 4.2. Since PEG is hydrophilic and acrylate is hydrophobic, the acrylate groups from different molecules cluster together when dispersed in an aqueous solution. When the polymerisation is initiated, crosslinking centers form, which are connected by a backbone of PEG molecules, see Figure 4.3. The crosslinking terminates when the PEGDA chain comes into contact with another free radical produced by a PI molecule [29].

The crosslinked PEGDA molecules forms a hydrogel, that is a mesh of hydrophilic polymers. The size of the ions that can pass through the hydrogel is determined by the size of the gaps in the mesh, the mesh size, which depends on the molecular weight of the PEGDA and the amount of UV exposure to the material [30]. As the name suggests, polyethylene glycol consists of ethylene glycol molecules. A larger molecular weight indicates that one PEGDA molecule contains more ethylene glycol molecules, which means that the crosslinking centers will have longer strands of PEG backbone between them, resulting in a larger mesh size. The amount of UV exposure determines how many free radicals are created, which affects how much of the PEGDA that crosslinks. The right amount of UV exposure is worth investigating. Too much will decrease the mesh size since a high crosslinking density will produce a tightly woven network of polymers, while too little exposure will yield a weak and unstable hydrogel.



(a) (b)

(c) (d)

Figure 4.2: Illustration of PEGDA crosslinking. a) The molecular structure of PEGDA. b) The photoinitiator (PI) radical binds to the molecule, opening up the double bond and generating an unbound electron, pictured with a dot. c) The unbound electron opens up a double bond on another PEGDA molecule, which binds to the chain. d) PEGDA molecules attach until the process is terminated by another photoinitiator radical. The angles between adjacent PEGDA molecules are not correct: this picture is a rough illustration of the mechanism.

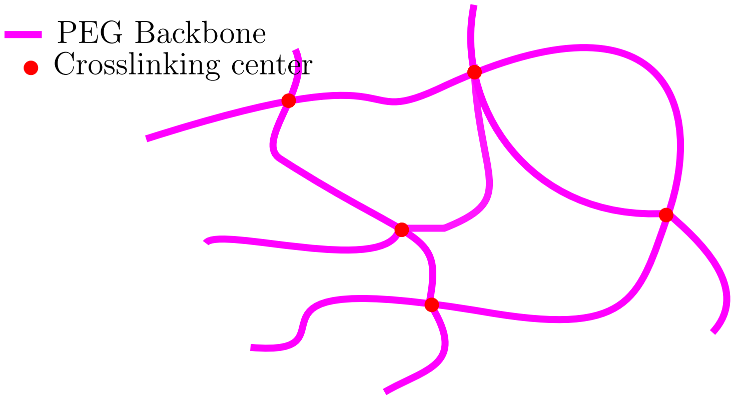


Figure 4.3: A schematic of the PEGDA hydrogel mesh network after polymerisation. Acrylate clusters crosslink and form crosslinking centers. The PEG backbone connects the centers, forming the mesh.

4.2 Making the membrane

The membrane making procedure began by putting the PEDOT:PSS solution Clevios™ PH 1000, which contains 1.15 wt% of the polymer, in an ultrasonic bath and filtering it through an 0.45 µm filter. This will minimize any aggregation of the PEDOT:PSS. PEGDA was added and the solution was sonicated in water with a temperature of 40° to ensure that the PEGDA dissolves. If other materials were incorporated into the membrane, they were added during the previous step. The photoinitiator was added and the solution was mixed. With the finished solution at hand, 2-3 droplets were put between two glass slides separated by approximately 0.3 mm, see Figure 4.4, and the glass sandwich was put into a UV oven. After the desired amount of exposure, the glass sandwich was extracted and submerged in DI for 15-30 minutes to allow the membrane to hydrate, which makes it easier to pry the glass slides from each other without damaging the membrane. The membrane was then stored in DI water for at least 24 hours to allow it to fully swell before experiments were conducted.

Another crosslinking mechanism was briefly investigated. (3-glycidyloxypropyl) trimethoxysilane (GOPS) is a common crosslinker for PEDOT:PSS as it binds the PSS units from different polymers to each other. However, it also binds PSS to glass [31] which could make removing the membrane from the glass substrate difficult. Since the GOPS crosslinking mechanism is activated by heat, the glass slide substrate with membrane solution was put

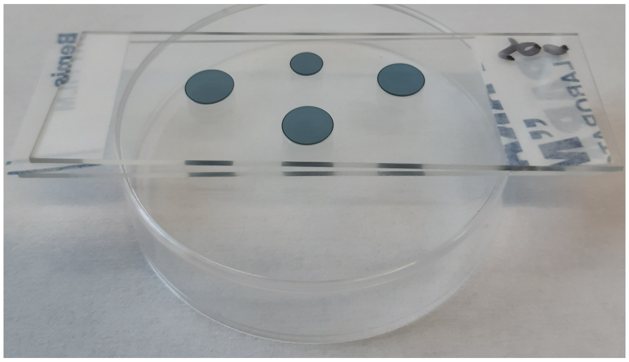


Figure 4.4: Membrane solutions sandwiched between two glass slides separated by 0.3 mm.

on a hotplate with a temperature of 70°C for one hour.

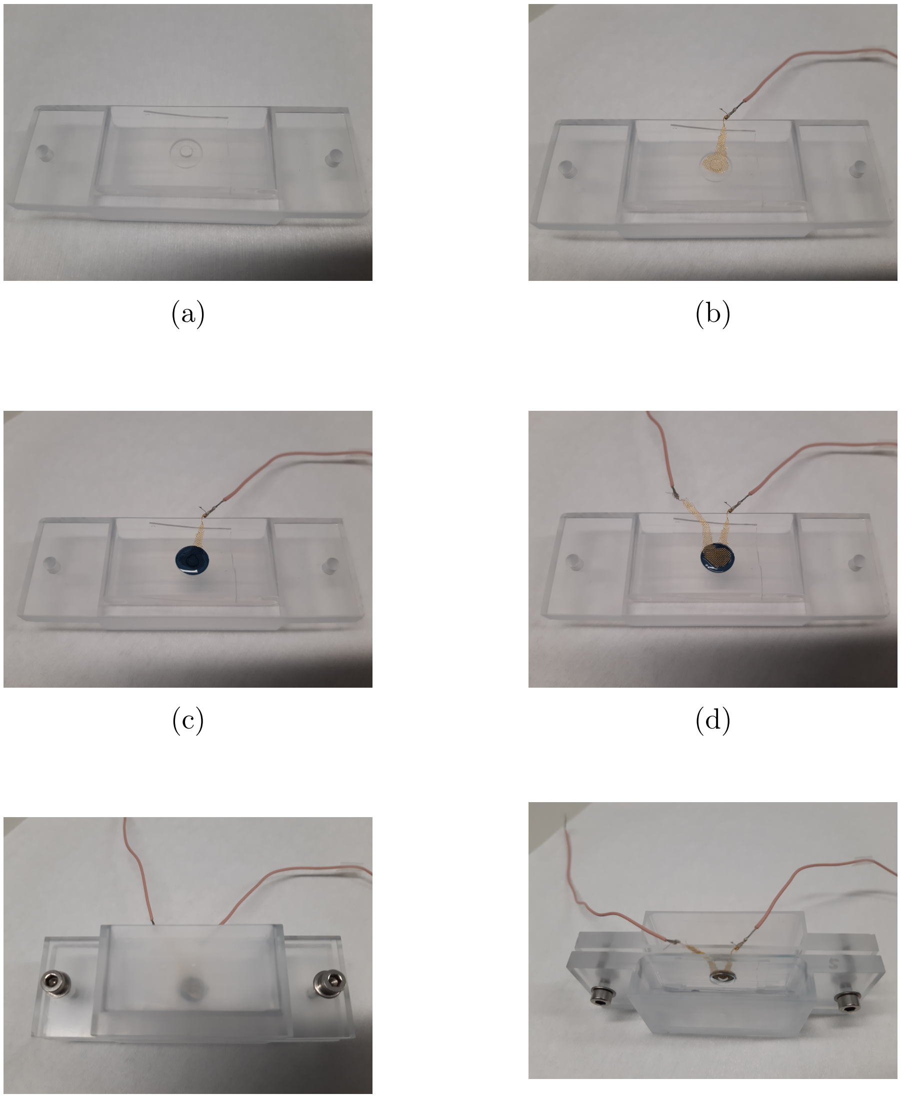
4.3 Experimental setup

4.3.1 Cell setup

The cell used for membrane characterisation and ion transport experiments consists of two acrylic containers, two gold mesh electrodes and a membrane. A piece of the polymer polydimethylsiloxane (PDMS), made with the SYLGARD 184 silicone elastomer, was added to each container to create a soft and elastic surface that prevents leakage and lessens the pressure on the membrane. The thickness of the piece was 2 mm. Assembly of the cell is shown in Figure 4.5.

4.3.2 Ion transport experiments

Ion transport experiments were carried out by filling the source reservoir with a solution containing the ion to be transported, and filling the target reservoir with de-ionized (DI) water. To ensure that the diffusion rate does not change during the experiments, the liquid-filled cell was left for 2 hours to achieve diffusion equilibrium. Subsequently, the target was refilled with clean DI water and the diffusion experiment was conducted. The ions were allowed to diffuse into the target for the experimental duration, after which the target solution was collected and the reservoir was refilled for the electromigration experiment. A potential of +0.8 V was applied across the electrodes, using



(a)

(b)

(c)

(d)

(e)

(f)

Figure 4.5: Assembly of the cell used for testing membrane properties. a) The PDMS covered hole in the acrylic container is b) covered with an electrode. c) The membrane and d) the second electrode is added. e) The second container is attached by two screws and f) the cell is ready to be filled with liquid.

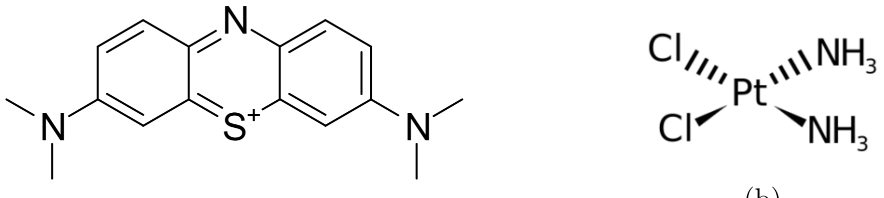
the target electrode as the reference, for the same duration and the target was collected. Note that diffusion is also present while a potential is applied, but for the sake of brevity, experiments involving an applied potential will be referred to as an electromigration experiment. The two target samples were compared in order to measure the electromigration of ions. Two different ions were transported: methylene blue and Na^+. The source reservoir in these experiments consisted of DI water with a concentration of either 10 mM methyleneblue or 100 mM Nacl.

4.4 Characterisation

4.4.1 Evaluating membrane compositions

Which materials, and what molecular weight of those materials, produced a membrane composition capable of transporting cancer drugs? This question was answered by investigating whether an analogue to a known cancer drug passed through the membrane. Methylene blue is a positively charged organic dye with a molar mass of 319.85 g/mol, which is comparable to the commonly used cancer drug cisplatin with a molar mass of 300.01 g/mol. Cisplatin in itself is neutral, but when in contact with water, H_2O molecules replace one of the Cl atoms in a process termed aquation. This can transform the cisplatin molecule $[Pt(NH_3)_2Cl_2]$ into various charged compounds, for example $[Pt(NH_3)_2Cl(OH_2)]^+$, which has a molar mass of 279.58 g/mol [32]. The methylene blue molecule is composed of three benzene molecules and is significantly larger than any aquated cisplatin molecule, see Figure 4.6. If methylene blue passes through the membrane, then so should the aquated form of cisplatin. The membranes ability to pass methylene blue was examined ocularly by filling the source in the cell with methylene blue solution and observing whether any dye passed through the membrane and into the target, which was filled with DI water. Once a membrane composition that successfully transported methylene blue was found, the amount of UV exposure was chosen to allow for as much methylene blue transport as possible.

Furthermore, the membranes had to be robust and homogeneous. Robust enough to withstand being sandwiched between the gold electrodes in the cell, and homogeneous enough to ensure that any coupling between electronic and ionic transport that might be responsible for continuous ion transport was present in the entire membrane.



(a) (b)

Figure 4.6: a) Methylene blue and b) cisplatin.

4.4.2 Multistep amperometry

Once suitable membrane materials were found, the optimal ratio of the materials involved was still to be decided. The steady-state current through the membranes with different ratios was measured using a Palmsens4 potentiostat, and used to compare their performance. This was determined by putting the membranes in the cell with a 100 mM NaCl solution in both reservoirs and conducting multistep amperometry. Amperometry measures the current through a sample due to a specified applied potential, and multistep amperometry allows multiple different potentials to be applied in succession. One multistep amperometry cycle consisted of applying 0.8 V for 30 seconds followed by −0.8 V for 30 seconds. As can be seen from Figure 4.7 a), the current response from the membrane changes with successive cycles. Note that the behaviour of the transients seems to saturate within 20 cycles. The 20 positive current transients from Figure 4.7 a) are plotted overlapping each other in Figure 4.7 b). By zooming in around the 30s mark, as is done in Figure 4.7 c), it is seen that 20 cycles are indeed enough for the behaviour of the current transients to saturate. Even though the transients are still declining over time, the steady-state current after 30s of applied voltage was deemed stable enough to use for comparing membranes. The average of the last four data points of the positive transient from the last cycle is taken as the value of the steady-state current through the membrane, which for the example in 4.7 results in $(0.144\,\mu\text{A}+0.138\,\mu\text{A}+0.145\,\mu\text{A}+0.137\,\mu\text{A})/4=0.141(4)\,\mu\text{A}$. The margin of error is also affected by the inexact nature of the cell assembly process. Every time the cell is assembled, the overlap of the electrodes and the distance between them is slightly different, which affects the strength of the electric field across the membrane. The error due to this variation, 0.015 µA, was estimated by comparing steady-state current values before and after reassembling the cell. This is the most significant error. The multistep amperometry described above was conducted three times on every membrane to ensure reproducibility.

4.4.3 Absorption

The target solutions produced by the methylene blue transport experiments were characterised using a AvaSpec-ULS2048CL-EVO (CMOS) spectrometer. The absorbance peak of methylene blue at 300 nm was measured for in order to compare the ion concentration of the samples. Note that the linear relationship between ion concentration and absorbance breaks down at high ion concentrations. The spectrometer measures transmittance, T, which can be converted into absorbance, A, by the relation

$$T = 10^{-A}.$$

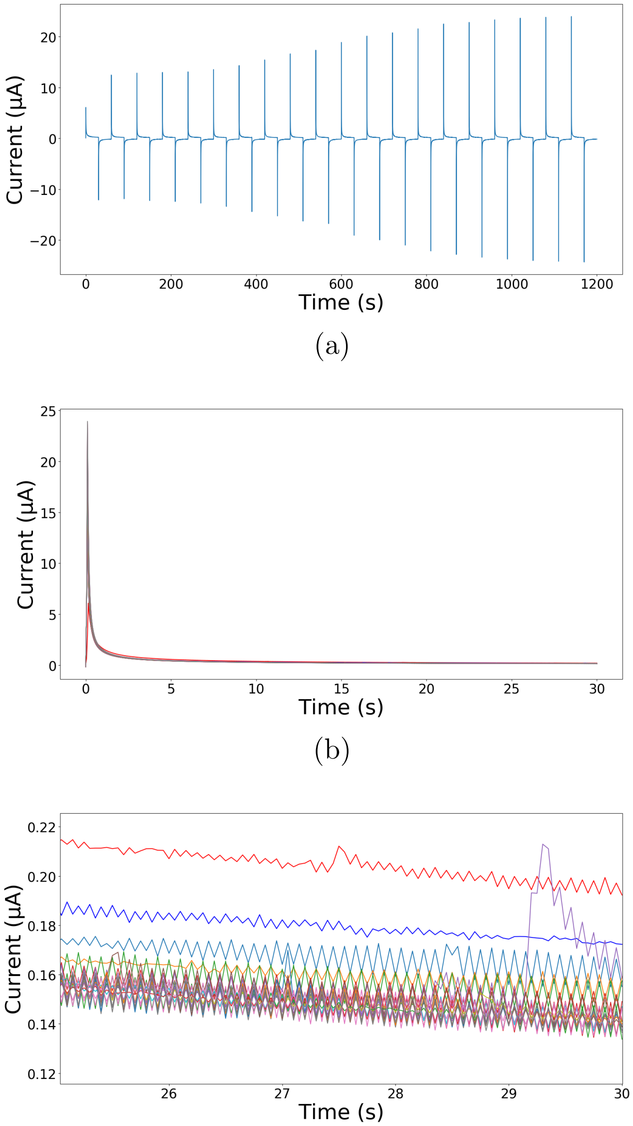
Furthermore, the relationship between ion concentration and absorbance is described in a version of Beer-Lambert's law:

$$A = \epsilon l c,$$

where ϵ is the absorptivity, l is the optical path length and c is the concentration of the species [33]. It is generally advised to keep the absorbance below a value of one to ensure this linear relationship.

4.4.4 Conductivity measurement

The ion concentration of the target solutions in the Na^+ transport experiments was quantified using a Mettler-Toledo Inlab 731 conductivity probe, which runs an alternating current through the solution and measures the ionic conductivity.



(a)

(b)

(c)

Figure 4.7: a) A multistep amperometry experiment showing the membrane response changing with successive cycles. b) The positive voltage responses from a) overlapped. c) Illustration of how the steady state current changes with successive cycles. The red line is from the first cycle, the blue line is from the second and so on. The steady-state current reaches an equilibrium within 20 cycles.

5 Results and Discussion

5.1 Membrane material composition

The search for a membrane composition that produced robust, homogeneous membranes that could pass methylene blue began with a membrane consisting of a PEDOT:PSS solution, low molecular weight PEGDA, and the photoinitiator (PI) 2-hydroxy-2-methylpropiophenone. PEGDA, with a molecular weight (MW) of 250 MW, was found not to mix with the PEDOT:PSS at all while the 575 MW PEGDA did. A homogeneous and robust membrane was successfully produced, however, methylene blue did not pass through it. Too small mesh size was deemed to be the problem and hence different ways of increasing the mesh size was investigated.

First up was reducing the crosslinking density by introducing sodium acrylate. The idea was that replacing some of the PEGDA, which has an acrylate group at both ends, with sodium acrylate, which has an acrylate group only at one end, would decrease the crosslinking density. Less available crosslinking points should increase the mesh size and allow for a larger selection of ions to pass through. A 1 M solution of sodium acrylate had been shown by Dr. Christopher Proctor to blend well with PEGDA, but unfortunately the addition of PEDOT:PSS did not produce a homogeneous solution or a robust membrane.

Instead of reducing the crosslinking density, the project proceeded with adding larger molecules, PEG 1500 MW, to the mix in order to introduce larger pores in the membrane. When properly mixed, the solution produced robust membranes, but no methylene blue was able to pass through them.

GOPS was used as the crosslinking mechanism with a PEDOT:PSS and PEG 1500 MW solution, which did produce homogeneous robust membranes, but no methylene blue passed through.

A membrane that successfully transported methylene blue was made by using the larger PEGDA 2000 MW. Dissolving PEGDA 2000 MW in only PEDOT:PSS did not allow dye to pass, but introducing DI water produced homogeneous, robust membranes that showed successful methylene blue transport. The ratios of these materials were free to experiment with in order to optimize the membrane. For the sake of simplicity, the amount of PEGDA 2000 MW was kept fixed to 0.05 g per 500 µL total solution and the ratio of the liquids, PEDOT:PSS and DI, was varied in the recipe. The PI amount was kept at 2 wt%. For example, the first membrane that was used in an actual ion transport experiment was made from a recipe with 0.05 g of PEGDA 2000 MW, 12 µL PI, 100 µL PEDOT:PSS and 400 µL DI. A short-hand notation for the recipe will be used, expressed as amount of PEDOT:PSS per 500 µL solution. For the recipe above, this would take the form 100 P:PSS/500.

Varying the amount of UV exposure was investigated by subjecting a 100 P:PSS/500 solution to an exposure of either 9.6 J/cm^2 or 48 J/cm^2. Less exposure should produce a membrane with a larger mesh size, and therefore higher ion transport capabilities. However, methylene blue transport experiments conducted with the different exposures showed that the membrane with a higher exposure transported more dye (with absorbance values of 0.86 for diffusion and 1.06 for electromigration) than the membrane with less exposure (0.57 for diffusion and 0.53 for electromigration). Diminishing the UV exposure provided no benefit and therefore the exposure of 48 J/cm^2 was kept as the standard for all membranes.

5.2 Multistep amperometry

Multistep amperometry was performed on the membrane composition containing PEGDA 2000 MW, with recipes varying from 0 P:PSS/500 to 450 P:PSS/500 and the results are presented in Figure 5.1. This result characterises the membranes and indicates that adding PEDOT:PSS significantly changes the steady-state current through the membrane. The steady-state current is seen to increase with the addition of PEDOT:PSS up until a maximum at 400 P:PSS/500. There was reason to believe that a higher steady-state current correlated with a larger electromigration of ions, which will be investigated in the next section.

Note the error bar for the 450 P:PSS/500 membrane in Figure 5.1. For this recipe, successive multistep amperometry measurements did not provide a reproducible steady-state current value until the fifth round, with a total of 100 cycles. With this high amount of PEDOT:PSS, the membrane swelled to such a degree that it became unstable and prone to breaking while in the cell, and the error bars illustrates the resulting unreliable performance of the membrane.

To investigate whether there is an correlation between steady-state current and electromigration of ions, methylene blue transport experiments were conducted.

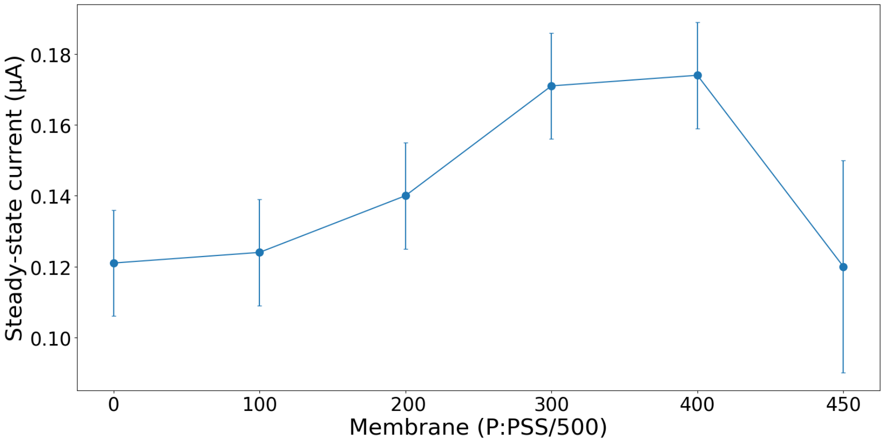


Figure 5.1: Steady-state current values for different membrane recipes.

5.3 Methylene blue experiment

Data from the ion transport experiments with methylene blue in the source are presented in Figure 5.2. The diffusion and electromigration experiments that are to be compared are referred to as an experimental set and are placed adjacently in the graph. Note that a higher absorbance indicates a higher concentration of ions.

The 0 P:PSS/500 membrane contains no PEDOT:PSS and hence no electronically conducting material. If mixed conduction is necessary for significant electromigration, this membrane should not exhibit any difference between diffusion and electromigration experiments. This is indeed the case. The addition of PEDOT:PSS, resulting in a 100 P:PSS/500 membrane, produced promising results. A significant difference can be seen between diffusion and electromigration in the three sets of experiments that were conducted. Note that only one set keeps the absorbance below a value of one, since this restriction was not known at the time. The resulting nonlinearity between absorbance and concentration might explain why the difference between diffusion and electromigration seems to diminish with each successive set of experiments. Lastly, the 200 P:PSS/500 membrane also shows a difference between diffusion and electromigration, but with an overall decrease in methylene blue transport capabilities. It seems that adding PEDOT:PSS diminishes the methylene blue transport capabilities of the membrane.

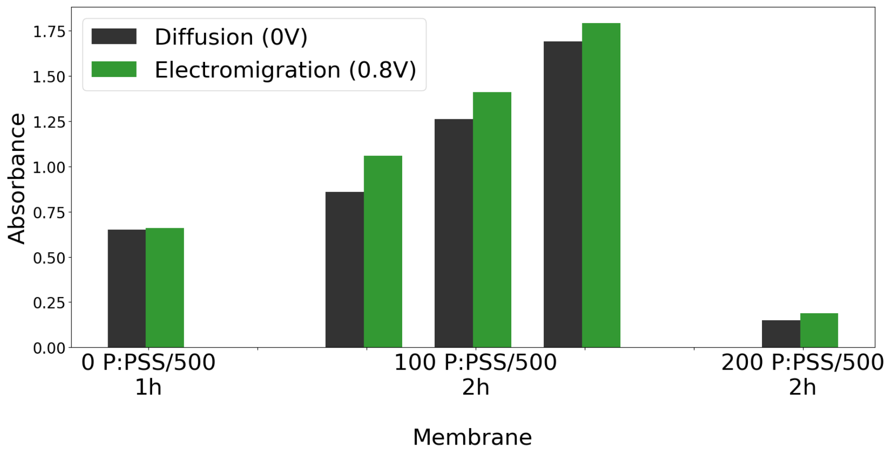


Figure 5.2: Ion transport experiments with methylene blue in the source and DI water in the target. Three different membranes were tested. The duration of the experiments are indicated underneath the membrane recipe.

Note that the 100 P:PSS/500 membrane shows an increase in dye transport with each successive set of experiments. For example, the absorbance of electromigration varies from 1.0 to 1.75 between sets. The membrane was stored in DI water between sets of experiments, which were conducted on different days due to their long duration. This could allow the membrane to swell with water over time, increasing its ion transport capabilities. An attempt to prevent this was made by storing the membranes for 24 hours in DI water before the first set of experiments, but apparently it was not enough.

From one set of experiments, we can get an on/off ratio for our setup by taking the ratio of the absorbance from the electromigration experiment and the absorbance from the diffusion experiment. The on/off ratio can be used as a measure of how much ions were transported due to the applied potential. Unfortunately due to the spectrometer becoming unavailable, only the few experiments presented in Figure 5.2 were available to be investigated. The on/off ratio for the 100 P:PSS/500 membrane was calculated as the average of the on/off ratios from the three sets of experiments. Plotting the on/off ratio and the steady-state current as a function of membrane ratio gives us Figure 5.3, which indicates a positive correlation between steady-state

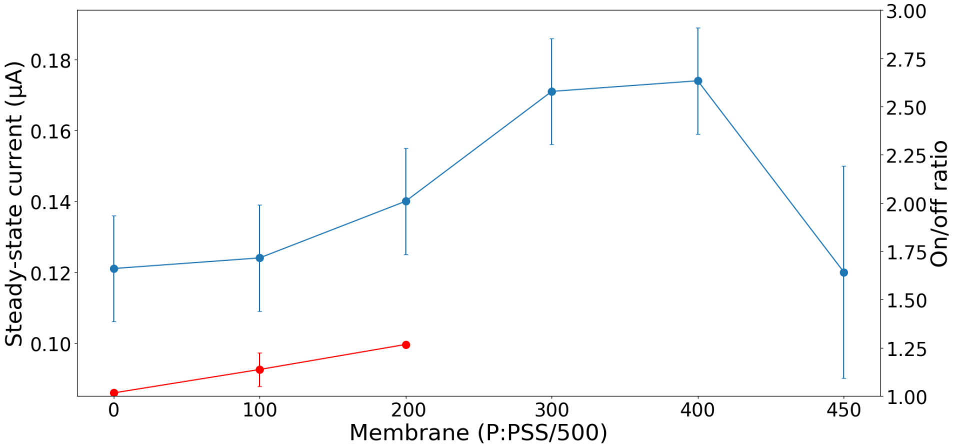


Figure 5.3: Steady-state current (blue) and on/off ratio (red) as a function of membrane recipe. Unavailability of the spectrometer prevented more data points to be collected for the on/off ratio.

current and on/off ratio. With the assumption that the highest steady-state current would result in the largest on/off ratio, 400 P:PSS/500 was chosen as the most promising membrane ratio for exhibiting electromigration of ions due to an applied potential.

5.4 Sodium experiment

Na^+ ion transport experiments conducted through a 400 P:PSS/500 membrane are presented in Figure 5.4. The 100 mM NaCl solution used in the source had a conductivity of ca. 10 000 µS/cm, while the DI water in the target had a conductivity of 0.03 µS/cm. Unlike the experiments with methylene blue, electromigration experiments were conducted before the diffusion experiments. The reason will be discussed later.

From the figure, experiments with a 20 minute duration transport slightly more ions during electromigration experiments. This difference could be due to an initial ion transport that quickly ceases after the electrical double layer forms, or it could be due to a very small continuous electromigration of ions that could be enhanced by further optimizing the membrane. If the difference is due to continuous electromigration, the difference should increase with a longer duration. Unfortunately, this is not what is observed. The one hour

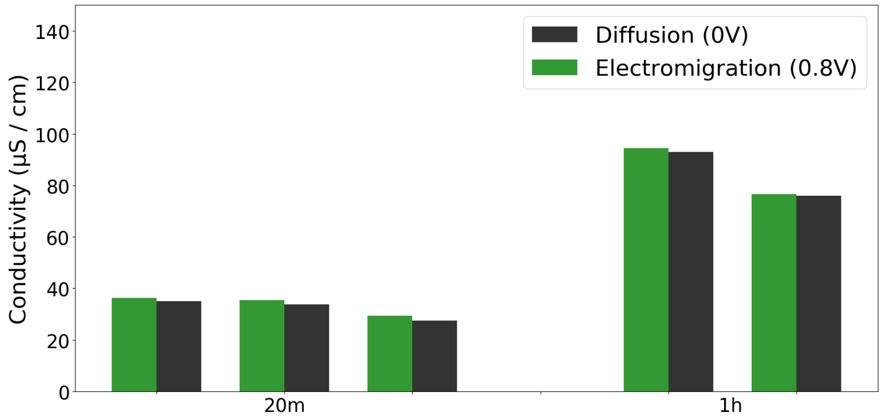


Figure 5.4: Comparing electromigration and diffusion of Na^+ ions through a 400 P:PSS/500 membrane. The duration of a single experiment is indicated underneath.

long experiments shows a similar difference between diffusion and electromigration. All sets of experiments shows an on/off ratio of approximately one: 1.04 ± 0.02 for the 20m experiments and 1.012 ± 0.006 for the one hour experiments. Since a slight difference is present for all sets of experiments, it is likely due to the small amount of ions transported by the applied potential before the electrical double layer forms. Note that the one hour long experiments shows a conductivity ca. three times that of the 20m experiments, indicating a linear relationship between duration and ion transport.

Initially, the Na^+ experiments were conducted in the same order as for methylene blue, diffusion followed by electromigration. However, this produced inconsistent results: sometimes there was no difference between diffusion and electromigration, and sometimes diffusion actually transported more ions than electromigration. Performing multiple sets of experiments back to back showed that performing an electromigration experiment before the diffusion experiment eliminated this irregular phenomena. The order of the experiments should not affect the experimental outcome since continuous ion transport due to electromigration is assumed to only depend if there is an applied potential or not. Hence, the order was changed for the Na^+ experiments.

6 Conclusions and future outlook

An organic mixed ionic-electronic conducting membrane was developed by mixing PEDOT:PSS and PEGDA 2000 MW, which passed a molecular analog to a known cancer drug. The membranes were characterised with multistep amperometry and ion transport experiments. A small, and perhaps significant, on/off ratio was found when transporting methylene blue, but this was not reproducible with Na^+ ions. The size difference between the two ions could explain this difference in behaviour. The data is inconclusive as to whether the hypothesis is correct an more experiments are needed to investigate whether a continuous electromigration of ions due to an applied potential exists in these kinds of membranes.

With the knowledge gained from the unfruitful Na^+ transport experiments, the promising methylene blue transport experiments could be redone to investigate their reproducibility and fill in the missing on/off ratios and ensure that the 400 P:PSS/500 membrane actually was the optimal choice. Performing the electromigration experiment before the diffusion experiment and keeping the absorbance below a value of one could provide more reliable data.

Future experiments should also take into account memory resistance, which refers to the ability of mixed conducting materials to change their resistance if they have recently experienced a potential. [34]. This means that the conductivity in the membranes presented in this thesis could change depending on if diffusion or electromigration experiments were conducted first, which would explain why the experimental order mattered in the Na^+ experiments and why it took 20 cycles for the multistep amperometry measurements to reach an equilibrium.

No continuous ion transport due to electromigration was found and the complexity of OMIECs makes it difficult to formulate a theory of the mechanism that would be responsible for such transport, if any exists. More in-depth knowledge of the chemistry of these types of materials is needed in order make progress and uncover the potential of OMIECs.

7 Svensk sammanfattning: Bland-ledande material för kontinuerlig läkemedelstranport

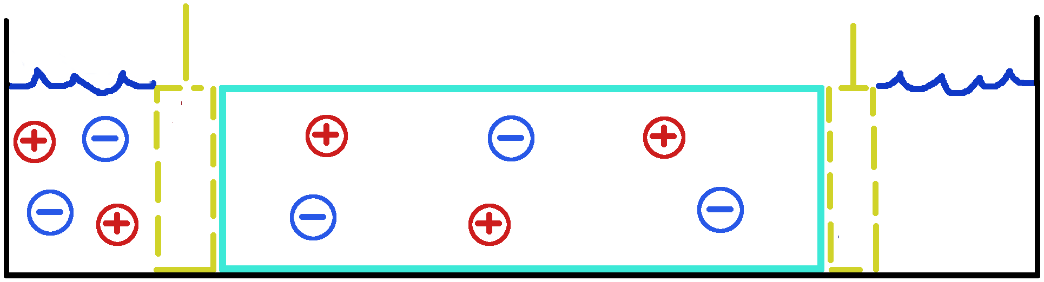
7.1 Bakgrund

Organiska blandledare (Eng. Organic mixed ionic-electronic conductor) är böjbara material med förmågan att transportera både joner och elektroner. Elektrontransport sker via tunnling mellan konjugerade polymerkedjor medan jontransport sker via jonhoppning mellan fixerade laddningar i materialet [5] eller fri transport i vattenfyllda kanaler [10]. Eftersom mekanismer i människokroppen styrs med joner finns det ett stort intresse inom läkemedelsindustrin för att kontrollera jontransport med hjälp av elektrisk ström, vilket är precis det som en organisk blandledare kan tillhandahålla.

En möjlig tillämpning finns inom cancerbekämpning, speciellt för hjärntumörer. Behandlingen av hjärntumörer försvåras på grund av blod-hjärnbarriären som förhindrar de flesta molekyler, inkluderat läkemedel, att överföras från blodomloppet till hjärnan [22]. Konvektionsförbättrad transport (Eng. Convection enhanced delivery) har utvecklats för att förbigå denna barriär. Detta uppnås genom att med tryck transportera läkemedelslösning direkt in i tumören genom en kateter insatt genom skallen. Nackdelar med denna metod är att lösningen kan flöda ut genom skallhålet istället för att fylla tumören, och ifall tumören fylls så kan tryckskillnaden som uppstår i hjärnan på grund av tumörsvällningen ha allvarliga bieffekter för patienten [24]. En jonpump baserad på ett organiskt blandledande material är en lovande lösning på problemet eftersom den transporterar endast joner och ingen vätska.

En jonpump är i dess enklaste form ett halvporöst membran omgivet av två reservoarer fyllda med vätska. Den ena innehållande jonerna som ska transporteras, källreservoaren, och den andra innehållande endast vatten, målreservoaren. Genom att applicera en potential med hjälp av elektroder kan man transportera jonerna från källan genom membranet till målet. Idealt transporteras endast jonerna och dess vattenskikt på grund av halvporositeten [14]. Detta gör att en tillämpning inom läkemedelstransport inte skulle orsaka en tryckökning vid målområdet, och skulle därför undgå bieffekterna förknippade med konvektionsförbättrad transport.

Att få en stor mängd laddat läkemedel genom en jonpump förhindras av bildningen av det elektriska dubbellagret. Allt eftersom joner transpor-

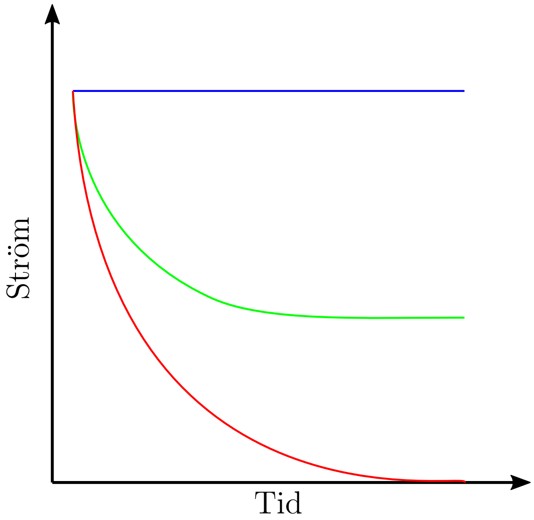


Figur 7.1: En jonpump baserad på två elektroder gjorda av guldnät, illusterade i guld, som är i kontakt med ett membran, illustrerad i ljus blått. Membranet är i kontakt med en källreservoar till vänster, fylld med en vätska innehållande jonen som skall transporteras och dess motjon, och en målreservoar till höger, fylld med avjoniserat vatten.

teras genom membranet kommer laddningen hos elektroderna som orsakar elfältet att avskärmas. Elfältet försvinner när jonlagret runt elektroden balanserar elektrodladdningen fullständigt och den aktiva jontransporten avstannar. Målet med detta arbete är att erhålla ett blandledande membran i en jonpumps konfiguration som uppvisar kontinuerlig jontransport på grund av elektromigration av joner. Elektromigration används här som ett samlingsbegrepp för alla jontransportmekanismer som händer när en potential appliceras.

7.2 Teori

Materialen som används i detta arbete är blandledaren PEDOT:PSS och jonledaren PEGDA, som även fungerar som stomme för membranet. Hypotesen för detta arbete är att en signifikant kontinuerlig elektromigration av joner, på grund av en applicerad spänning, sker genom en jonpump baserad på detta membran. Jonpumpsuppställningen illustreras i Figur 7.1. Berättigandet för denna kommer från opublicerade data från Dr. Christopher Proctor. Genom att ha undersökt olika förhållanden mellan PEDOT och PSS i ett PEDOT:PSS-membran hävdar han sig ha hittat en blandledande jämvikts-



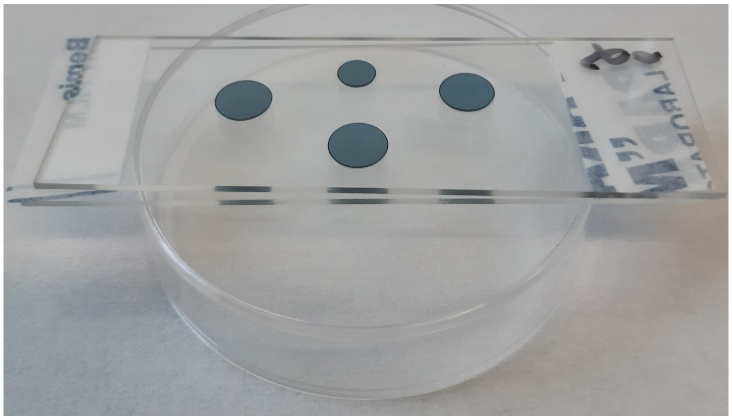
Figur 7.2: Ström som funktion av tid för membran med olika transporttyper. Endast elektron transport (blå), blandad transport (grön) och endast jon transport (röd).

ström. En förklaring följer. Ifall membranet leder elektroner väldigt bra kommer strömmen, som funktion av tid, hållas konstant. Ifall membranet leder joner väldigt bra kommer strömmen minska exponentiellt p.g.a. det elektriska dubbellagret. En optimal blandning av dessa två ledningstyper har visat en ström som i början avtar exponentiellt men som planar ut till en jämviktsström efter en stund, se Figur 7.2. Denna jämviktsström antas bestå av både elektroner och joner, vilket skulle indikera en kontinuerlig jontransport. Målet är alltså att uppnå samma fenomen men istället för att ändra förhållandet mellan PEDOT och PSS ändras förhållandet mellan PEDOT:PSS och PEGDA.

7.3 Material och metoder

7.3.1 Membranet

Membranet som användes bestod av PEGDA med en molekylvikt på 2000, blandat med PEDOT:PSS och en fotoinitator. Fotoinitiatorns uppgift är att sammanbinda PEGDA-molekylerna för att bilda ett vattenfast membran. Mängden PEGDA hölls konstant som 0,05 g per 500 µL lösning. Likaså hölls fotoinitiatorn som 2 viktprocent. Lösningen bestod av flytande PEDOT:PSS



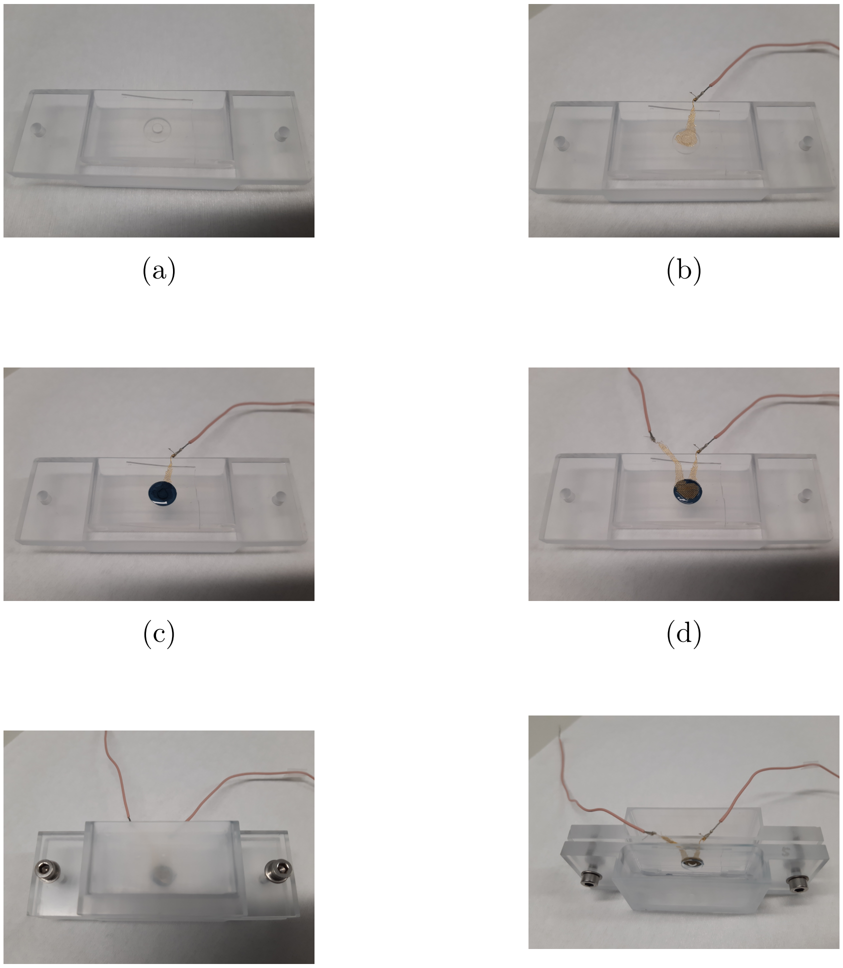
Figur 7.3: Membranlösning mellan två glasplattor, separerade med 3 mm.

med en koncentration på 1,15 viktprocent samt avjoniserat vatten. Proportionen mellan PEDOT:PSS och det avjoniserade vattnet ändrades för att optimera membranet. Således ändrades förhållandet mellan PEDOT:PSS och PEGDA medan mängden lösning hölls konstant. Exempelvis var det första membranet som testades gjort enligt ett recept med 0,05 g PEGDA, 12 µL fotoinitator, 100 µL PEDOT:PSS och 400 µL avjoniserat vatten. För att hänvisa till olika membran kommer enheten mängd PEDOT:PSS-lösning per 500 µL lösning användas, förkortat som P:PSS/500. Exempelvis är den förkortade versionen av benämningen på det ovanstående membranet 100 P:PSS/500. För att skapa membranet placeras ett par droppar av lösningen mellan två separerade glasplattor, se Figur 7.3, och läggs in i en UV-ugn och utsätts för 48 J/cm^2. Därefter lagras membranet i avjoniserat vatten.

7.3.2 Experimentell uppställning och karakterisering

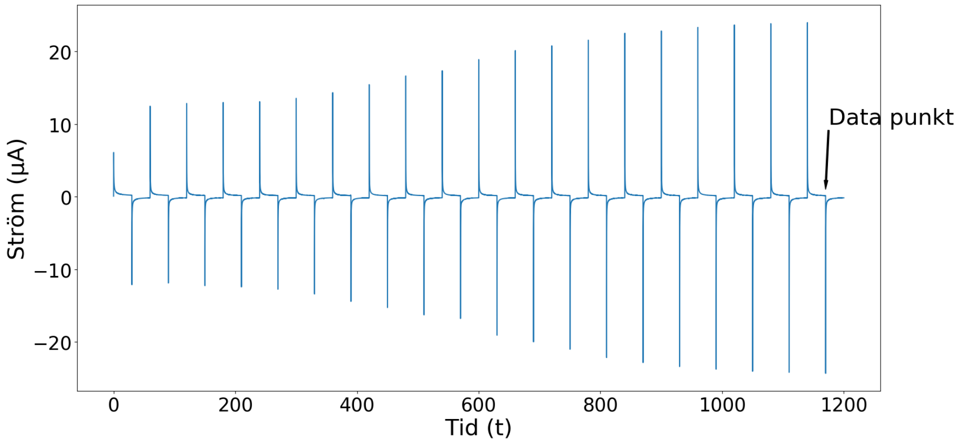
För att karakterisera membranet utvecklades en experimentell cell som tillät membranet att komma i kontakt med elektroderna. Detta tillåter en elektronisk ström att passera genom membranet samtidigt som jontransport sker, vilket ansågs vara en nödvändighet för kontinuerlig transport. Cellen beskrivs i Figur 7.4.

För att undersöka jämviktsströmmen genom membran med olika proportioner av PEDOT:PSS och PEGDA användes flerstegsamperometri, vilket innebär att en spänning på +0,8 V och -0,8 V turvis applicerades över membranet i 30 sekunders intervaller. Detta upprepades i 20 cykler för att nå



(a) (b) (c) (d) (e) (f)

Figur 7.4: Ihopsättning av cellen. Ena reservoarens hål täcks av en elektrod (b), membranet (c) och slutligen en till elektrod (d). Den andra reservoaren skruvas fast (e) och cellen är färdig (f).

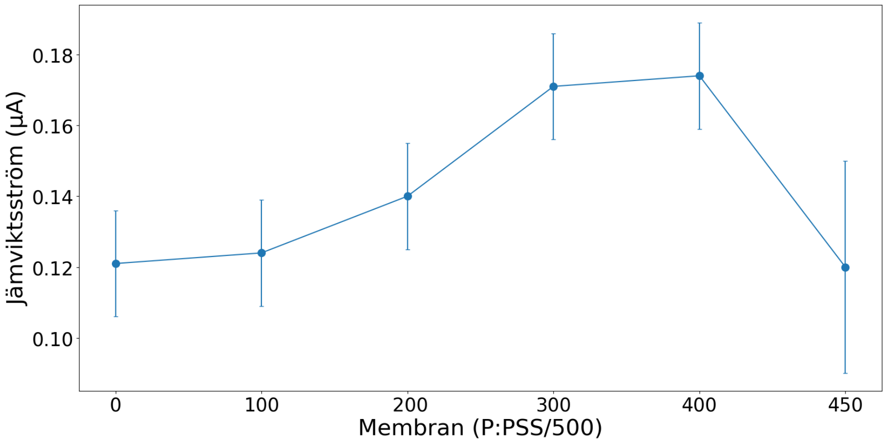


Figur 7.5: Exempel på en flerstegsamperometrikurva. Datapunkten som används som mått på membranets jämviktström tas under den sista cykeln, vid pilen. Notera att 20 cykler är tillräckligt för att erhålla jämvikt.

jämvikt, varefter jämviktsströmmen i den sista cykeln noterades och användes för att jämföra membranen, se Figur 7.5. Osäkerheten uppskattades genom att mäta ett membran, plocka isär och plocka ihop celluppställningen, och mäta igen. Skillnaden mellan dessa två mätningar, 0,015 µA, togs som ett mått på felet som introduceras av att de två elektrodernas överlapp och avstånd ändrar mellan ihopsättningar av cellen.

Det första jontransportexperimentet gjordes genom att sätta den positiva molekylen metylenblått i källreservoaren och avjoniserat vatten i målreservoaren. Metylenblått användes eftersom den har en liknande storlek som cancermedicinen cisplatin. Transporten genom membranet genom diffusion jämfördes med transporten genom membranet under en spänning på +0,8 V. Det senare experimentet refereras till som ett elektromigrationsexperiment. Mängden metylenblått som transporterats kvantifierades med hjälp av spektroskopi.

Jonen ändrades sedan till Na^+ och transport experiment gjordes på samma sätt som ovan, men mängden joner man transporterat mättes genom att mäta konduktiviteten i målreservoaren.



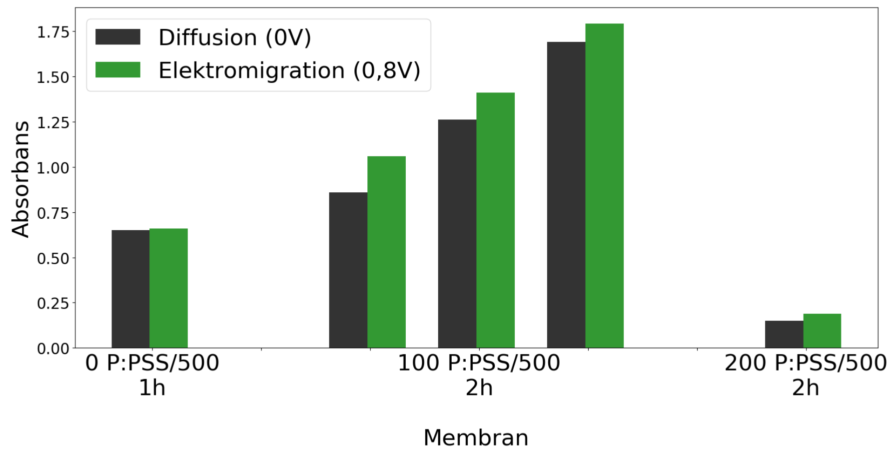
Figur 7.6: Jämviktsströmmen för olika membran.

7.4 Resultat

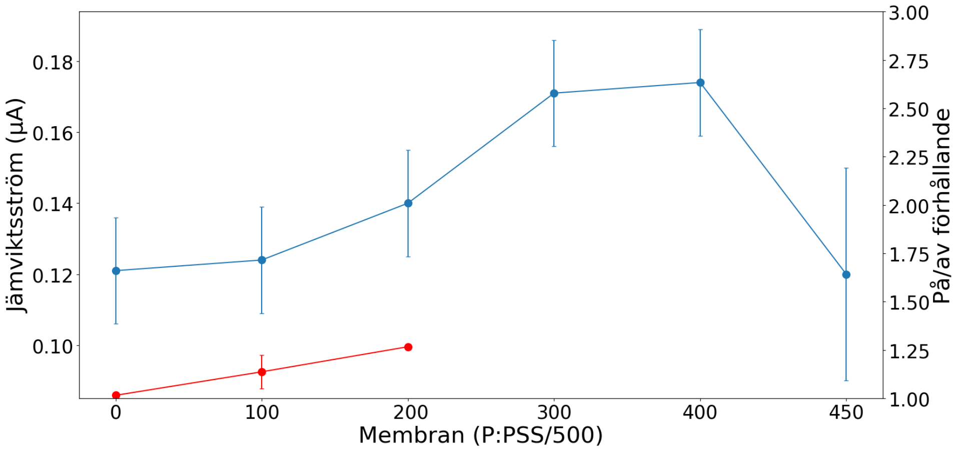
Resultatet av flerstegsamperometrin på membran varierande från 0 P:PSS/500 till 500 P:PSS/500 visas i Figur 7.6. Det kan ses att 400 P:PSS/500 visar högst jämviktsström. För att undersöka ifall jämviktsström korrelerar med elektromigration av joner genom membranet, utfördes transport experiment med metylenblått.

Jämförelse mellan diffusion och elektromigration av metylenblått för olika membran presenteras i Figur 7.7. Från denna figur ses ingen skillnad mellan diffusion och elektromigration för ett membran utan PEDOT:PSS i sig, dvs. 0 P:PSS/500-membranet. 100 P:PSS/500-membranet visar en skillnad mellan diffusion och elektromigration, vilket är väldigt lovande speciellt eftersom resultatet upprepades tre gånger. Ett 200 P:PSS/500-membran testades också, vilket visade avsevärt mindre transport av metylenblått. En skillnad mellan diffusion och elektromigration kan dock ses.

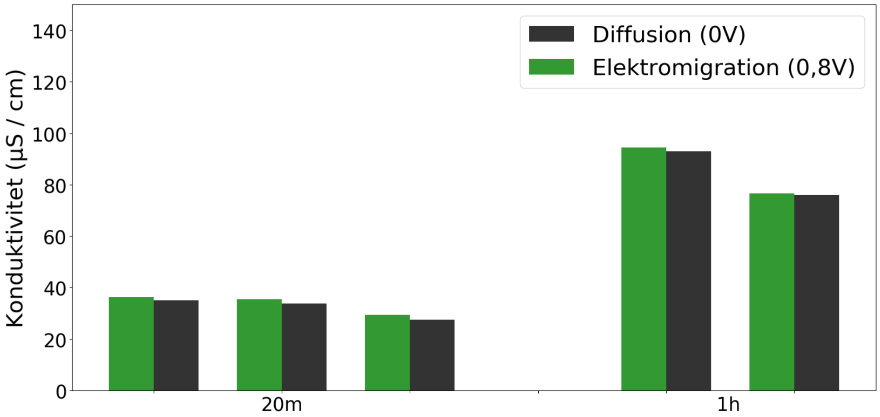
Genom att dividera absorbansen från elektromigration och diffusion experimenten får man ett på/av förhållande (Eng. on/off ratio) som indikerar hur mycket jontransport som skett på grund av den applicerade potentialen. Genom att plotta detta förhållande i samma graf som jämviktsströmmen från flerstegsamperometrin, se Figur 7.8, ses att jämviktsströmmen verkar ha en positiv korrelation med elektromigrationen. Därför valdes 400 P:PSS/500-membranet som det mest lovande membranet för att uppvisa elektromigra-



Figur 7.7: Diffusion- och elektromigrationstexperiment för olika typer av membran. Högre absorbans innebär högre jonkoncentration. Längden per experiment indikeras under respektive membran.



Figur 7.8: Jämviktsströmmen (blå) och på/av förhållandet (röd) för olika membran.



Figur 7.9: Diffusionexperiment jämfört med elektromigrationsexperiment för ett 400 P:PSS/500-membran, för två olika tidslängder.

tion av joner. I nästa experimentserie ändrades jonen som transporterades till Na^+, eftersom spektrometern som användes för metylenblått experimenten blev otillgänglig.

Data från Na^+ transport experiment med ett 400 P:PSS/500-membran visas i Figur 7.9. Märk att elektromigration utfördes före diffusion denna gång. En liten skillnad ses mellan diffusion och elektromigration, men skillnaden växer inte med en ökning av längden på experimenten, vilket indikerar att det inte sker kontinuerlig jontransport på grund av elektromigration genom membranet.

7.5 Diskussion och sammanfattning

Ett membran baserat på PEDOT:PSS och PEGDA producerades och visades kunna passera metylenblått, en analog till cancermedicinen cisplatin. Variationer av detta membran karakteriserades med flerstegsamperometri och jontransport experiment. Det är möjligt att metylenblått experimenten uppvisar tecken på kontinuerlig elektromigration av joner, men Na^+ experimenten var inte lika lovande. Storleksskillnaden mellan dessa joner kanske är en del av förklaringen till varför de beter sig olika. Det är oklart ifall hypotesen stämmer. Mera experiment behövs för att säkerställa ifall det existerar en signifikant kontinuerlig elektromigration av joner genom denna typ av membran på grund av en applicerad potential.

Metylenblått experimenten visade lovande resultat och skulle med fördel kunna göras om. Kunskapen som erhölls under Na^+ experimenten skulle kunna inkorporeras för att få mer tillförlitlig data: utför elektromigrationsexperimentet före diffusionsexperimentet och håll absorbansen under värdet ett. Att undersöka på/av förhållanden för alla sorters membran skulle även göra nytta genom att ge en mera omfattande bild av situationen, och säkerställa ifall 400 P:PSS/500-membranet faktiskt var det optimala valet.

En annan sak att ta i beaktande i framtida experiment är att blandledande material uppvisar en föränderlig resistans som ändras beroende på ifall en ström nyligen gått igenom membranet eller inte [34]. Detta skulle kunna förklara varför ordningen av diffusion och elektromigration hade en inverkan på experimenten, samt varför det tog 20 cyklar för multistep amperometrin att nå jämvikt.

En teoretisk modell för kontinuerlig jontransport med hjälp av elektromigration existerar ej och skulle vara nyttig för att framskrida med experimenten. Mera djupgående information om bland-ledare och deras mekanismer behövs för detta, och skulle vara ovärderligt för att kunna utnyttja dessa material till fullo.

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