Interface Engineering of Ion Exchange Membranes

Grenzflächen-Engineering an Ionenaustauschermembranen

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Said Abdu

Berichter: Univ.-Prof. Dr.-Ing. Matthias Wessling
Prof. Dr. Ir. Rob G.H. Lammertink

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Abstract

Surface properties of membranes play decisive roles in the overall membrane separation processes. Membrane surfaces are elaborately altered during membrane formation or in a separate step afterward with the objective of enhancing some desired performances or mitigating drawbacks that are inherent to membrane separation processes.

The work at hand investigates the surface/interface modification of both monopolar- and bipolar ion exchange membranes for electrodialysis applications. The ion transport phenomena investigated are particularly influenced by the state of the membrane surface/interface. The phenomena studied are overlimiting mass transfer through electrodialysis membranes, monovalent ion permselectivity of cation exchange membranes, and water dissociation catalysis at the interface of bipolar membranes. For the non-covalent surface modification of the membranes, two classes of polymers are applied: polyelectrolyte multilayers and microgels.

The polyelectrolyte multilayers and microgels are successfully implemented – as homogeneous- and micropatterned layers – to tailor the interface of the ion exchange membranes without any prior treatment of the membranes. Their depositions are subsequently characterized with several surface analytical techniques.

Results of the interface modification of bipolar membranes indicate enhanced performance when the anion exchange layer of the membranes are coated with certain polyelectrolytes, and more so when polyelectrolytes of higher charge density are applied. Out of the investigated Layer-by-Layer (LbL) assembly parameters, ionic strength and number of layers show the largest influence on the catalytic activity and surprisingly on the membrane ionic permselectivity as well. The membrane permselectivity was previously assumed to be only influenced by the bulk thickness of the anion- and cation exchange layers.

Furthermore, the possibility of applying polyelectrolytes to induce monovalent ion permselectivity on standard cation exchange membranes is studied. Permselectivity comparable to that of a commercial monovalent-ion-permselective membrane is obtained with only six bilayers of polyelectrolytes, yet with significantly lower energy consumption per mole of Na\(^+\) ions transported through the membranes. At overlimiting current densities, the study further shows that polyelectrolyte multilayers allow switching on and turning off water splitting at the surface of ion exchange membranes. These
membranes could be beneficial for applications in which ion permselectivity and pH regulation are needed at the same time.

This thesis, in addition, attempts to answer the question whether polyelectrolytes can also be utilized to modulate overlimiting current phenomena in electrodialysis membranes. The study proves that controlled adsorption of polyelectrolyte multilayers at the interface between the ionic solution and membrane surface triggers a significantly earlier onset of electroconvection (as the main driver for the overlimiting current) at lower polarization potential. It further proves that their uniform regio-selective adsorption imposed by microcontact printing is even more effective, and enhances macroscopic electro-osmotic chaotic fluid instabilities. The experimental techniques, guided by theoretical studies, may pave the way for potentially ‘smart’ design of electrodialysis membranes for intense-current desalination.

Apart from electrodialysis, the findings of this thesis may provide equally valuable insights to other areas of applications of ion exchange membranes, which require membranes with tailored surface properties.
Zusammenfassung

Die Oberflächeneigenschaften von Membranen spielen eine entscheidende Rolle in Membrantrennprozessen. Um gewünschte Membraneigenschaften zu erzeugen oder nachteilige Charakteristiken zu mildern, werden die Oberflächen während oder nach der Membranherstellung aufwendig verändert.


Die Polyelektrolyt-Multilagen und Mikrogele werden ohne Vorbehandlung der Ionenaustauschermembranen als homogene Schicht oder Mikrostruktur aufgebracht und zeigen eine erfolgreiche Oberflächenmodifikation. Die Beschichtungen werden anschließend mit verschiedenen Methoden zur Oberflächenanalyse charakterisiert.


Weiterhin wird die Aufbringung von Polyelektrolyten auf herkömmliche Kationenaustauschermembranen zur Schaffung von Permselectivität für monovalente Ionen untersucht. Dabei wird gezeigt, dass bereits mit sechs Polyelektrolyt-Doppellagen Permselectivität generiert wird, die mit kommerziellen für monovalente Ionen selektiven Membranen vergleichbar ist. Der Energieverbrauch pro durch die Membran transportiertem Mol Na⁺ Ionen wird im Vergleich jedoch deutlich reduziert. Es wird
ferner gezeigt, dass bei überlimitierenden Stromdichten, Polyelektrolyt-Multilagen die Entstehung bzw. das Unterdrücken von Wasserspaltung an der Membranoberfläche wesentlich beeinflussen können. Diese Art von Membranen ist somit nützlich für Anwendungen, in denen Ionenpermselektivität und zugleich pH-Regulierung gefordert sind.


Die Ergebnisse aus dieser Doktorarbeit könnten, neben der Anwendung in der Elektrodialyse, ebenfalls wertvolle Einblicke für andere Verwendungsbereiche von Ionenaustauschermembranen bieten, welche Membranen mit angepassten Oberflächeneigenschaften benötigen.
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Chapter 1

General Introduction

Ion exchange membranes are used in a number of key engineering technologies, such as mass separation processes, chemical synthesis as well as energy conversion and storage processes [1]. This thesis deals with electrodialysis – a major separation application of ion exchange membranes, which has been for decades mainly applied to produce potable water from brackish water sources as well as to desalinate seawater [2].

There are two major types of monopolar ion exchange membranes: the positively-charged anion exchange membranes and the negatively-charged cation exchange membranes. These membranes consist of polymeric films bearing covalently-bound ionic fixed charges that enable the transport of electrolyte ions with opposite charge sign (counterions) through the membrane structure. Ions with the same charge sign (co-ions) are electrostatically repelled and retained in the feed compartment.

Bipolar membranes, on the other hand, are a laminate of anion- and cation exchange membranes that dissociate water molecules at their interface very efficiently upon application of an electric field. They are utilized in an electrodialytic cell arrangement, along with monopolar membranes, to produce acids and bases from their corresponding salt solutions.

The ion transport phenomena investigated in this thesis are principally influenced by the state of the membrane surface/interface. The phenomena studied are namely: overlimiting mass transfer through electrodialysis membranes, monovalent ion permselectivity of cation exchange membranes and water dissociation catalysis at the interface of bipolar membranes. In general, surface properties of membranes play decisive roles in the overall membrane separation processes. Membrane surfaces are elaborately altered during membrane formation or in a separate step afterward with the objective of enhancing some desired performances or mitigating drawbacks that are inherent to membrane separation processes [3], [4].
Two classes of materials are applied in this work for the non-covalent surface modification of the ion exchange membranes: polyelectrolyte multilayers and microgels. The layer-by-layer (LbL) assembly of polyelectrolytes is a generic and versatile technique used to modify surfaces; it allows the formation of thin films with tunable composition, thickness, and morphology [5]. In dipping LbL deposition technique of polyelectrolytes, a charged substrate is alternately immersed in polyanions and polycations, to form multilayers with properties controllable on the nanoscale.

Microgels, on the other hand, are soft particulate cross-linked polymer networks swollen in suitable solvents with typical sizes of about 50 nm–5 µm [6]. Microgels exhibit stimuli-responsive behavior, i.e., they undergo swelling and de-swelling transitions in response to external stimuli, such as temperature, pH, ionic strength etc. [7], [8]. Of particular interest to the combination of microgels with membranes is that presynthesized microgels also retain their responsiveness in the adsorbed state [9], [10].

Surface modification using polyelectrolytes/presynthesized microgels entail a number of advantages: The surface modification is a relatively easy physical process requiring no pretreatment of most membranes [11]. With polyelectrolytes/microgels, a rigorous control of the membrane surface properties at the nanometer-scale can be achieved [12]. Other advantages include stimuli-responsiveness, the applicability to different membrane geometries etc. [9].

### 1.1 Scope and Outline of the Thesis

The work at hand aims at applying polyelectrolyte multilayers as a tool to tune ion transport through electrodialysis membranes. The study further explores the potential application of functional microgels to modify the surface of ion exchange membranes. The scope of this thesis is:

- Establishing techniques for ‘homogeneous’ as well as micropatterned deposition of the polyelectrolytes/microgels without any prior treatment of the membranes.
- Characterizing the state of the membrane surfaces with surface analytical techniques.
- Identifying the influencing mechanisms in light of the most recent theories on the ion transport phenomena and elucidating the effects qualitatively or quantitatively with the help of several electrochemical methods and to some extent with theoretical models.
For the polyelectrolyte multilayers, the following questions are to some extent investigated for the respective ion transport phenomena: What type of polyelectrolytes to use? How to enhance the effect of LbL-assembled multilayers? What are the most important LbL deposition parameters?

Chapter 2 gives a brief overview of ion exchange membranes – their structure, properties, preparation methods, and applications. The chapter is closed by giving a short background about polyelectrolyte multilayers and microgels.

Chapter 3 generally outlines the materials and methods used that are applicable to the entire thesis. Further chapter-specific experimental conditions, additional materials or techniques are detailed in the respective chapters.

Chapter 4 investigates the layer-by-layer (LbL) deposition of polyelectrolyte multilayers as a tool to introduce molecularly thin catalyst groups at the interface of bipolar membranes. The study reports the effect of LbL architecture on the water splitting efficiency and membrane selectivity. The latter is surprisingly a strong function of the interface architecture. A number of commercial polyelectrolytes are compared for their water dissociation capability. Further, the study reveals the difference in coating the polyelectrolytes on the anion- or the cation exchange layer as well as the influence of different deposition parameters. Besides, the experimental results are compared with a complete water dissociation model to help explain the main effect.

Chapter 5 focuses on imparting monovalent ion permselectivity on a standard commercial cation exchange membrane. The modified membranes are characterized by several surface analytical methods, and their surface characteristics are correlated with their electrochemical transport behavior. Their performance is investigated and compared with that of other commercial membranes by galvanostatic permselectivity experiments, current–voltage curves, and electrochemical impedance spectroscopy (EIS) measurements. Monovalent ion permselectivity and water dissociation behavior of the membranes are found that are dependent on the number of bilayers. These findings could be key to applications requiring both ion permselectivity and pH regulation at the same time.

Chapter 6 sets to investigate whether polyelectrolytes can also be utilized to modulate overlimiting current phenomena in electrodialysis membranes. LbL assembly of polyelectrolytes is used to tailor the interface of the membranes: to alter the chemical nature of the surface and to increase the degree of membrane surface hydrophobicity. In
addition, microcontact printing (µCP) is also applied to introduce uniform electrochemical heterogeneity on the surface of the membranes. The results provide valuable insights on the possibility of reducing the detrimental effect of concentration polarization for intense-current desalination.

Chapter 7 aims at exploring the potential application of functional microgels to modify the surface of ion exchange membranes. Both highly-charged aqueous polyelectrolyte microgels and their uncharged precursor latex particles are used to modify the surface of ion exchange membranes. Within the scope of this study, methods to form a dense confluent- and micropatterned microgel monolayers on top of ion exchange membranes are developed. The study is rounded off with preliminary performance tests of the membranes modified with the above-mentioned methods. The polarization behavior and the monovalent ion permselectivity of the modified membranes are characterized. In addition, application of the microgels as catalysts for water dissociation at the interface of bipolar membranes is also investigated.

Finally, Chapter 8 summarizes the main outcomes and conclusions of the thesis.
Chapter 2

Background on Ion Exchange Membranes, Poly-electrolyte Multilayers, and Microgels

2.1 Ion Exchange Membranes

2.1.1 Structure and Properties of Ion Exchange Membranes

Synthetic membranes are defined as permselective barriers separating two phases – feed and permeate [13]. Upon applying a driving force, membranes allow certain components of a feed solution to pass through selectively to the permeate phase while retaining other components in the feed phase. The membranes investigated in this thesis are a subclass of synthetic membranes called ion exchange membranes, which are polymeric films carrying fixed charges attached to their polymer matrix.

The two main types of ion exchange membranes are cation exchange membranes containing negatively-charged groups attached to their polymer matrix, and anion exchange membranes having positively-charged moieties in their polymer matrix. Ion exchange membranes enable the transport of electrolyte ions with opposite charge sign (counterions) through the membrane structure. Ions with the same charge sign (co-ions) are electrostatically repelled and retained in the feed compartment. Schematic representation of the structure of ion exchange membranes is shown in Figure 2.1.

Other types of ion exchange membranes are amphoteric, bipolar and charge-mosaic membranes. Amphoteric membranes encompass positive and negative charges randomly distributed throughout the membrane. Charge-mosaic membranes consist of positive and negative domains across the thickness of the membranes, and these domains are possibly separated by a neutral polymer matrix. Whereas bipolar membranes consist of anion- and cation exchange layers laminated back to back.
If for instance, a cation exchange membrane is brought in contact with an electrolyte solution, the concentration of the co-ions (anions) in the membrane becomes lower than in the bulk solution. Due to the concentration difference, the natural tendency of the anions is to diffuse from the bulk solution into the membrane. However, to maintain electroneutrality, an electric field is created (Donnan potential) to counterbalance the diffusional flows so that an electrochemical equilibrium is achieved (Donnan equilibrium). The opposite effect is true for the counterions in the membrane. Distribution of the co- and counterions between the membrane and bulk solutions and the resulting Donnan potentials at a cation and an anion exchange membrane are shown in Figure 2.2.
Ion exchange membranes are primarily characterized by their ability to reject ions of the same charge sign (co-ions), commonly referred to as Donnan exclusion in honor of the pioneer work of Donnan [14]. Donnan put this property of ion exchange membranes into a mathematical expression as given by Equation 2.1.

\[
\varphi_{Don} = \varphi_m - \varphi^* = \frac{RT}{z_i F} \ln \frac{a_i^s}{a_i^m}
\]  

(2.1)

where \( \varphi_{Don} \) is the Donnan potential, which is the potential difference between the membrane \( \varphi^m \) and the solution \( \varphi^* \); \( R \) is the universal gas constant; \( T \) is the absolute temperature; \( F \) is the Faraday constant; \( z_i \), \( a_i^s \) and \( a_i^m \) refer to the valency, and the activity in the solution and in the membrane of the ion \( i \), respectively.

The permselectivity of ion exchange membranes thus depends on the fixed charge concentration, the electrolyte solution concentration, the valency of the co-ions, and the affinity of the ion exchange material towards the counterions [1].

For the case of a completely dissociated dilute monovalent salt solution (NaCl), the concentration of the co-ions (Cl\(^-\)) in a cation exchange membrane can be derived from the Donnan equilibrium to a first approximation as [15]

\[
C_{Cl^-}^m = \frac{(C^s)^2}{X}
\]  

(2.2)

where \( C_{Cl^-}^m \) is the co-ion concentration in the membrane; \( C^s \) is the bulk electrolyte concentration; \( X \) is the fixed charge concentration of the membrane.

Equation 2.2 indicates that Donnan exclusion is most effective at low bulk electrolyte concentrations and at high fixed charge concentration of the membranes.

Given the above working principles, the most desired properties of ion exchange membranes for practical applications are:

- **High permselectivity** for the permeation of counterions while excluding co-ions
- **Low electrical resistance** for the permeation of counterions under applied potential to maintain reasonable operating costs in the form of electrical energy
- **Good mechanical strength and form stability** during operations involving strong changes in electrolyte concentrations
- **High chemical stability** towards extreme pHs and a variety of oxidizing agents
The above four properties are essentially common to all ion exchange membranes. Other special properties may be required for certain applications. Hence, application-oriented optimization of the membrane properties is then necessary. In fact, there are commercial membranes for monovalent and divalent ion fractionation, membranes with high proton permselectivity, membranes with high proton retention, membranes with anti-fouling properties, membranes with high alkaline stability etc. [1].

Even the above-mentioned basic features of ion exchange membranes demand making trade-offs. For instance, a high degree of cross-linking results in good mechanical stability but leads to an increase in the electrical resistance. A high concentration of the fixed charges results in low electrical resistance but causes a high degree of swelling, hence, poor mechanical stability [15].

**Bipolar membranes.** Bipolar membranes are composed of an anion- and a cation-selective layer joined together, and usually also a third catalytic intermediate layer in between. Under the influence of a high electric field, bipolar membranes split water molecules into protons and hydroxyl ions at their bipolar interface. Figure 2.3 shows a schematic of the structure and function of bipolar membranes.

![Figure 2.3: Schematic of the structure and function of bipolar membranes.](image_url)

Two anomalous phenomena observed in bipolar membranes are (a) a very rapid water dissociation and (b) water transport against pressure gradient by diffusion. A properly functioning bipolar membrane must be able to dissociate water molecules at very high rates and at the same time draw water to the interface against pressure gradient. The adjacent ionic liquid solutions may comprise concentrated acid and alkali while the water at the interface is deionized: the flow of the water into the bipolar interface hence
occurs against an osmotic pressure difference of two orders of magnitude [16]. More theory about water dissociation in bipolar membranes can be found in Chapter 4.

Therefore, the most desired properties of bipolar membranes are low electric resistance, high selectivity for counter-ions, excellent stability in acids and bases, high water dissociation capacity, and high water permeability of the monopolar layers [1].

2.1.2 Ion Transport through Ion Exchange Membranes

Ion transport through ion exchange membranes is usually described by the extended Nernst-Planck equation, which consists of three contributions: convection, diffusion, and migration. Convection is driven by a hydrostatic pressure difference, diffusion by concentration gradient and migration by electric potential difference [1], [15].

\[ J_i = vC_i - D_i \frac{dC_i}{dx} - z_i \frac{FC_iD_i}{RT} \frac{d\varphi}{dx} \]  

(2.3)

where \( J_i \) is flux of the ion i, \( v \) is the convective velocity; \( C_i, D_i \) and \( z_i \) are the concentration, the diffusion coefficient and the valency of the ion i, \( x \) is the distance coordinate across the membrane; \( R \) is the universal gas constant; \( T \) is the absolute temperature; and \( F \) is the Faraday constant.

Ions carry the current through ion exchange membranes, and it follows from Faraday’s law that

\[ i = \frac{I}{A} = F \sum_{i}^{n} z_i J_i \]  

(2.4)

where \( i \) is the current density; \( I \) is the applied current; and \( A \) is the active membrane surface area.

Part of the current that is carried by a certain ion is expressed by the term transport number \( (t_i) \), which is given by

\[ t_i = \frac{z_i J_i}{\sum_{i}^{n} z_i J_i} \]  

(2.5)

Permselectivity of commercial ion exchange membranes for counterions is normally quite high up to a reasonable electrolyte concentration. Therefore, the transport number of the counterions approaches close to 1 while the transport number of co-ions is approximately 0.
On the other hand, the permeability of the counterions can be different, which is the product of their concentration and mobility. Remarkably high mobility of $H^+$ and $OH^-$ is observed in ion exchange membranes due to a different transport mechanism. Contrary to other ions that move with their hydration shells, these ions hop from one hydronium ion to another. This transport mechanism is called tunneling or Grotthuss mechanism [1].

Like all other membrane processes, concentration polarization also hampers the use of ion exchange membranes at higher current densities, and thus limiting mass flux is reached beyond which no further mass transfer is theoretically possible. Considering only the migration part of the extended Nernst-Planck equation and making few other assumptions, this limiting current density ($i_{lim}$) can be derived to a first approximation as

$$i_{lim} = \frac{FD}{(\bar{t}_+ - t_+)} \frac{c^b}{\delta}$$

(2.6)

where $F$ is the Faraday constant; $D$ the electrolyte diffusion coefficient; $\bar{t}_+$ and $t_+$ are the counterion transport number in the membrane and in the solution, respectively; $c^b$ is the bulk solution concentration; and $\delta$ is the thickness of the stagnant diffusion boundary layer formed in the vicinity of the membrane.

Therefore, $i_{lim}$ is directly proportional to the bulk concentration of the electrolyte and its diffusion coefficient; and $i_{lim}$ is inversely proportional to the counterion transport number and the boundary layer thickness. The boundary layer thickness is in turn dependent on the hydrodynamic conditions – determined by geometry of the membrane module, temperature, solution viscosity and flow rate etc. [15], [17], [18].

Unlike other membrane processes, so-called overlimiting current can be realized in electrodialysis, which is peculiar to ion exchange membranes. Industrially, however, ion exchange membranes have been normally operated in underlimiting currents to avoid complications arising with overlimiting currents. With the emergence of new applications that make use of intense electric currents, there is recently an increased interest in exploring the overlimiting currents. In addition, it is also desirable to operate ion exchange membranes at the highest possible current density to save investment costs of the costly ion exchange membranes. More theory about the origin of the overlimiting current and a separate study about this topic can be found in Chapter 6.
2.1.3 Preparation of Ion Exchange Membranes

According to their preparation methods, consequently their microstructure, ion exchange membranes are subdivided into homogeneous and heterogeneous types. Homogeneous ion exchange membranes consist of the ion exchange groups about homogeneously distributed. Whereas in the heterogeneous ion exchange membranes, ion exchange resin beads provide the ion exchange sites. Here, one of the possible methods to form the membranes is by co-extruding ion exchange resin powders that are premixed with polymer binders.

Most of the commercially-available ion exchange membranes are of the homogeneous type. In general, the techniques used to prepare homogeneous membranes can be categorized as [1], [19], [20]:

1. Polymerization or polycondensation of monomers; at least one of them must contain a moiety that either is or can be made anionic or cationic, respectively.

2. Introduction of anionic or cationic moieties into a polymer or polymer blends followed by the dissolving of the polymer and casting it into a film. Here, engineering polymers are chosen, such as polysulfone, poly(ether ether ketone) or poly(phenylene oxide) due to their high chemical and mechanical stability.

3. Introduction of anionic or cationic moieties into a preformed solid film, such as poly(ethylene) by irradiation- or plasma-induced grafting polymerization.

According to the materials used for the preparation of homogeneous membranes, they can be further classified, the main ones being hydrocarbon-type membranes and perfluorocarbon membranes [21]. The perfluorocarbon membranes are used in applications where high chemical and thermal stabilities are required. These kinds of membranes are the main components in chloro-alkali process and fuel cells.

A method widely used to prepare commercial homogeneous hydrocarbon-type membranes for electrodialysis is the copolymerization of styrene and divinylbenzene. Subsequent sulfonation and quaternization then yield cation- and anion exchange membranes, respectively [1]. Sulfonation is carried out using chlorosulfonic acid or concentrated sulphuric acid in dichloroethane using silver sulfate as a catalyst [19]. Quaternization is conducted in two steps: chloromethylation followed by quaternization with a tertiary amine. The reaction schemes for the preparation of styrene-divinylbenzene-based ion exchange membranes are shown in Figure 2.4.
These type of membranes can be industrially produced by a procedure called coating- or paste method [21]. Here, linear polymers, such as poly(vinyl chloride), polyethylene etc. are added to the mixture of vinyl monomers to provide mechanical stability to the membranes. Additionally, initiators (such as benzoyl peroxide) and plasticizers are added – all components then forming a pasty mixture. Unlike ion exchange resins, the practical handling of industry-size ion exchange membranes inside membrane modules necessitates high mechanical and dimensional stability. Therefore, they are normally backed with reinforcing materials. During production, the pasty mixture is then continuously coated on a backing fabric (woven cloth or net) and shielded on both sides with a separating film. Afterward, the mixture is heated for the mixture of vinyl monomers to copolymerize into a film. Charges are subsequently introduced by sulfonation or amination. This way, membranes with very good electrical and mechanical properties can be produced.
In addition to the base polymers, the nature and concentration of charged groups affect the membrane transport properties. In most commercially-available ion exchange membranes, sulfonic acid groups provide the fixed negative charge and quaternary ammonium groups the fixed positive charge. These two fixed charge groups are dissociated over the entire pH range and maintain high conductivity of the membranes. Cation exchange membranes with carboxylic acid groups are as well commercially available [21]. Other proposed charged groups include –SO$_3^-$, –COO$^-$, –PO$_4^{3-}$, –PHO$_2^-$, –AsO$_3^{3-}$, –SeO$_3$ providing negatively-charged moieties; and –N$^+$H$_2$R, –N$^+$HR$_2$, –N$^+$R$_3$, –P$^+$R$_3$, –S$^+$R$_3$ providing positively-charged moieties [1].

**Bipolar membranes.** With respect to preparing bipolar membranes, the easiest way is to bond two commercial ion exchange membranes, by gluing, pressing or laminating. An alternative method is to prepare bipolar membranes from a single inert film by introducing ion exchange groups by plasma- or radiation-induced grafting polymerization. However, with these methods, there is little control on the final membrane properties. The best method is to prepare bipolar membranes by the sequential casting of all the layers [22].

Some types of catalysts used in bipolar membranes are mentioned in Chapter 4. The catalysts can be immobilized before or after the film formation. There have been several methods applied: spray or dip-coating [23], incorporating in the polymer material by even dispersion [24], by electrochemical methods after formation of the layers or by in-situ polymerization [25], electrospray deposition, [26] etc. There exist also reports of some polymer materials that inherently contain the required catalytic functional groups in their repeating units [24].

### 2.1.4 Applications of Ion Exchange Membranes

Ion exchange membranes are used in a number of key engineering technologies, such as mass separation processes, chemical synthesis as well as energy conversion and storage processes [1]. In the following, the principles of electrodialysis using monopolar and bipolar membranes are treated in more detail.

In an electrodialysis stack, a number of cation- and anion exchange membranes are placed in alternating series in between a pair of electrodes. The ion exchange membranes are separated from one another by spacers forming compartments for the solution flow. Feed is introduced in all compartments, and under applied electric potential cations migrate towards the cathode and anions towards the anode. Due to Donnan
exclusion, the cation exchange membranes allow the selective passage of cations while rejecting anions. Similarly, anion exchange membranes allow anions to pass through selectively while rejecting cations. Therefore, the overall outcome in electrodialysis is an alternate depletion and concentration of ions. The stream depleted of ions, diluate, which is many of the times the product is collected from every other compartment; and the stream enriched with ions, concentrate, is collected from the rest of the compartments. A simplified process scheme of electrodialysis for the case of sodium chloride as a feed solution is shown in Figure 2.5.

![Figure 2.5: Simplified process scheme of electrodialysis.](image)

Electrodialysis has been for more than 50 years mainly applied to produce potable water from brackish water sources. The largest of such an application, with an average capacity of 200,000 m³/day, provides drinking water to about 4.5 million inhabitants of the Barcelona metropolitan area [27]. In Japan, a large-scale application of electrodialysis has been realized for the purpose of edible salt production from seawater. Other important industrial applications are process water demineralization and wastewater treatment. These applications include boiler feed water demineralization, recycling of cooling tower blowdown water, the recovery of spent acids generated in metal finishing industries. Several applications of electrodialysis are also in the food industry and biotechnology [2].

Electrodialysis using bipolar membranes (EDBM), on the other hand, combines the conventional electrodialysis with the water dissociation function of bipolar membranes. EDBM is utilized to produce acids and bases from neutral salt solutions. The principle of three-compartment EDBM (there are also two-compartment designs) for the example of sodium chloride feed solution is depicted in Figure 2.6. Many membrane repeating-units are stacked in one pair of electrodes and the feed salt solution is introduced in
between the monopolar membranes. By applying a potential difference, sodium ions are forced across the cation-exchange membranes and form sodium hydroxide with the hydroxyl ions from the bipolar membranes. Similarly, chloride ions pass the anion-exchange membranes and with the protons form hydrochloric acid.

A large number of applications have been identified for EDBM for pollution control/resource recovery and chemical processing. They range from battery acid recovery, sodium alkali recycling in pulping and bleaching operations, acid and base production from saline wastewater streams, and high-purity water production to organic acid recovery from fermentation broths [28].

![Figure 2.6: Schematic representing electrodialysis using bipolar membranes (EDBM) to produce acids and bases from their corresponding salt solutions.](image)

Other desalination applications of ion exchange membranes related to electrodialysis are continuous electro-deionization and membrane capacitive deionization. Continuous electro-deionization enables the production of ultrapure water by filling the diluate cell of electrodialysis with ion exchange beads to reduce the electrical resistance [29]. Membrane capacitive deionization removes ions from a solution into oppositely-charged porous electrodes in front of which are ion exchange membranes that help increase the process efficiency [30].

Established large-scale application of ion exchange membranes is in the chlor-alkali process to produce caustic soda and chlorine. The application of ion exchange membranes in energy conversion and storage is increasingly gaining momentum. They are traditionally used in chemical fuel cells. And recently in microbial fuel cells, which are devices that degrade organic and inorganic matter and generate electricity [31]. They are further applied to generate power from the salinity gradient between fresh and salt.
water using ion exchange membranes in a process called reverse electrodialysis [32]. For electrochemical energy storage, ion exchange membranes are the main components of the recently-developed redox flow batteries [33].

Other novel applications of ion exchange membranes in the research phase are in the area of microfluidics, where several innovative microfluidic devices have been designed, such as electroosmotic pumps [34], protein preconcentration devices [35] and microfluidic chips for direct seawater desalination [36] etc. Fundamental researches on ion-selective interfaces for- and their integration in microfluidic devices are currently underway [37].

A number of reviews covered the recent advances in ion exchange membranes and related processes [2], [19], [20], [38] etc. Some theories about the ion transport phenomena studied in this thesis are given in the respective chapters. Reviews specific to these phenomena have also been published: overlimiting conductance [39], [40]; monovalent cation permselectivity [41]; water dissociation in bipolar membranes [22], [42].

2.2 Polyelectrolyte Multilayers

2.2.1 Layer-by-Layer Assembly

The layer-by-layer (LbL) assembly of polyelectrolytes is a generic and versatile technique used to modify surfaces; it allows the formation of thin films with tunable composition, thickness, and morphology [5]. LbL assembly is based on sequential adsorption of polyanions and polycations onto a charged substrate, which was introduced in the early 1990s by Decher et al. [43]. The process is now considered to be not only driven by electrostatic interactions but more generally by entropy gain due to the release of counterions and waters of hydration [44], [45].

Apart from electrostatic interactions, other interactions can also be utilized for the multilayers construction, such as hydrogen bonds, covalent bonds, halogen bonds, coordination bonds, charge-transfer interactions, biospecific interactions, guest–host interactions etc. [46]. And in addition to polyelectrolytes, the multilayer films can comprise other building blocks, such as (bio)macromolecules, clay platelets, virus particles, colloids, microgels etc. [5], [47].

For the electrostatic LbL assembly with polyelectrolytes, the procedure is as follows. A simplified scheme of the method is presented in Figure 2.7. With the first deposition step, electrostatic attractions anchor the first polyelectrolyte layer on the oppositely-
charged substrate. What propagates multilayer film formation is that the amount of adsorbed polyelectrolytes is self-limiting and that a charge reversal of the membrane surface occurs, thus leaving the surface prepared for the next adsorption step. The adhesion of the subsequent polyelectrolyte layer is ensured through a high number of electrostatic bonds created with the opposite charges of the previously deposited polyelectrolyte. In between the adsorption steps, rinsing of the substrate is necessary to remove any loosely-bound polyelectrolytes. In this manner, the thickness and functional properties of the membrane coating can be finely tuned by adjusting the adsorption parameters and the number of deposited bilayers.

![Figure 2.7: A schematic representation of an ultrathin film deposition process using the layer-by-layer (LbL) assembly of polyelectrolytes (adapted from ref. [5]).](image)

Two main aspects give LbL assembly an advantage over other comparable techniques: (a) precise control over the thickness and chemical composition of the layers and (b) no limitation with respect to the size or geometry of the substrates [47]. It is further a cost-effective, environment-friendly method that is carried out at normal room conditions without any special instruments.

### 2.2.2 Growth and Internal Structure of Polyelectrolyte Multilayers

A number of parameters can be varied to tune properties of the polyelectrolyte multilayers: number of layers, type of polyelectrolyte, charge density of the polyelectrolyte, ionic strength (addition of salt), type of salt [44]. Variables such as polyelectrolyte molecular weight and concentration, and deposition time are known to be less important [48].

In explaining charge balance and transport in polyelectrolyte multilayers and the effect of deposition parameters, especially ionic strength, Schlenoff and co-workers introduced the terms *intrinsic* and *extrinsic* charge compensation [48]–[51]. Intrinsic charge compensation occurs when charges of a polymer chain are compensated by opposite charge
of another polyelectrolyte. It is termed extrinsic charge compensation when salt ions of
the depositing solution take part in balancing charges of the polyelectrolytes (see
Figure 2.8).

By decreasing charge density and increasing ionic strength, polyelectrolyte chains go
from a stretched to a coiled conformation due to reduced electrostatic repulsion along
the polyelectrolyte chains. If deposited as such, give rise to thicker layers with higher
roughness [52]. For weak polyelectrolytes whose dissociation properties (charge density)
depend on pH, pH can be used as an additional parameter to finely tune the LbL film
properties [53]. Screening of the charges of the polymer backbone by extrinsic compensa-
tion also implies that the polymer chains are more mobile, thus show a higher degree
of swelling [54]. For the effect of the type of salt counterions, a complex interplay of a
set of contributions has to be considered but generally depends on the polarizability of
the ions [44], [55]. Figure 2.8 summarizes the preparation conditions and post-
deposition treatments affecting the chain mobility [44].

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Preparation conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial dissolution of complexes by increasing ionic strength</td>
<td></td>
</tr>
<tr>
<td>Partial dissolution of complexes by increasing temperature</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>Increasing temperature</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2.8:** Summary of parameters that affect the chain mobility in polyelectrolyte multilayers (adapted from ref. [44]).

Purely extrinsic compensation is unlikely. When the LbL film is exposed to a certain
critical salt concentration, the remaining ion-pairing between the polyelectrolyte chains
become too weak to hold the assembly together. Hence the multilayer decomposes back
into individual polymer strands or loosely-associated complexes [56]. The critical salt
concentration that leads to the deconstruction of the assembly seems to depend on the
used polyelectrolyte pairs. It was, for example, reported to be 0.3 M NaCl for
PAA/PDADMA and 2 M NaCl for PSS/PDADMA [57].

The internal structure of polyelectrolyte multilayer assemblies has been extensively
studied [44]. A number of surface analytical techniques, especially neutron reflectome-
try, reveal that polyelectrolyte multilayers are not distinct strata, but rather fuzzy nanoassemblies with interdigitation between the polymer chains [5], [58]. At least for the case of polyions that form a 1:1 stoichiometric complex, three gradual zones are thought to form with growing number of layers: precursor zone (I), core zone (II) and outer zone (III) [59]. Zone I formed from the first few layers is largely influenced by the underlying substrate. Zone II makes up the charge neutral bulk of the assembly, which forms only after a sufficiently high number of layers were being deposited. The outer zone III comprises the few outer layers at the surface of the film carrying excess charges, which are in direct contact with the ambience.

Physico-chemical properties of the outer zone are different from the core zone. The outer layers and especially the terminating layer switch the surface properties. After zones I and III have reached their final thickness, the thickness of only the core zone increases with an increase in the number of layers. The number of layers that belong to zone I and III is unknown but depends on the substrate, the polyelectrolyte pairs and the deposition conditions [60].

### 2.2.3 Techniques for LbL Assembly

LbL assembly is mostly carried out by alternate dipping of the substrate into polyelectrolytes of different charge. Dipping creates uniform and reproducible films. The assembly involves diffusion, adsorption, and rearrangement of the polymer chains. The process is usually finished after 20 min for polyelectrolytes with a concentration of $10^2$ monomol/L (concentration of the corresponding monomer units) [44]. Assembly of a high number of layers by dipping is, nonetheless, time-consuming. Hence, techniques such as spray-assisted and spin-assisted coating have been pursued, especially for rapid fabrication of thick layers [47]. This will likely enhance wider acceptance of the LbL method [60].

In addition, lateral micropatterning of the deposited polyelectrolyte layers is also vital for certain applications. Hammond and co-workers advanced the non-lithographic microcontact printing technique into transferring polyelectrolytes onto a substrate using polydimethylsiloxane (PDMS) stamps with micron-sized features [61]. Subsequently, Hammond lab has further demonstrated a multilayer transfer printing [62]. Here an entire polyelectrolyte multilayer assembled on a PDMS stamp is transferred onto a substrate provided that the interaction of the first polyelectrolyte layer with the PDMS is finely tuned and conducive conditions are maintained for the printing.
2.3 Microgels

Microgels are particulate cross-linked polymer networks in a typical size range of about 50 nm–5 µm [6]. They differ from rigid colloidal particles, in that microgels are soft and can be swollen in suitable solvents, have a diffuse boundary and can be penetrated by smaller molecules [63], [64]. Depending on their type, microgels also exhibit stimuli-responsive behavior, i.e., they undergo swelling and de-swelling transitions (change in dimensions and structure) and variation in their interactions in response to external stimuli, such as temperature, pH, ionic strength etc. [7], [8]. They are thus, as smart materials, candidate for a number of different applications, such as drug delivery, sensing, separation and purification technologies, catalysis etc. [7], [65].

The swelling and de-swelling of water-swollen microgels is the result of expulsion or imbibition of water. This transition is dictated by the imbalance between repulsive and attractive forces acting on the particles. Microgels swell when ionic repulsion and osmotic forces exceed attractive forces, such as hydrogen bonding, van der Waals interactions, and hydrophobic and specific interactions [7]. For example, the most widely-studied microgel system – poly(N-isopropylacrylamide) (poly(NIPAM)) – undergoes thermally-induced de-swelling when the solution temperature is increased above the lower critical solution temperature (LCST) (Figure 2.9). The LCST of poly(NIPAM) polymer in water is 32 °C [6].

![Image of microgel swelling and de-swelling](image)

Figure 2.9: Thermally-induced swelling and de-swelling of microgels (adapted from ref. [7]).

Below the LCST, water is a good solvent for poly(NIPAM) due to the hydrogen bonding between water molecules and the amide residue of the polymer. But as the temperature of the solution is increased, the hydrogen bonds are broken and the hydrophobic interactions within the polymer chain are dominating, causing poly(NIPAM) to under-
go a coil-to-globule transition, thus the microgel size shrinks significantly. This transition occurs in a very short time period and within a narrow range of temperature called volume phase transition temperature (VPTT) [6], [7].

Of particular interest to the combination of microgels with membranes is that presynthesized microgels also retain their responsiveness in the adsorbed state as shown in a number of previous publications [9], [10], [66].
Chapter 3

Materials and Methods

This chapter generally outlines the materials and methods used that are applicable to the entire thesis. Further chapter-specific experimental conditions, additional materials or techniques are detailed in the respective chapters.

3.1 Materials

3.1.1 Membranes

In this study, commercial ion exchange membranes, modified- or tailor-made membranes were used. Properties of the commercial membranes are listed in Table 3.1.

3.1.2 Polyelectrolytes

The LbL multilayers were formed from the following polyelectrolytes; the polycations: poly(ethylenimine) (PEI), poly(diallyldimethylammonium chloride) (PDADMAC), poly(allylamine hydrochloride) (PAH); and the polyanions: poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), poly(sodium styrene sulfonate) (PSS) and poly(acrylic acid) (PAA). The chemical structures of the polyelectrolytes and their respective molecular weights (MW) are shown in Figure 3.1. All the polyelectrolytes were obtained from Sigma-Aldrich (Germany), and were used as received without any further purification. If not mentioned otherwise, the polyelectrolyte solutions were prepared in ultrapure water with a concentration of 1 g/L. The pH of PAA (pH 3.0) and PAH (pH 10.0) solutions were adjusted with HCl and NaOH solutions, respectively.
<table>
<thead>
<tr>
<th>Name</th>
<th>Manufacturer</th>
<th>Type</th>
<th>Ion exchange capacity (meq/g)</th>
<th>Membrane thickness (mm)</th>
<th>Area resistance (Ω.cm²)</th>
<th>Selectivity (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMX</td>
<td>Astom Corp., Japan</td>
<td>Standard</td>
<td>1.66&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.16&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.50&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMS</td>
<td>Astom Corp., Japan</td>
<td>Monovalent-ion-permselective</td>
<td>2.30&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.13&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.49&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CSO</td>
<td>Asahi Glass, Japan</td>
<td>Monovalent-ion-permselective</td>
<td>2.55&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.09&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.09&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FKB</td>
<td>FuMA-Tech GmbH, Germany</td>
<td>Stable in acidic and caustic environment (PEEK-reinforced)</td>
<td>0.9-1.0</td>
<td>0.08 – 0.10</td>
<td>&lt;4</td>
<td>&gt;98</td>
<td></td>
</tr>
<tr>
<td>FAA</td>
<td>FuMA-Tech GmbH, Germany</td>
<td>Stable in acidic and caustic environment (PEEK-reinforced)</td>
<td>&gt;1.2</td>
<td>0.13 – 0.15</td>
<td>&lt;2</td>
<td>&gt;92</td>
<td>Used in Chapter 4</td>
</tr>
<tr>
<td>FAA</td>
<td>FuMA-Tech GmbH, Germany</td>
<td>Stable in acidic and caustic environment (PEEK-reinforced)</td>
<td>1.43</td>
<td>0.13</td>
<td>1.9</td>
<td>96.6</td>
<td>Used in Chapter 7</td>
</tr>
<tr>
<td>Bipolar membrane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FBM</td>
<td>FuMA-Tech GmbH, Germany</td>
<td>Stable in acidic and caustic environment (PEEK-reinforced)</td>
<td>-</td>
<td>0.2 – 0.25</td>
<td>&lt;3</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Measured
<sup>b</sup>Membrane thickness measured in swollen state.
<sup>c</sup>Characterized in 0.5 M NaCl at 25 °C.
3.1.3 Microgels and Microgels Synthesis

The microgels poly(methacrylic acid) (PMAA) and quaternized poly(2-vinylpyridine) (qP2VP) and also the latex precursor of qP2VP, i.e., P2VP, were used in this study to modify the membranes. Aqueous dispersions of the particles were provided by DWI – Leibnitz Institute for Interactive Materials (Aachen, Germany). They were synthesized and characterized by Rahul Tiwari. The latex dispersion P2VP was synthesized by surfactant-free emulsion polymerization. The microgel qP2VP was prepared post-deposition by quaternizing the assembled P2VP with methyl iodide vapor for about 24 h. Similarly, the PMAA microgel was prepared from its latex precursor poly(t-butyl methacrylate) (PtBMA) by acid hydrolysis using methane sulfonic acid. Chemical structures of the used microgels are shown in Figure 3.2.

Average particle size of the P2VP particles is 210 nm with a polydispersity index of 1.02 as determined by dynamic light scattering (DLS). Zeta potential of the qP2VP
Materials and Methods

Microgels vary between 55 mV at pH 3.0 and 38 mV at pH 9.0, and their particle size varies between 506 nm at pH 3.0 to 346 nm at pH 7.0 as determined by DLS. These qP2VP microgels were prepared by first redispersing freeze-dried P2VP particles in dichloromethane and then quaternizing by adding methyl iodide. The reaction was carried out for 48 h at room temperature. Particle size and zeta potential of the qP2VP microgels prepared by quaternizing in the gas phase are yet to be determined.

The PMAA particles also show pH-dependent variation of the particle size and zeta potential. Their average particle size varies between 420 nm at pH 2.0 and 960 nm at pH 10.0 as determined by DLS. Their zeta potential similarly varies between -5 mV at pH 3.0 and -55 mV at pH 10.0.

![Chemical structures of the used microgel precursor (a) and microgels (b and c).](image)

**Figure 3.2**: Chemical structures of the used microgel precursor (a) and microgels (b and c).

### 3.1.4 Materials for Micropatterning Polyelectrolytes and Microgels

The Sylgard 184 kit of elastomeric poly(dimethyl siloxane) (PDMS) (DOW Chemical) was used to prepare PDMS stamps for microcontact printing (µCP). Silicon molds were used to prepare structured PDMS stamps. The molds were partly manufactured at the Chair of Micro Structure Integration of the RWTH Aachen University and partly obtained from the University of Twente. Standard photolithographic techniques were used to machine the patterns into the silicon wafers. Trichloro(1H,1H,2H,2H-perfluorooctyl)silane was obtained from Sigma-Aldrich (Germany) to hydrophobize the surface of the silicon molds in order to facilitate the release of the PDMS stamps after curing.
3.2 Membrane Preparation and Modification

3.2.1 Layer-by-Layer (LbL) Assembly of Polyelectrolytes

Polyelectrolyte multilayers were applied to modify membranes or PDMS stamps. To introduce the polyelectrolyte multilayers, the membranes normally stored in 0.5 M NaCl were typically first rinsed with ultrapure water and coated on only one side with the desired polyelectrolyte multilayers. This was carried out in an in-house-built coating cell (for single or multiple membranes) by the LbL assembly method, by sequential dipping of, e.g. a cation exchange membrane in 1 g/L solution of a polycation for 30 min, followed by 1 g/L polyanion solution for 30 min, for each bilayer. In between the coating steps, the membranes were thoroughly rinsed with ultrapure water to remove any loosely bound polyelectrolytes. Concentration and pH of the polyelectrolytes, as well as coating times vary slightly, and they are mentioned in the corresponding chapters.

3.2.2 Microcontact Printing of Polyelectrolytes

Preparation of Silicon Molds. The stamps for the µCP were prepared by curing the Sylgard 184 PDMS kit. The surface of the silicon molds was treated beforehand by perfluorination to facilitate the peeling off of the PDMS stamp from the silicon mold.

The PDMS prepolymer and the crosslinking agent were manually mixed in a 10:1 ratio, and degassed in a vacuum oven 2–3 times, before being centrifuged at 4000 rpm for 1 min. The PDMS mixture was then slowly poured onto the silicon mold placed in a Petri dish. After casting, the thin film was again degassed 2–3 times in a vacuum oven, afterwards cured at 60 °C for 2 h. Finally, the microstructured PDMS film was carefully peeled off the silicon mold.

Microcontact Printing. The polyelectrolyte micropatterns were printed either directly on the CMX membrane or on a previously assembled LbL layers (atop the CMX membrane), where the PAA was left as the outermost layer. To ink the PDMS stamp, it was immersed in PAH for 1 h and then rinsed. The rinsing lasted for only a few seconds to maintain the degree of ionization of the PAH. Then the stamp and the membrane were blown dry with a gentle stream of nitrogen. The stamp was afterward pressed against the membrane for 1 min (20 min) to print the patterns. A schematic representation of the followed µCP protocol is shown in Figure 3.3.
3.2.3 Slip Coating of Microgel Monolayers

In this thesis, a method of modifying membranes with confluent and micropatterned monolayers of microgels has been developed – formed by a method similar to dip-coating (henceforth referred to as slip-coating method) and by microcontact printing (µCP) technique, respectively. Further details about the methods developed to pattern the microgels on top of ion exchange membranes are presented in the Results Section of Chapter 7.

3.3 Surface Characterization of the Modified Membranes

The deposition of the polyelectrolyte layers was monitored by contact angle measurements (DSA10-MK2, Krüss, Germany), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Thermo Nicolet, Nexus 470) and X-ray photoelectron spectroscopy (XPS) (Axis Ultra, Kratos Analytical, UK). The deposited homogeneous polyelectrolyte multilayers were visualized using field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi, Japan) and scanning electron microscopy (SEM) (S-3000N, Hitachi, Japan). Whereas confocal- and fluorescence microscopy were employed to visualize the µCP-ed polyelectrolyte patterns.

3.4 Electrochemical Characterization of the Modified Membranes

3.4.1 Measurement Setup

Figure 3.4 and Figure 3.5 show the assembled single-membrane experimental setup for the electrochemical characterization of the membranes. The setup contains four tanks.
from which the solutions are pumped through the six-compartment module by MCP Standard peristaltic pumps fitted with SB 2V pump heads (Ismatec, Switzerland). The flow rate through each compartment was maintained at 1000 mL/min (a cross-flow velocity of approximately 2 cm/s). The temperatures of the feed solutions are controlled by a Julabo F25 ME laboratory thermostat (Julabo, Germany) connected to four glass-coil heat exchangers (Normag, Germany). To ensure the right working conditions and to acquire the related process/membrane properties, pH and conductivity of the solutions adjacent to the membrane under investigation are measured. Data acquisition of the system is implemented on DASYLab software.

**Figure 3.4:** Schematic flow diagram of the single-membrane characterization setup. 1. Membrane cell; 2. Power supply; 3. Measurement of the membrane voltage drop; 4. Data acquisition board; 5. Solution tanks; 6. Glass coil heat exchangers connected to a thermostat; 7. Measurement of pH and conductivity.

The membrane module of the measurement setup is made of poly(methyl methacrylate) and consists of six separate compartments, shown schematically in Figure 3.6. The two outer compartments contain two working electrodes used to apply potential. The anode and cathode are made of mixed-metal-oxide-coated titanium and stainless steel, respec-
tively. The membranes are placed between the individual cell compartments; arrangement of the membranes inside the module depends on the test performed, and they are shown separately for each test. The active area of each membrane in the cell varies between 49 and 10.5 cm². The membrane under investigation is placed in the middle of the cell. The other membranes are auxiliary membranes that are used to limit interference of the electrode reactions on the measurement.

An electrical current was applied to the module using the EA-PS 9065-20 DC power supply (maximum 65 V, 20 A) (Elektro-Automatik, Germany). The voltage drop across the test membrane was measured using two calomel reference electrodes (QM712X, ProSense, the Netherlands). The reference electrodes were extended close to the membrane surface using Haber-Luggin capillaries. The capillaries were filled with a 3 M KCl solution and each connected to a small reservoir in which the reference electrodes were placed. A schematic of the voltage measurement system is shown in Figure 3.7.

Figure 3.5: Single-membrane electrodialysis setup for membrane characterization and for screening application tests.
Figure 3.6: Schematic representation of a six-compartment measurement module for the measurement of the electrochemical performance of the membrane placed in the middle. The arrangement of the membranes in the module and the salt solutions can vary; the schematics are presented separately in each chapter.

Figure 3.7: Measuring system of the voltage drop across the membranes.

3.4.2 Measurement of Polarization Curves

The current–voltage (i–V) polarization curves of the membranes were measured using the four-point method: the two working electrodes were used to apply the current while the voltage drop across the membrane was measured using the two calomel reference electrodes. The membranes were characterized in salt solutions of varying concentrations (mentioned separately in each chapter). Prior to any measurement, the membranes were conditioned in the salt solution for about 24 h outside the membrane module. During the experiments, the temperature was maintained at 25 °C and the applied
current density was increased stepwise (every 30 s) to allow the membrane reach a steady state.

The pH changes in the central compartments were simultaneously recorded during the $i$–$V$ measurements to quantify the percentage of the current carried by the water-splitting products as

$$\frac{J_{OH^-}}{J_{total}} \cdot 100$$

where $J_{OH^-}$ is the fraction of the current carried by hydroxyl ions; and $J_{total}$ is the total ion flux, i.e., the sum of the flux of hydroxyl and sodium ions, and was obtained from Faraday’s law as

$$J_{total} = \frac{A}{V \cdot F} \int_0^t i \cdot dt$$

where $A$ is the effective membrane area; $V$ is the volume in each compartment; $i$ is the current density; and $F$ is the Faraday constant.

For the experiments with bipolar membranes, the water-splitting capacity of the membranes was additionally determined by titration.

The transition of the $i$–$V$ curves of the monopolar membranes from the plateau to the overlimiting region is marked by the scatter of the voltage drop readings, but the transition was also determined with the aid of Cowan-Brown plots. In Chapter 7 the transition was as well defined according to a mathematical sigmoid method recently reported. Then the plateau lengths were read off the $i$–$V$ curves, which have had their ohmic parts subtracted.

### 3.4.3 Chronopotentiometry

In Chapter 5, chronopotentiometry measurements were carried out to get an insight into the hydrodynamic instabilities caused by the electroconvective vortices, and the concentration-polarization-related potential losses. The chronopotentiograms were obtained by applying a step input in current of 30 mA/cm² (which is in the overlimiting region of the investigated membranes), and recording evolution of the voltage drop across the membranes at a sampling rate of 600/min.
3.4.4 Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were carried out to get further insight about the influence of the interface layers of the membranes. These experiments were conducted using IviumStat XR, a potentiostat/galvanostat with frequency response analyzer (Ivium Technologies, the Netherlands). Similar to the DC $i-V$ measurements, a four-point system was applied to measure the impedance of the membranes. All the impedance measurements were performed with an AC signal of 10 mA amplitude in the frequency range of 0.03 Hz−1 kHz. The complex nonlinear least-squares fitting of the impedance data was performed with the Zview 3.0 software package.

3.4.5 Permselectivity Measurements

The permselectivity measurements in Chapter 5 were carried out in galvanostatic mode under the application of a current density of 15 mA/cm$^2$, which is in the underlimiting range for all the studied membranes. These experiments were conducted using the same six-compartment module (Figure 3.6) and for the same mixture of NaCl and CaCl$_2$ in both compartments next to the membrane, to avoid any influence of concentration gradients between both sides of the membrane. The experiments lasted for 6 h, and samples were drawn every hour from both compartments adjacent to the membrane being tested. Na$^+$ and Ca$^{2+}$ concentrations were determined by HPLC (1100 Series, Agilent Technologies, USA). This technique has ~2% error limit.

The permselectivity of the membranes between sodium and calcium ions ($P_{Ca}^{Na}$) was calculated according to the equation

$$P_{Ca}^{Na} = \frac{t_{Na^+} / t_{Ca^{2+}}}{C_{Na^+} / C_{Ca^{2+}}} = \frac{J_{Na^+} / J_{Ca^{2+}}}{C_{Na^+} / C_{Ca^{2+}}}$$  \hspace{1cm} (3.3)

$$t_{Na^+} = \frac{J_{Na^+}}{\sum J_i}$$  \hspace{1cm} (3.4)

$$t_{Ca^{2+}} = \frac{J_{Ca^{2+}}}{\sum J_i}$$  \hspace{1cm} (3.5)

where $C$ is the concentration of the ions on the diluate side of the membranes expressed in mol/L; $J$ is the flux of the ions through the membrane expressed in mol/(m$^2$ s); and $t$ is the transport number of the ions through the membrane. The flux of ions was obtained from the change in concentration of the ions on the diluate side according to
where $V$ is the volume of the treated batch of the electrolyte, which was 1 L; and $A_m$ is the active area of the membranes, which was 10.5 cm$^2$.

Furthermore, the specific energy consumption in the membrane region per mole of transported Na$^+$ ions ($E_m$) was calculated according to the relation

$$E_m = \frac{\int U_m \cdot Idt}{(C_o - C_t) V} \quad (3.8)$$

where $I$ is the applied current; $U_m$ is the voltage drop across the membrane measured by the reference electrodes; $C_o$ and $C_t$ are the concentrations of Na$^+$ ions initially and at a specific time $t$, respectively.
Chapter 4

Catalytic Polyelectrolyte Multilayers at the Bipolar Membrane Interface

4.1 Introduction

Electrodialysis has been a mature electromembrane process for more than 50 years and has been mainly applied for the production of potable water from brackish water and seawater desalination [2]. The potential of the process in new industrial applications has been strongly extended by the development of bipolar membranes [67]. Bipolar membranes are special types of ion exchange membranes composed of laminated polymeric films with fixed charges of opposite polarity. Under the influence of a high electric field, bipolar membranes split water molecules into protons and hydroxyl ions at their bipolar interface. They are utilized in an electrodialytic cell arrangement, together with cation and anion exchange membranes, to produce acids and bases from their corresponding salt solutions. Figure 4.1 shows a schematic of the structure and function of bipolar membranes.

The water dissociation reaction takes place at the interface of the ion exchange layers, either on the anion, on the cation, or within a separate contact layer. The water dissociation observed in bipolar membranes is about 7 orders of magnitude higher than in free solutions [68]. The actual mechanism of water splitting is still controversial. There are, however, two theories to explain this phenomenon.

This chapter has been published as:

The enhanced water dissociation at the interface of bipolar membranes can be explained by the increase in the degree of dissociation of weak electrolytes, like water, by high electric field strengths, which is referred to as the second Wien effect [69]. Model estimations, however, attribute the second Wien effect to be responsible for only 3 orders of magnitude of the experimentally observed increase in water dissociation [68]. This led investigators to suggest the so-called proton transfer reaction mechanism, which is strongly supported by theory and experimental evidence [70]. According to the reaction model, the proton and hydroxyl ions are believed to be a result of protonation and deprotonation reaction between water molecules and the fixed charge groups (especially the anion exchange groups) according to the following scheme [68], [71], [72]

\[
B + H_2O \rightleftharpoons BH^+ + OH^- \\
BH^+ + H_2O \rightleftharpoons B + H_3O^+ \\
A^- + H_2O \rightleftharpoons AH + OH^- \\
AH + H_2O \rightleftharpoons A^- + H_3O^+ 
\]  

(4.1) 
(4.2) 
(4.3) 
(4.4)

where \( A^- \) and \( BH^+ \) are the catalytic sites.

Following the proton transfer reaction mechanism, to improve the water splitting capability of bipolar membranes, the chemical composition and structure of the transition region are elaborately modified. In the presence of catalysts, the rate of water dissociation is enhanced, for a fixed electric potential across the transition region [73]. Catalysts reduce the usually high activation energy of water dissociation, by providing alternative reaction paths, i.e., by forming reactive activated complexes [71], [73].
As catalysts in the bipolar junction, immobile weak acids or bases with an equilibrium constant of the acid/base pair close to that of the water dissociation reaction ($pK_a = 7$) could be used [74], such as suitable phosphoric acids [75], carboxylic acids [73], amino acids [68] or pyridines [76]. As alternative catalyst types, immobilized heavy metal ion complexes like those of iron, chromium, zirconium, or others could be utilized [16], [77]. They are immobilized by placing their insoluble salts in the intermediate layer or using a soluble salt with a subsequent treatment [73]. Hydroxides of the most suitable multivalent metal ions are immobilized due to their low solubility [73]. The actual location of the water dissociation and consequently the preferred location of the catalyst (to the anion or cation exchange layer) are still open questions [78].

In order to demonstrate the catalytic activity of different macromolecules, a series of fundamental studies have been carried out by Xu and co-workers [79]–[83] on bipolar membranes whose anion exchange layers were modified with a variety of (bio)macromolecules beforehand. The list includes hydrophilic substances such as polyethylene glycol (PEG) [79] and polyvinyl alcohol (PVA) [80], polyamphoteric bovine serum albumin (BSA) [81], a dendrimer molecule polyamidoamine (PAMAM) which possesses higher amino groups [82] and hyperbranched aliphatic polyesters of the Boltorn series [83].

The catalysts can be immobilized before or after the film formation. There have been several methods applied: spray or dip-coating [23], incorporating in the polymer material by even dispersion [24], by electrochemical methods after formation of the layers or by in-situ polymerization [25], electrospay deposition, [26] etc. There exist also reports of some polymer materials that inherently contain the required catalytic functional groups in their repeating units [24].

With the methods of catalyst immobilization applied thus far, a precise control of thickness and architecture of the catalytic interface is still unsatisfactory today. In response to this need, the objective of this study is to investigate interface modification of bipolar membranes using the consecutive dipping layer-by-layer (LbL) deposition technique of polyelectrolytes. The LbL assembly of polyelectrolytes is a generic and versatile technique used to modify surfaces; it allows the formation of thin films with tunable composition, thickness, and morphology [5]. For bipolar membranes, the LbL technique offers an attractive tool to introduce molecularly thin catalyst groups at the interface of the ion exchange layers of a bipolar membrane, after formation of the films. In LbL assembly, a charged substrate is alternately immersed in polyanions and poly-
cations, to form multilayers with properties controllable on the nanoscale. To the best of our knowledge, this is the first study to report LbL assembly of polyelectrolyte multilayers to tailor the interface of bipolar membranes. We report the effect of LbL architecture on the water splitting efficiency and membrane selectivity. The latter is surprisingly a strong function of the interface architecture.

4.2 Experimental

4.2.1 Materials

The commercial Fumasep membranes, obtained from FuMA-Tech (Germany) or tailor-made membranes were used in the experiments. Properties of the commercial membranes are shown in Table 3.1. The LbL interface layers were formed from these polyelectrolytes obtained from Sigma-Aldrich (Germany): poly(ethyleneimine) (PEI), MW = 750 000 g/mol, poly(diallyl dimethylammonium) chloride (PDADMAC), MW = 250 000 g/mol, poly(4-vinylpyridine) (P4VP), MW = 60 000 g/mol and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). Chemical structures of the polyelectrolytes are shown in Figure 3.1.

Polymer materials used for the membrane preparation are sulfonated poly(ether ether ketone) (SPEEK), with an ion exchange capacity (IEC) of 1.4 meq/g (SPEEK 1.4), kindly provided by FuMA-Tech (Germany) and a SPEEK with an IEC of 1.8 meq/g (SPEEK 1.8), and poly(ether sulfone) (PES) obtained from BASF (Germany). Sulfonation of the 450PF PEEK powder (Victrex, UK) to prepare the SPEEK 1.8 was carried out according to a method described elsewhere [24]. N-Methyl-2-pyrrolidone (NMP), obtained from Merck (Germany), was used to dissolve the polymers.

4.2.2 Preparation of Bipolar Membranes

The bipolar membranes were prepared either by lamination of two commercial ion exchange membranes or by casting. Lamination of LbL-modified ion exchange membranes to prepare bipolar membranes was preferred in the first place to quickly screen and preselect viable polyelectrolyte combinations. In a second stage, bipolar membranes were realized by casting, to investigate actual performance and to study the effect of some polyelectrolyte deposition parameters. Here the preparation procedure of the membranes prepared by casting is described.
The bipolar membranes prepared by casting were composed of four layers of polymers as shown in Figure 4.2(a). The commercially available anion exchange membrane FAA (anion exchange layer) was first modified by the LbL assembly, with the desired number of polyelectrolyte layers (LbL interface layer). The LbL-coated membrane was allowed to dry for some time and fixed on a glass plate with the polyelectrolyte layers facing the airside. A thin intermediate layer (SPEEK 1.8) was then cast on top with a casting knife and dried for some time, to a dry membrane thickness of ~15–25 µm. The cation exchange layer (a blend polymer of SPEEK 1.4/PES) was cast afterward with a 500 µm casting knife (dry membrane thickness of ~130 µm). The dry film thicknesses were measured with a Vernier caliper after casting the films separately. The assembled bipolar membrane was then placed in an oven at 70 °C for 2 h and then allowed to dry at room temperature for several days before it was finally stored in a 2 M NaCl solution. The sequence of steps is depicted in Figure 4.2(b).

The cation exchange layer was cast from a 20 wt% blend of SPEEK 1.4 and PES in 60:40 weight ratio [84]. The highly charged intermediate layer was prepared from 12.5–20 wt% pure SPEEK 1.8 solution. Both polymers were dissolved in NMP with continuous stirring at 70 °C for 24 h and afterward filtered over a metal filter.

PEDOT:PSS and PEI were selected to form the LbL interface layer of the bipolar membranes prepared by casting. PEDOT:PSS was selected as the polyanion due to its high ionic conductivity as well as its ability to transport electrons to a certain degree, and PEI as a polycation due to its hyperbranched structure and highly positively charged amine groups, which can catalyze water dissociation reaction. Their chemical structures are shown in Figure 3.1.

The polyelectrolyte interface layers were introduced on the FAA membrane with LbL assembly of polyelectrolytes (cf. Section 3.2.1) by sequential dipping of the FAA mem-
brane in 1 g/L solution of PEDOT:PSS for 30 min, followed by 1 g/L PEI solution for 30 min, for each bilayer. In between the coating steps, the membrane was thoroughly rinsed with ultrapure water to remove any loosely bound polyelectrolytes.

### 4.2.3 Characterization of the Monopolar Layers

The deposition of the polyelectrolyte layers was monitored by ATR-FTIR and XPS measurements (cf. Section 3.3). Furthermore, permselectivity of the monopolar layers was checked by static permselectivity measurement, by measuring the potential difference across the monopolar layers placed between 0.1 and 0.5 M KCl solutions.

### 4.3 Characterization of the Prepared Bipolar Membranes

The prepared bipolar membranes were mainly compared in terms of their $i$–$V$ polarization curves, by DC electrical resistance measurements. The measurements were performed in the six-compartment electrodialytic cell shown schematically in Figure 4.3, with the setup described in Section 3.4.1. The membranes were characterized in a 2 M NaCl solution. Prior to any measurement, the membranes were conditioned in the salt solution for about 24 h outside the membrane module. Most of the results are an average of three runs; the average standard deviation was observed to be within 5%.

![Figure 4.3: Schematic representation of a six-compartment measurement module for the measurement of electrical resistance of membranes.](image)

The water dissociation principle of bipolar membranes can be revealed by their typical steady-state current–voltage ($i$–$V$) curve. For the sake of understanding the data presented in the Results Section, the curve is depicted schematically in Figure 4.4, with
current density per unit active membrane area on the y-axis and the electrical potential drop across the membrane on the x-axis.

When a current of the correct polarity (reverse bias) is applied, i.e., the cation exchange layer facing the cathode and the anion exchange layer facing the anode, there is at first a linear increase in electrical current, carried by salt ions initially present at the interface of bipolar membranes. The curve then plateaus at a given current generally known as the first limiting current density ($i_{\text{lim}1}$); this is when salt ions are driven out of the bipolar junction and when the interface is mostly depleted of mobile ions. This first limiting current density is also considered to be a measure of the selectivity of a bipolar membrane. The higher this limiting current density, the more unselective co-ion leakage occurs. Up to now, it is proven that the thickness and charge density of the monopolar layers are mainly responsible for the extent of co-ion leakage, expressed by the equations below [85], [86].

$$J_{\text{lim}}^{M^+} = \frac{D_{M^+,\text{AEL}}(C^s)^2}{d_{\text{wet},\text{AEL}}C_{\text{char},\text{AEL}}} \quad J_{\text{lim}}^{X^-} = \frac{D_{X^-,\text{CEL}}(C^s)^2}{d_{\text{wet},\text{CEL}}C_{\text{char},\text{CEL}}} \quad (4.5)$$

$$i_{\text{lim}} = F\left(\frac{D_{M^+,\text{AEL}}(C^s)^2}{d_{\text{wet},\text{AEL}}C_{\text{char},\text{AEL}}} + \frac{D_{X^-,\text{CEL}}(C^s)^2}{d_{\text{wet},\text{CEL}}C_{\text{char},\text{CEL}}}\right) \quad (4.6)$$

where $J_{\text{lim}}$ is the flux of co-ions; $i_{\text{lim}}$ is the first limiting current density; $C^s$ is the solution concentration; $D$ is the diffusion coefficient; $d_{\text{wet}}$ is the wet thickness of the ion exchange layers; $C_{\text{char}}$ is the charge density; subscripts AEL and CEL denote anion and
cation exchange layers, respectively; $M^+$ and $X^-$ are salt cation and anion, respectively; and $F$ is the Faraday constant.

Accordingly, the $i_{\text{lim1}}$ and co-ion leakage are directly dependent on the square of the solution concentration, the diffusion coefficients in the membrane layers, the fixed charge density, and the thickness of the monopolar layers of the bipolar membrane.

Above $i_{\text{lim1}}$, there is a steep increase in current—the region of active water dissociation. Here, the current corresponds to the production and transport of protons and hydroxyl ions. At very high current densities, a second plateau is reached, at the so-called second limiting current density ($i_{\text{lim2}}$) [87], a point at which the water dissociation reaction in bipolar membranes becomes mass transfer-limited: water transport from the electrolyte compartment through the monopolar membranes to the interface of bipolar membranes can no longer replenish the water consumed in the reaction. Hence, the membrane dries out and in fact, becomes irreversibly damaged [88].

4.4 Results and Discussion

In the following, the results of bipolar membranes modified by LbL assembly of polyelectrolytes are presented. As it was mentioned in the Experimental Section, the bipolar membranes prepared by casting were composed of four layers of polymers. The parameters of the LbL interface layer deposition varied to optimize the performance of the membranes were: number of layers, molecular weight and concentration of the polycation, as well as the ionic strength of the polyelectrolyte solution. Furthermore, an additional highly charged ionomer intermediate layer was incorporated in between the cation and the anion exchange layers.

4.4.1 Monitoring the deposition of polyelectrolyte layers

In Figure 4.5(a), the ATR-FTIR spectra of the FAA membrane, coated with various number of bilayers of PEDOT:PSS and PEI, are shown. The formation and growth of the multilayers were monitored after each of the PEDOT:PSS coatings in the multilayers: the signal at 1033 cm$^{-1}$ representing the vibrational mode of the sulfonate group from the PSS. The thickness of the layers obtained is very thin, hence the weak intensity of the sulfonate signal. Figure 4.5(b) zooms in on the sulfonate groups signal, and it can be seen that such a peak is absent in the uncoated FAA membrane but present on the LbL-coated membranes, a clear indication of successful LbL deposition of the polyelectrolyte layers.
ATR-FTIR measurements were supported with XPS measurements. With XPS, it was further demonstrated that the first layer of PEDOT:PSS was indeed successfully deposited on the membrane surface. From elemental analysis of the XPS data (Table 4.1), it can be seen that there is an increase in the O-content and S-content of FAA coated with PEDOT:PSS in comparison with the uncoated FAA. This is in agreement with the O present in the sulfonate groups as well as the dioxy groups of the PEDOT:PSS, and the S again present in the sulfonate groups, and the thiophene rings of the PEDOT:PSS, respectively.

![Figure 4.5: FTIR spectra of the FAA membrane coated with polyelectrolyte multilayers formed from PEDOT:PSS and PEI: (a) whole spectra and (b) zoomed to wavenumbers around 1033 cm$^{-1}$. Indicated in the legends are the number of bilayers, 0 being the pristine FAA membrane.](image)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position BE (eV)</th>
<th>Atomic conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>532.00</td>
<td>Pristine FAA: 10.11</td>
</tr>
<tr>
<td>S 2p</td>
<td>168.50</td>
<td>2.25</td>
</tr>
<tr>
<td>C 1s</td>
<td>285.00</td>
<td>81.20</td>
</tr>
</tbody>
</table>
4.4.2 Morphology characterization of the membranes

Morphology of the four-layered bipolar membranes was characterized using FE-SEM (Hitachi, S-4800). Figure 4.6(a) shows a cross-section micrograph of one of the four-layered membranes. Three of the four distinct polymer layers, namely, anion exchange layer (with the reinforcing fibers), cation exchange layer, as well as the intermediate layer, can be clearly distinguished. As it can be seen in the figure, a sharp junction between the anion- and the cation-exchange layers was formed, as a result of the sequential casting of the intermediate and the cation exchange layers.

Independently, 10 bilayers of PEDOT:PSS/PEI, where both polyelectrolytes were dissolved in 0.5 M NaCl solution, were assembled atop the anion exchange layer, to visually confirm their deposition using FE-SEM (Figure 4.6(b)). In addition to the ATR-FTIR and XPS measurements, FE-SEM provided supplementary evidence of the presence of the LbL interface layers.

![Figure 4.6: FE-SEM micrographs of (a) a four-layered bipolar membrane. Indicated on the micrograph - AEL, Anion exchange layer; IL, Intermediate layer; and CEL, cation exchange layer. (b) LbL interface layers atop a reinforced FAA membrane without the cation exchange layer.](image)

4.4.3 Screening of Possible Polyelectrolytes for the LbL Assembly Method

First, to quickly screen the possible polyelectrolyte combination for further study, bipolar membranes were prepared by laminating either the LbL-modified FAA with FKB or the LbL-modified FKB with FAA. A summary of the results is shown in Figure 4.7, which shows the comparison of the various membranes studied compared on their voltage drop at a constant current density of 40 mA/cm². The membrane voltage drops were read off their respective \( i-V \) curves. It can be seen from Figure 4.7 that all single polyelectrolyte layers coated on the FKB show increased electrical resistance in comparison to the membrane without any interface. This was in spite of the fact that the polycations coated on the FKB contain amine groups, which were shown in a number
of previous studies to be catalytically active. On the other hand, one layer of PEDOT:PSS coated on FAA shows a slight decrease in the electrical resistance. PEDOT:PSS bears sulfonic acid groups, which in itself are not catalytic to water dissociation reaction [89].

After optimizing the coating procedure, a polyelectrolyte combination with the least electrical resistance was obtained for the interface (PEI/PEDOT:PSS)$_2$, deposited on FAA (i.e., FAA coated with two bilayers of PEDOT:PSS and PEI - a total of 4 single polyelectrolyte layers). It is noteworthy that coating the same bilayers on FKB (now (PEDOT:PSS/PEI)$_2$), however, showed increased electrical resistance.

![Graph showing membrane voltage drop](image)

**Figure 4.7**: Bipolar membranes composed of two laminated commercial ion exchange membranes, FAA and FKB (FuMA-Tech, Germany), and a combination of a number of polyelectrolytes as interface layers.

The collective outcomes of these screening experiments were (a) polyelectrolyte multilayer structures at the interface of bipolar membranes do catalyze water dissociation, (b) bipolar membranes with enhanced performance can be prepared by introducing polyelectrolyte interface layers on the anion exchange layer rather than on the cation exchange layer, confirming also that water splitting occurs near the anion exchange layer [90], [91], and (c) polyelectrolyte pairs of higher charge density should be selected: PEDOT:PSS and PEI are viable candidates and have been selected for our experiments where the bipolar membranes are prepared by casting the layers rather than by laminating them.
4.4.4 Addition of LbL-Assembled Interface Layers

From the membranes prepared by lamination, the best catalytic activity was obtained with two bilayers of PEDOT:PSS and PEI coated on FAA. The commercial membrane FAA is an alkali-stable anion exchange membrane from the company FuMA-Tech, based on quaternary ammonium groups [92]. From previous studies, particularly from the work of Balster et al. [24], it was evident that the type of anion groups on a bipolar membrane plays a major role in its performance. Quaternary ammonium groups are normally not catalytically active for water dissociation. However, at high electric field and in alkaline conditions they degrade to tertiary and secondary amines, which then become more reactive [70]. Hence, FAA was chosen for LbL modification for all the experiments, due to it being alkali stable and because it bears quaternary ammonium groups [92], which are important factors when preparing high-performance bipolar membranes.

Figure 4.8 illustrates the effect of the addition of (1) LbL-assembled interface layers and (2) highly charged intermediate layer on the $i$–$V$ curves of the prepared bipolar membranes. The interface layers were two bilayers of PEDOT:PSS and PEI coated on FAA. In comparison to the electrical resistance curve of the bipolar membrane prepared from only the anion and the cation layer, the membrane with an extra LbL interface shows a more defined profile of the $i$–$V$ curve. Especially the $i_{\text{lim1}}$ plateau is flatter (Figure 4.8(b)), which is an indication of the uniform onset of the water splitting. At the practical working current densities, it even shows lower electrical resistance than the membrane with no interface.

In the polyelectrolyte multilayers, the prime catalytic effect could stem from the hyperbranched PEI, which comprises 50% secondary and 25% tertiary amines in the backbone and 25% primary amine side groups [93]. These functional groups facilitate the proton transfer between water molecules and the fixed ion exchange groups of the anion exchange layer. These rapid protonation and deprotonation reactions proceed according to the reaction schemes in equations (4.1) and (4.2) as proposed by Simons [71]. In accordance with the reasoning of the proton transfer reaction mechanism, the effect of the molecular weight (MW) and concentration of PEI was investigated. The base case of PEI solutions applied was 1 g/L and a MW of 750 000 g/mol. Hence bipolar membranes, wherein the LbL-coated layers were formed from (a) 1 g/L of PEI with a low MW of 1300 g/mol and (b) with a varied concentration of 0.1 g/L and 0.5 g/L of the high MW PEI of 750 000 g/mol, were prepared and compared to the base case.
However, these variations did not significantly affect the voltage drop across the bipolar membranes, in the active water dissociation area of the $i$–$V$ curve (refer to Figure A4.1 in the Appendix).

Figure 4.8: Effect of the addition of intermediate and interface layers and their combined effect on the electrical resistance of tailor-made bipolar membranes, characterized in 2 M NaCl solution. The LbL interface was made up of two bilayers of PEDOT:PSS/PEI coated on the FAA. (a) Complete curve. (b) Lower current density region; lines added to the data points to guide the eyes.

4.4.5 Synergy of LbL Interface Layers with Highly Charged Intermediate Layer

Balster et al. [24] demonstrated that increasing the amount of ion exchange groups at the interface of bipolar membranes significantly lowers the electrical resistance of bipolar membranes. This decrease in electrical resistance was achieved by casting a thin pure SPEEK intermediate layer with a high fixed ion concentration. Such a film naturally has high water uptake, hence higher co-ion leakage. However, since it is sandwiched in between the anion and cation exchange layers, the function of ion rejection is ensured by an outer cation exchange layer, which possesses a lower swelling degree and larger thickness. In the present study, such a method of the thin intermediate layer inclusion was also employed, while the cation exchange layer was formed from a blend of SPEEK 1.4/PES, with a dry film thickness of ~130 µm and a permselectivity of ~93%.

As expected, the addition of such a highly charged intermediate layer indeed lowers the electrical resistance as shown in Figure 4.8. This is a clear indication that the thin in-
intermediate layer of pure SPEEK 1.8 facilitates the polarization of water molecules at the interface. Due to its high charge density, the intermediate layer also increases the electric field present at the interface of bipolar membranes and as a result also enhances the water activity there, by drawing more water toward the interface [16]. Water supply toward the interface of bipolar membranes is debated to be the result of an inward-directed Maxwell pressure whose magnitude increases with the strength of the electric field. With the electric fields encountered in bipolar membranes, Maxwell pressure is strong enough to supply water against an osmotic pressure. The adjacent ionic liquid solutions may comprise concentrated acid and alkali, while the water at the interface is deionized: the flow of the water into the bipolar interface hence occurs against an osmotic pressure difference of 2 orders of magnitude [16].

Finally, the bipolar membrane with the four distinct polymer layers shows a synergetic effect of the added LbL interface and the intermediate layer. At 100 mA/cm$^2$ current density, the voltage drop across the membrane drops from ~5 to 2.5 V, by adding both the LbL interface and the intermediate layers. These results clearly demonstrate the applicability of LbL interface layers to act as catalysts, in combination with intermediate layers, in preparing high-performance bipolar membranes; that is to say a synergistic effect of the second Wien effect (manifested by the intermediate layer) and a catalysed proton transfer reaction (manifested by the LbL interface layers). This batch of experiments had the intermediate layers prepared from 12.5 wt% SPEEK 1.8 solutions. The adhesion of the SPEEK 1.8 layer to the FAA membrane was significantly improved by forming the film from 20 wt% polymer solution. Therefore, further experiments were carried out with 20 wt% SPEEK 1.8 solutions.

**4.4.6 Effect of Number of Interface Layers**

It has been discussed that macromolecules, vis-à-vis, polyelectrolytes with the right functional groups, act as water dissociation catalysts at the interface of bipolar membranes by different mechanisms. The presence of functional groups could, for example, increase the electric field generated at the transition region or increase hydrophilicity of the interface layer, thus increasing water activity and the looseness of the bonds of water. These are some desired effects of added catalysts as discussed by Kang et al. [25].

Figure 4.9 shows $i$–$V$ curves of the bipolar membranes with two, four and six bilayers of PEDOT:PSS/PEI. From Figure 4.9(b), it is obvious that the number of deposited polyelectrolytes at the interface of bipolar membranes has indeed a significant effect on
the water splitting. In the cases studied the bipolar membrane with two bilayers of PEDOT:PSS/PEI has the lowest water splitting potential ($V_{\text{diss}}$) as well as the lowest operating electrical resistance ($R_{\text{op}}$), approximated at a current density of 100 mA/cm$^2$.

The trend observed was that increasing the number of layers will increase the electrical resistance of the bipolar membranes. The $V_{\text{diss}}$ and $R_{\text{op}}$ of the membranes are summarized in Table 4.2. Furthermore, Table 4.2 shows that the relationship between the number of layers and the water splitting potential ($V_{\text{diss}}$) does not correlate linearly. The difference in the water-splitting potential ($V_{\text{diss}}$) between two and four bilayers is not as high in comparison to the difference between four and six bilayers, which could be resulting from the growth behavior of PEDOT:PSS/PEI multilayers.

![Figure 4.9](image)

**Figure 4.9:** Effect of the number of the deposited polyelectrolyte layers on the electrical resistance of tailor-made bipolar membranes, characterized in 2 M NaCl solution. The LbL interface layers were made up of PEDOT:PSS and PEI. (a) Complete curve. (b) Lower current density regime; lines added to the data points to guide the eyes.

**Table 4.2:** Variation of water dissociation potentials and $R_{\text{op}}$ with the number of interface layers$^a$

<table>
<thead>
<tr>
<th></th>
<th>Two bilayers</th>
<th>Four bilayers</th>
<th>Six bilayers</th>
</tr>
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<tbody>
<tr>
<td>$V_{\text{diss}}$ (V)</td>
<td>1.4</td>
<td>1.7</td>
<td>3.6</td>
</tr>
<tr>
<td>$R_{\text{op}}$ ($\Omega \cdot \text{cm}^2$)</td>
<td>30</td>
<td>36</td>
<td>54</td>
</tr>
</tbody>
</table>

$^a$Approximate values given here obtained from the $i-V$ curves in Figure 4.9.

With an increase in the number of layers, it was expected that the active catalytic sites available for water dissociation would increase, thereby causing the electrical resistance to decrease. Experimentally, however, it is shown that the electrical resistance increased with the number of layers. The increase in electrical resistance could probably
be resulting from the opposing effects of the effective contact area ($A_{eff}$) and the bipolar junction thickness ($2\lambda$), a notion used by Alcaraz et al. [94] to characterize interface structure of bipolar membranes using impedance spectroscopy. With an increase of the LbL interface layers, the effective contact area of the two ion exchange layers would increase. The effective contact area ($A_{eff}$) is implied here to be the active catalytic site at the interface of the two ion exchange layers of the bipolar membranes. These active catalytic sites are provided by the amine groups of the PEI forming the LbL interface layers. On the other hand, the bipolar junction thickness (i.e., the region depleted from ions) would increase too. For effective water dissociation, the bipolar junction should be very sharp, preferably less than 5 nm [19].

In previous publications [15], [95], scanning electron micrographs and X-ray spectrometry show that the typical thickness of the contact region is in the order of micrometers. Nonetheless, this distance does not correspond to the space charge layer at the bipolar junction ($2\lambda$), which is believed to extend from the effective contact zone to some nanometers within the ion exchange layers [94], especially the anion exchange layer [96].

The effect of excessive junction thickness enlargement by catalysts can be understood as a screening effect, which would weaken the electric field present at the interface of the ion exchange layers. Since under reverse-bias conditions the depleted bipolar junction is mainly responsible for the majority of the voltage drop across bipolar membranes, any catalytic additive should not increase the thickness of the depletion layer by its own presence [81]. In other words, the enhancement of the catalytic effects achieved by catalysts according to the proton transfer reaction mechanism should not undermine the capability of generating a high electric field at the bipolar membrane interface, which is approximated by [96]

$$E = \left| \frac{\varphi_D + U_{bm}}{2\lambda} \right|$$

where $E$ is the electric field strength; $2\lambda$ is the bipolar junction (transition) thickness; $\varphi_D$ is the Donnan potential across the transition region; and $U_{bm}$ is the externally applied voltage.

As mentioned before, the enhanced water dissociation at the interface of bipolar membranes can be explained by the increase in the degree of dissociation of weak electrolytes, like water, by high electric field strengths, which is referred to as the second Wien effect [69]. According to Onsager’s treatment of the second Wien effect, the in-
crease in dissociation rate constant at high electric field (>10⁹ V/m), can be approximated by [68], [69]

\[
\frac{K_d(E)}{K_d} = \sqrt{\frac{2}{\pi}} \cdot (8b)^{-\frac{3}{4}} \cdot e^{\sqrt{8b}}
\] (4.8)

For a monovalent electrolyte, \(b\) is given by

\[
b = 0.096 \frac{E}{\varepsilon_r T^2}
\] (4.9)

Where \(K_d(E)\) and \(K_d\) are the water dissociation constants with and without the electric field effects, respectively; \(E\) is the electric field strength (V/m); \(\varepsilon_r\) is the relative permittivity of the medium; and \(T\) is the absolute temperature. In the above description, it is assumed that the recombination rate constant of \(H^+\) and \(OH^-\) ions is unaffected by the electric field, and lies approximately in the range of 10⁹ mol⁻¹s⁻¹.

Applying the Maxwell–Boltzmann and the Poisson equations to ion exchange membranes, by drawing an analogy to the p–n semiconductor junctions, the bipolar junction thickness can be approximated by the equation below. It is assumed here that the entire voltage drop across a bipolar membrane falls across the junction [97].

\[
2\lambda = 2 \sqrt{\frac{(2|\varphi_{Dom}^{tr}| + U_{bm})\varepsilon_o \varepsilon_r}{XF}}
\] (4.10)

where \(2\lambda\) is the bipolar junction (transition) thickness; \(\varphi_{Dom}^{tr}\) is the Donnan potential across the transition region; \(U_{bm}\) is the externally applied voltage; \(\varepsilon_o\) is the permittivity of free space; \(\varepsilon_r\) is the relative permittivity; \(X\) is the fixed charge density of the ion exchange layers; and \(F\) is the Faraday constant.

The bipolar junction thickness thus depends on the applied reverse-bias external voltage. Applying higher voltage would increase the bipolar junction thickness.

Apart from the simpler form of the above equation for junction thickness, the experimental data in Figure 4.9(a) were fitted according to a complete water dissociation model which incorporates the second Wien effect and the proton transfer reaction mechanisms [96]. The apparent bipolar junction thickness was computed according to the given experimental data by keeping all other factors constant and varying the junction thickness to fit the experimental voltage drop, at a constant current density of 100 mA/cm². Accordingly, based on estimations of the model, the apparent bipolar junction thickness may have increased from 16.3 to 23 nm to 42.5 nm by depositing two, four,
and six bilayers of PEDOT:PSS/PEI, respectively, for a current density of 100 mA/cm$^2$ (Table 4.3). It is likely that the presence of the LbL interface layers has increased the bipolar junction thickness by the estimated magnitude, thus acting as constant thickness spacers. For more detailed information about the water dissociation model, the reader is referred to the paper of Strathmann et al. [96] The used model parameters and initial conditions are listed in Table A4.1 in the Appendix.

Table 4.3: Model estimation of the bipolar junction thickness without taking into account $A_{el}$ increase by the catalyst groups

<table>
<thead>
<tr>
<th></th>
<th>Two bilayers</th>
<th>Four bilayers</th>
<th>Six bilayers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computed apparent bipolar junction thickness (nm)</td>
<td>16.3</td>
<td>23</td>
<td>42.5</td>
</tr>
</tbody>
</table>

To sum up, the quantity of catalyst should be finely optimized to maximize water-splitting properties of a bipolar membrane. Catalysts may reduce the polarization effect between the sulfonic acid and quaternary ammonium groups (typical functional groups of ion exchange membranes) if present in too high concentrations [25]. In this regard, LbL assembly comes into play as an attractive tool to immobilize catalysts in bipolar membranes, whereby layer properties can be finely tuned by modifying various deposition parameters.

A further remarkable effect observed with an increase in the number of layers is the permselectivity of the bipolar membranes. It was theoretically, as well as experimentally, shown in the paper of Balster et al. [86] that the first limiting current density ($i_{lim1}$) directly correlates with the co-ion leakage through the membranes. Furthermore, from the ion transport model, the $i_{lim1}$ and the salt transport across a bipolar membrane are directly dependent on the square of the solution concentration, the diffusion coefficients in the membrane layers, the fixed charge density, and the thickness of the ion exchange layers of the bipolar membrane.

In addition to the factors mentioned above, we have clearly observed an effect of the bipolar membrane interface layer on the $i_{lim1}$. In Figure 4.9(b), $i-V$ curves of the tailor-made bipolar membranes are depicted in the lower current density region. The results clearly illustrate that the $i_{lim1}$ increased with the number of layers, which directly translates to an increase of the co-ion leakage through the membranes. The $i_{lim1}$ read from the $i-V$ curves are tabulated in Table 4.4. Therefore, both in terms of electrical re-
istance and permselectivity, the membrane with the two bilayers of LbL interface was the optimal one.

Table 4.4: Variation of the first limiting current density with the number of interface layers

<table>
<thead>
<tr>
<th>Number of Interface Layers</th>
<th>$i_{\text{lim1}}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two bilayers</td>
<td>~2.5</td>
</tr>
<tr>
<td>Four bilayers</td>
<td>~3.5</td>
</tr>
<tr>
<td>Six bilayers</td>
<td>~8</td>
</tr>
</tbody>
</table>

*Approximate values given here obtained from the $i$–$V$ curves in Figure 4.9.

4.4.7 Effect of the Ionic Strength of the PEI Depositing Solution

To analyze the steric effect of the junction thickness enlargement, two bipolar membranes were prepared with four polymer layers (as shown in Figure 4.2(a)), whereby the LbL interface was prepared from two bilayers of (PEDOT:PSS/PEI); in one the PEI was in aqueous solution, while in the other the PEI was prepared in 0.5 M NaCl solution. Figure 4.10(a) shows a comparison of the $i$–$V$ curves of three bipolar membranes: the above-mentioned four-layered membranes and the commercial membrane FBM (FuMA-Tech, Germany).

It is well known that in salt solutions with increasing ionic strength, polyelectrolyte chains go from a stretched to a coiled conformation and, if deposited as such, give rise to thicker layers than those obtained from polyelectrolytes in aqueous solutions [98]. Nevertheless, the bipolar membrane obtained with PEI in 0.5 M NaCl solution showed an improved performance somehow, having electrical resistance comparable to the commercially available bipolar membrane FBM as shown in Figure 4.10(a).

Such an improved performance could be due to an increase in the accessibility of the ion exchange sites of the catalytic amine groups of PEI [99]. The presence of salt results in the screening of the charges along the backbone of the polyelectrolyte causing the PEI chains to adopt a coiled conformation, which implies an enlarged bipolar junction thickness. However, with only four layers of polyelectrolytes, we are in a regime where the entire film is swollen and full of voids [100], which provides higher accessibility to the catalytic sites. It was demonstrated in the work of Wakamatsu et al. [26] that the effective contact area of the intermediate layers of a bipolar membrane does play a crucial role. This effect was investigated by preparing intermediate layers from highly porous fabrics, of different specific surface areas by electrospray deposition.
To validate this finding, the water-splitting capacity of this membrane was compared to that of the commercial bipolar membrane FBM at a constant current density of 100 mA/cm$^2$, over a period of 2.5 h (Figure 4.10(b)). It was found that our bipolar membrane has an appreciable water splitting capacity close to 90% of the commercial membrane (average values of $\sim 8.33$ mmol/(m$^2$ s) vs $\sim 9.43$ mmol/(m$^2$ s) of the commercial membrane FBM).

To check reproducibility, we prepared another membrane with the above recipe and found very similar results. We carried out experiments with these membranes for longer periods, with no stability problems. In general, the membranes prepared by casting were mechanically stable.

![Graph](image1)

![Graph](image2)

**Figure 4.10:** (a) Effect of the ionic strength of PEI on the electrical resistance of tailor-made bipolar membrane, characterized in 2 M NaCl solution. (b) Water splitting flux of the tailor-made membrane, in comparison to a commercial FBM, characterized in 2 M NaCl solution at constant current density of 100 mA/cm$^2$.

### 4.5 Conclusions

In conclusion, LbL assembly of polyelectrolyte multilayers was successfully implemented to tailor the interface of bipolar membranes. Bipolar membranes were fabricated in a first step by lamination of two commercial monopolar membranes, which were coated with various polyelectrolyte combinations, to quickly screen the best polyelectrolyte architecture. The outcomes of the lamination experiments demonstrated that coating the anion exchange membrane yields better performance as compared to coating the cation exchange membranes, confirming that water splitting occurs near the anion ex-
change layer. Moreover, it was shown that polyelectrolyte pairs of higher charge density should be selected.

For the membranes prepared by casting, in addition to the effect of the polyelectrolyte catalytic layers, an additional highly charged thin intermediate layer helps enhance water splitting.

Several parameters of the LbL interface deposition were varied: the molecular weight, the concentration, and the ionic strength of the polycation as well as the number of polyelectrolyte layers. Out of the investigated LbL-assembly parameters, ionic strength and number of layers have shown the largest influence. In terms of the interface layer, the bipolar membrane consisting of the anion exchange layer modified with two bilayers of PEDOT:PSS and PEI, wherein the PEI was dissolved in 0.5 M NaCl, gave rise to the best performance. Such a bipolar membrane has a water-splitting capacity close to 90% of the commercial membrane FBM (FuMA-Tech, Germany).

Furthermore, it was observed that not only the ion exchange layers (as investigated in previous studies) but also the interface layers of a bipolar membrane play a major role in its permselectivity. Increasing the number of interface layers increased the co-ion leakage through the tailor-made membranes, characterized at the same concentration.
4.6 Appendix for Chapter 4

4.6.1 Effect of MW and Concentration of PEI

- Effect of MW and concentration of PEI on the electrical resistance of the bipolar membranes

![Graph showing the effect of MW and concentration of PEI on electrical resistance.]

**Figure A4.1:** Electrical resistance of tailor-made bipolar membranes with added LbL interface layers, characterized in 2 M NaCl solution. The LbL interface layers were made up of 2 bilayers of PEDOT:PSS/PEI. (a) Effect of MW of PEI (b) Effect of concentration of PEI.

4.6.2 Model Parameters and Initial Conditions

- Parameters and initial conditions of the applied model of water dissociation in bipolar membranes

In Table A4.1 parameters and initial conditions of the water dissociation model used in Section 4.4.6 are listed. The complete water dissociation model based on the paper of Strathmann et al. [96] was used to estimate the thickness of the interface layers of the prepared membranes. The model was implemented in gPROMS (version 3.3.1).
Table A4.1: Parameters and initial conditions of the applied model for water dissociation in bipolar membranes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{H_2O}^b$</td>
<td>6000 mol/m$^3$</td>
<td>Water in the bulk phase</td>
</tr>
<tr>
<td>$C_i^b$</td>
<td>2000 mol/m$^3$</td>
<td>Concentration of salt in the bulk phase$^{*1}$</td>
</tr>
<tr>
<td>$C_{H_2O}^{tr,0}$</td>
<td>6000 mol/m$^3$</td>
<td>Water in the transition region at $t = 0$</td>
</tr>
<tr>
<td>$C_{H_3O^+}^{tr,0}$</td>
<td>$10^{-4}$ mol/m$^3$</td>
<td>$H_3O^+$ in the transition region at $t = 0$</td>
</tr>
<tr>
<td>$C_{OH^-}^{tr,0}$</td>
<td>$10^{-4}$ mol/m$^3$</td>
<td>OH$^-$ in the transition region at $t = 0$</td>
</tr>
<tr>
<td>$C_B^{tr,0}$</td>
<td>1500 mol/m$^3$</td>
<td>Unprotonated fixed charge in the transition region</td>
</tr>
<tr>
<td>$C_{BH^+}^{tr,0}$</td>
<td>$10^{-10}$ mol/m$^3$</td>
<td>Protonated fixed charge in the transition region</td>
</tr>
<tr>
<td>$u_{H_3O^+}$</td>
<td>$3x10^{-7}$ m$^2$/(V s)</td>
<td>Mobility of $H_3O^+$</td>
</tr>
<tr>
<td>$u_{OH^-}$</td>
<td>$3x10^{-7}$ m$^2$/(V s)</td>
<td>Mobility of OH$^-$</td>
</tr>
<tr>
<td>$D_{H_2O}$</td>
<td>$10^{-9}$ m$^2$/s</td>
<td>Diffusion coefficient of water</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>78.58</td>
<td>Relative permittivity of water</td>
</tr>
<tr>
<td>$k_1$</td>
<td>$3.36x10^{-10}$ m$^3$/(mol s)</td>
<td>Rate constant, water splitting forward reaction</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$10^{8}$ m$^3$/(mol s)</td>
<td>Rate constant, protonation backward reaction</td>
</tr>
<tr>
<td>$k_3$</td>
<td>$10^{8}$ m$^3$/(mol s)</td>
<td>Rate constant, deprotonation backward reaction</td>
</tr>
<tr>
<td>$K_b$</td>
<td>$1.58x10^{-5}$ mol/m$^3$</td>
<td>Base constant, corresponds to $pK_b = 4.8$</td>
</tr>
<tr>
<td>$K_w$</td>
<td>$10^{-8}$ molF/m$^6$</td>
<td>Dissociation constant of water; corresponds to $pK_w = 14$</td>
</tr>
<tr>
<td>$\delta_{cem}$</td>
<td>$1x10^{-4}$ m</td>
<td>Thickness of the cation exchange layer</td>
</tr>
<tr>
<td>$\delta_{aem}$</td>
<td>$1x10^{-4}$ m</td>
<td>Thickness of the anion exchange layer</td>
</tr>
<tr>
<td>$\Delta \varphi^{tr}$</td>
<td>From measurement</td>
<td>Potential drop across the transition layer</td>
</tr>
<tr>
<td>$2\lambda$</td>
<td>Fitted</td>
<td>Thickness of the transition layer (interface layers)</td>
</tr>
</tbody>
</table>

$^{*1}$Concentration of salt solutions in which the membranes were characterized
Chapter 5

Layer-by-Layer Modification of Cation Exchange Membranes Controls Ion Selectivity and Water Splitting

5.1 Introduction

Electrodialysis is an electrochemical separation technology used to separate inorganic salts from aqueous environments to desalinate water and treat wastewater [2]. It is also applied to separate solutions containing organic ionic species [101]. The heart of electrodialysis processes is ion exchange membranes which selectively pass ions of opposite charge under the application of an electric field. These membranes consist of polymeric films bearing covalently bound ionic fixed charges which enable the transport of the electrolyte ions with opposite charge sign (counterions) through the membrane structure. Ions with the same charge sign (co-ions) are electrostatically repelled and retained in the feed compartment. This technology can be integrated into industrial processes in which the separation of ions to recover valuable products is desired. Furthermore, the development of ion exchange membranes with increased permselectivity for specific ions may extend the applicability of electrodialysis to more demanding operations. In this regard, an important progress in the field of membrane technology is the development of membranes selective to monovalent ions, i.e., membranes capable of separating ions with the same charge sign but different valence.

This chapter has been published as:

Monovalent-ion-permselective membranes are of special utility for those applications in which monovalent cations are the product of interest to be separated from mixtures with multivalent ions. A large-scale application of this type of membranes has already been realized for the purpose of edible salt production from seawater, where multivalent ions are undesired in the product and scale formation on the membranes is prevented by rejecting the multivalent ions [102]. Other emerging applications include the recovery of spent acids generated in metal finishing industries [103], hardness removal to produce drinking water, [104] and electrochemical acidification of milk [78], [105].

Several aspects determine the permselectivity of ion-conducting membranes for cations of different valence. First, the affinity under equilibrium conditions between the fixed charges of the membranes and the solution counterions is strongly affected by electrostatic forces, so that the fixed ion exchange sites have usually larger attraction toward multivalent cations [106]. Another important factor is the size and mobility of ions under the application of current since the membrane structure could retard the transport of cations of larger size. In addition, depending on the applied current density and the hydrodynamic conditions the properties of the diffusion boundary layer developed near the membrane surface can favor the supply of specific cations from the bulk solution to the membrane surface [106]–[108].

Therefore, taking into account the above factors, different approaches can be considered to increase the membrane permselectivity for monovalent cations. An increased monovalent permselectivity can be induced by increasing the membrane’s cross-linking density and making the membrane matrix denser, which hinders the diffusion of large ions through the membrane structure [21], [109]. Alternatively, the deposition of a thin positively charged layer on the surface of cationic membranes has been applied to increase the repulsion toward multivalent species. The latter methodology entails an additional advantage since the electrostatic repulsion of multivalent ions would also prevent the formation of precipitates of multivalent metal species on the membrane surface, thus acting as an antifouling mechanism [110], [111].

The deposition of a thin layer of cationic polyelectrolytes on the surface of membranes has been previously accomplished in different studies [103], [112], [113]. However, new approaches are needed to further increase the membrane permselectivity and avoid problems related to the deterioration of the adsorbed films [112], [114], [115]. To this end, utilization of the layer-by-layer (LbL) assembly of polyelectrolyte multilayers, as a facile and precise method to tailor and control the electrostatic properties of the mem-
brane surface, arises as a viable and promising alternative to obtaining highly monovalent-ion-permselective membranes [116]. An increase in the proportion of positively charged groups on the membrane active layer can be obtained by using such a procedure, which is based on the alternate dipping of the cation exchange membrane in polycations and polyanions. With the first deposition step, electrostatic attractions anchor the first polyelectrolyte layer on the oppositely charged membrane surface. Simultaneously, a charge reversal of the membrane surface occurs, thus leaving the surface prepared for the next adsorption step [5]. The adhesion of the subsequent polyelectrolyte layer is ensured through a high number of electrostatic bonds created with the opposite charges of the previously deposited polyelectrolyte. In this manner, the thickness and functional properties of the membrane coating can be finely tuned by adjusting the adsorption parameters and the number of deposited bilayers.

In the field of membrane technology, this methodology has been recently applied to increase the solvent stability of nanofiltration membranes while maintaining good retention and permeability [117]. Previously we modified ultrafiltration membranes by LbL assembly without any prior treatment of their surface [118], and more recently we reported on the successful catalysis of water splitting in bipolar membranes via polyelectrolyte multilayers [119]. The performance of ion exchange membranes used in direct methanol fuel cells has also been improved, by reducing the methanol crossover with LbL polyelectrolyte assemblies [120]. Other studies report the increase of the multivalent ion rejection of pressure-driven as well as anion exchange membranes after being modified with polyelectrolyte coatings [110], [121].

In the present study, the LbL procedure was aimed to increase the monovalent permselectivity of cation exchange membranes. The modified membranes were characterized by several surface analytical methods, and their surface characteristics were correlated with their electrochemical transport behavior. Their performance was investigated and compared with that of other commercial membranes by galvanostatic permselectivity experiments, current-voltage curves, and electrochemical impedance spectroscopy (EIS) measurements.

**5.2 Experimental**

**5.2.1 Membranes, Materials, and Reagents**

The membranes used in the experiments were the commercial cation exchange membranes CMX (Astom, Japan), CMS (Astom, Japan) and CSO (Asahi Glass, Japan),
whose properties are given in Table 3.1. CMX is a standard cation exchange membrane used for electrodialysis, while CMS and CSO are monovalent-ion-permselective cation exchange membranes. CMS features monovalent ion permselectivity on both of its sides, whereas CSO is designated with an active side.

The LbL multilayers were formed from the following polyelectrolytes: poly(ethyleneimine) (PEI), molecular weight (MW) = 750 000 g/mol, and poly(4-styrenesulfonate) (PSS), MW = 70 000 g/mol. They were both obtained from Sigma-Aldrich and were dissolved in ultrapure water.

Synthetic solutions mixing 0.05 M NaCl and 0.05 M CaCl₂ (reagent grade dissolved in DI water) were used for electrochemical characterization of the membranes.

**5.2.2 Membrane Modification**

PEI and PSS were selected to form the polyelectrolyte multilayers on the surface of the membranes. PSS was selected as the polyanion because it is a strong polyelectrolyte, and PEI as the polycation due to its hyperbranched structure and the high density of its positively charged amine groups. Their chemical structures are shown in Figure 3.1.

To introduce the polyelectrolyte multilayers, the CMX membrane was first rinsed with ultrapure water and coated on one side with the desired polyelectrolyte multilayers. The membrane was prior to that stored in 0.5 M NaCl solution. The coating was carried out in an in-house-built coating cell by the LbL assembly method. First, the CMX was exposed to a 1 g/L solution of PEI for 1 h, followed by 1 g/L PSS solution for 30 min. Except for the first layer, where the membrane was brought into contact with PEI for 1 h, the rest of the layers were formed each for 30 min, PEI as well as PSS. In between the coating steps, the membranes were thoroughly rinsed with ultrapure water. The polyelectrolytes formed the active side on the CMX membrane – the side that faces the anode in subsequent experiments.

The nomenclature employed to designate the modified membranes is the following: (CMX)/(PEI/PSS)_N. The term CMX indicates the substrate membrane, PEI and PSS the polycation and the polyanion, respectively, and the subscript N the number of bilayers. Unless mentioned otherwise, both the PEI and PSS were prepared in ultrapure water.
5.2.3 Surface Characterization of the Membranes

The deposition of the polyelectrolyte layers was monitored by contact angle, XPS and FE-SEM measurements (cf. Section 3.3).

The contact angle measurements were performed immediately after modification. The images for analysis of the contact angles were taken 1 min after the water droplet had settled on the membrane surface. For each membrane, an average of at least five measurements of the contact angle was taken, measured at different locations of the samples. The contact angle was evaluated by the sessile drop method.

5.2.4 Electrochemical Characterization of the Membranes

Polarization current–voltage ($i$–$V$), electrochemical impedance spectroscopy (EIS) and galvanostatic permselectivity measurements were performed in order to characterize the electrochemical behavior of the modified membranes. The measurements were carried out in a six-compartment electrodialytic cell shown schematically in Figure 5.1. The membranes were characterized in 0.05 M equimolar mixtures of chloride salts of monovalent and divalent cations ($\text{Na}^+$ and $\text{Ca}^{2+}$ ions). Prior to that, the membranes were conditioned in the salt solution (0.05 M $\text{NaCl}$ and 0.05 M $\text{CaCl}_2$) for about 24 h outside the membrane module.

The $i$–$V$ and EIS measurements were performed using the four-point method (cf. Sections 3.4.2 and 3.4.4 for the details). Details of the permselectivity measurements are also mentioned in Section 3.4.5.

EIS measurements were carried out to get further insight about the influence of the interface layers of the membranes. EIS results are generally represented by plotting the imaginary part of the impedance against its real part, which is known as the Nyquist plot. Then, to understand impedance spectra, the experimental results obtained with an electrochemical cell can be fitted to an equivalent electrical circuit (EEC). EECs are the result of the combination of different electrical elements (resistance, capacitors, etc.) connected in a logical order to allow a coherent interpretation of the mass transfer processes occurring in the system. Consequently, the contribution of each mass transfer process to the behavior of the membranes, which are simultaneous in time but predominate at different frequency ranges, can be elucidated from the parameters associated with their analogous electric elements in the EEC.
Figure 5.1: Schematic drawing of a six-compartment measurement module for polarization curves, permselectivity, and impedance measurements.

5.3 Results and Discussion

5.3.1 Surface Characterization of the Modified Membranes

The effect of the deposition of LbL assemblies on the surface properties of the modified membranes was assessed by means of various techniques. For a high number of deposited layers, FE-SEM allows the identification of the LbL films coated on top of the membranes. Figure 5.2 shows the cross-sectional images of an unmodified and a modified CMX membrane, respectively. In both micrographs, the structure of the CMX membrane composed of the membrane matrix and the reinforcing fibers can be seen. In the case of the modified membrane, the deposited LbL film (10.5 bilayers) can be clearly distinguished from the membrane substrate. Normally, for membrane samples that are coated with few polyelectrolyte layers, the LbL film is very thin and cannot be clearly detected in the FE-SEM images.

In the case of a low number of deposited layers, XPS is a useful tool to monitor the deposition of the LbL films on top of the substrate membrane since the functional groups of PEI and PSS are composed of different elements. Figure 5.3(a) shows the evolution of the ratio of nitrogen to sulfur (N/S) atomic concentration for the first two bilayers. The alternating trend of the N/S ratio with the number of deposited bilayers reveals an increase in the presence of nitrogen when PEI is the last layer adsorbed and an increase in the concentration of sulfur when the last adsorption step is conducted with PSS. The increase in the atomic concentration of nitrogen is associated with the
amine groups present in the PEI top layer, whereas the sulfonic groups of PSS are responsible for the increase in the sulfur content.

**Figure 5.2:** Cross-sectional FE-SEM micrographs obtained for (a) an unmodified CMX membrane and (b) a CMX membrane modified with 10.5 bilayers of PEI/PSS (both polyelectrolytes prepared in 0.5 M NaCl solution).

![Cross-sectional FE-SEM micrographs](image)

**Figure 5.3:** Surface characterization of the modified membranes: (a) N/S ratio and (b) water contact angle values as a function of the number of bilayers.

![Surface characterization graphs](image)

In addition to the FE-SEM images and the XPS analysis, measurement of the contact angle provides an additional indication of the changes brought about on the membrane surface as a consequence of the polyelectrolyte deposition. The contact angle measurements as a function of the number of bilayers deposited are shown in Figure 5.3(b). In general, when the top layer is PEI the membrane hydrophobicity increases and when it is of PSS the membrane surface becomes more hydrophilic. This alternating trend confirms, as observed in the XPS analysis, the effective sequential deposition of both polyelectrolytes. It has to also be noted, that contact angle values increase somewhat for the samples modified with more than five bilayers. This behavior could be due to the increase in the thickness of the LbL assembly with increasing number of adsorption
steps. For the first adsorption steps, there may exist some coating defects with areas where the membrane substrate is not covered by the polyelectrolyte chains. Hence during the contact angle measurement of these membranes, part of the water droplets may reach the base membrane, thus resulting in contact angles closer to that of the unmodified membrane (45.4°). However, as the number of bilayers increases and the membrane surface gets completely covered, the contact angle is mostly dependent on the properties of the LbL coating. In the results obtained by other authors, a change in the trend of the contact angle measurements from approximately more than five bilayers was also reported [110], [121].

5.3.2 Electrochemical Characterization of the Modified Membranes

**Current–Voltage (i–V) Curves.** Polarization i–V curves are a necessary tool to characterize the behavior of ion exchange membranes over a wide range of currents. Typical i–V curves obtained for monopolar ion exchange membranes display three different membrane behaviors depending on the applied current. At low current densities, the current is directly proportional to the membrane voltage drop, and therefore, the transport through the membrane can be described by a quasi-ohmic behavior. As the current is further increased and the limiting current density ($i_{\text{lim}}$) for the membrane/electrolyte system is reached, the concentration of counterions in the diluate side of the ion exchange membrane strongly diminishes due to the more rapid transport through the membrane as compared to the diffusive supply out of the bulk liquid through the diffusion boundary layer. As a consequence, the resistance of the membrane system increases, and a plateau is formed in the curve. The increase in resistance stems from the continuous ion depletion of the diffusion boundary layer. The third part of the curves, known as the overlimiting region, appears at an advanced stage of concentration polarization. The membrane voltage drop reaches a certain threshold at which multiple phenomena occur that can destabilize the boundary layer [122]–[124]: supply of counterions to the membrane surface is enhanced and current density values increase again with the membrane voltage drop. The plateau length and the onset of the overlimiting current are not well understood yet but are not object of the current study. The reader is referred to Chapter 6 for a separate study on this topic.

Figure 5.4(a) and (b) show some of the curves obtained for the modified and unmodified commercial membranes. The curves exhibit the three characteristic regions described above, which are indicated for the CMS membrane in Figure 5.4(a). Different aspects of the ionic transport through ion-conducting membranes can be evaluated
from the curves. The ohmic resistance ($R_\Omega$) can be obtained from the inverse of the slope of the first ohmic part of the curves. An increase in the ohmic resistance of the modified membranes would be expected as the thickness of the LbL film increases with the number of deposited bilayers.

**Figure 5.4:** Current–voltage ($i$–$V$) curves obtained with mixtures of 0.05 M NaCl and 0.05 M CaCl$_2$ for (a) the two monovalent-ion-permselective membranes CMS and CSO and (b) unmodified CMX membrane and one modified with 11 bilayers of PEI/PSS, with the scatter of the overlimiting region of the graphs smoothed. (c) Dependence of the $R_\Omega$ values of the membrane/electrolyte system as a function of the number of bilayers.

The values of $R_\Omega$ are presented in Figure 5.4(c) for the commercial (CMX, CMS, and CSO) and various modified membranes ((CMX)/(PEI/PSS)$_N$). Among the commercial membranes, the lowest $R_\Omega$ value was calculated for the unmodified CMX membrane.
The resistance of the monovalent-ion-permselective CSO membrane is similar to that of CMX, whereas the highest resistance is that of the monovalent-ion-permselective CMS membrane. The increased $R_\Omega$ value obtained for CMS could not only be ascribed to the thin cationic layer deposited on its surface. Tuan et al. reported that the CMS membrane is characterized by having a higher degree of cross-linking in addition to the thin cationic layer deposited on its surface [125]. The enhanced cross-linking is another factor imparting monovalent ion permselectivity properties to this membrane. Therefore, the mobility of larger cations through its structure may be diminished due to ion-size impediments, which are also responsible for the high electrical resistance observed for this membrane.

In the case of the modified membranes, $R_\Omega$ values show a very slight increase with the number of adsorbed bilayers. As expected, among the modified membranes, those with the highest number of bilayers (10.5 and 11 bilayers) present the largest $R_\Omega$ values. Such an increase with respect to the unmodified CMX membranes starts to be noticeable for a number of bilayers higher than 6. These results could be related to the total coverage of the substrate membrane achieved from a certain number of bilayers in the LbL film. Moreover, it has to be noted that the highest $R_\Omega$ value calculated for the modified membranes ($60.06 \, \Omega \cdot \text{cm}^2$ for ((CMX)/(PEI/PSS)$_{11}$) is even lower than that of the monovalent-ion-permselective CMS membrane. As stated previously, the slight increase in the membrane resistance with the number of polyelectrolyte layers can be considered as an additional proof of the successful deposition of LbL assemblies on the cation exchange membranes.

With regard to the limiting current density, as can be seen from Figure 5.4 the $i_{\text{lim}}$ values lie approximately around 20 mA/cm$^2$ for all the investigated membranes. The slight variation in the $i_{\text{lim}}$ values and the less well-defined transition region could be explained as a consequence of the compensation between the effects of the increased hydrophobicity and the conducting heterogeneity of the LbL assemblies [126], [127].

**Impedance Measurements.** In addition to the changes promoted by the LbL modification of the membranes on the $i$–$V$ characteristics, the main contribution of the LbL films to the membrane permselectivity may be caused by the change in the attractive/repulsive forces existing between the surface of the modified membranes and the electrolyte counterions. In this context, EIS is an electrochemical technique that potentially provides information about the charging properties of interfaces. Particularly, a recent work shows that EIS can distinguish among the diffusion boundary layer re-
istance, the double-layer resistance, and the transfer resistance from the liquid into and through the membrane phase [128].

The EEC used to fit the EIS of the different membranes thus considers the combination in series of the contributions of the three different layers to the mass transfer resistance: the combined ohmic resistance of membrane and solution, the double layer formed at the membrane/solution interface, and the diffusion boundary layers [128]–[131]. The EEC and the schematic representation of the three transport layers considered are shown in Figure 5.5(a). This circuit has already been used in previous studies to investigate the behavior of ion exchange membranes [128], [130], [132].

![Figure 5.5](image.png)

**Figure 5.5:** (a) EEC for the cation exchange membrane with the solution used in this study and schematic diagram of the phenomena associated with each component of the circuit. At very high frequencies the impedance shows only the ohmic resistance due to the membrane and the solution; at medium frequencies, the heterogeneous transport layer originates the capacitive behavior; and at low frequencies, the transport of electroactive species through the solution layers is modeled with a constant phase element. (b) Nyquist plot representation of the impedance responses obtained for the unmodified CMX membrane and other modified membranes.

At the high-frequency range, the system behavior is purely resistive, which is defined by the combined ohmic resistance of the solution and the membrane ($R_1$).

As the frequency decreases, a phase shift between the voltage and current signals is usually observed. This response corresponds to a capacitive behavior modeled in the EEC with a resistor ($R_2$) and a capacitor ($C_2$) connected in parallel. The $R_2$–$C_2$ combination represents the mass transfer occurring at the electrical double layer formed at
the membrane/electrolyte interface, where the current is divided into its faradaic com-
ponent and another part used to charge the double layer. Finally, when the range of
low frequencies is reached, the transport in the solution layers becomes predominant in
the EIS response. This behavior can be adjusted to the parallel combination of a re-
sistance ($R_1$) and a constant phase element (CPE$_3$). The constant phase element is a
non-intuitive element, which can represent all types of impedance behavior and takes
into account nonhomogeneities in the material or nonideal behaviors [133].

An example of the Nyquist plots obtained with the unmodified CMX and some modi-
fied CMX membranes is presented in Figure 5.5(b). The resistance $R_1$ is calculated
from the intercept at high frequencies with the x-axis (no imaginary part). At decreas-
ing frequencies two overlapped semicircles corresponding to the $R_2$–C$_2$ and $R_3$–CPE$_3$
elements appear in the diagram. The fittings are represented in solid lines in Figure
5.5(b), and the best-fit estimates of the EEC parameters are tabulated with the chi-
square ($\chi^2$) values of the model fitting in Table 5.1. Since the operating conditions dur-
ing the experiments were the same (such as the volume flow rate or the 0 DC current),
we assume the properties of the solution layers to be approximately constant for all the
membranes. Accordingly, the values of the constant phase element ($CPE$–$Q_3$) were
fixed to the value obtained with the unmodified CMX membrane to get better estima-
tions for the rest of the parameters of the modified membranes.

From the fitting results, the parameter which is most influenced by the LbL coatings is
the capacitance of the double layer ($C_2$). $C_2$ values exhibit an abrupt decrease for the
first adsorbed layer of PEI, which may be associated with a charge reversal of the
membrane surface. Then, an alternating trend is observed for the first polyelectrolyte
bilayers, where the values of $C_2$ increase when the last adsorbed polyelectrolyte is PSS
and decrease when the last adsorbed polyelectrolyte is PEI. As an analogy, Sow et al.
reported a decreasing trend in the capacitance of the double layer of ion exchange
membrane systems with increasing temperature, which was attributed to a decrease in
the Donnan potential [133]. In the present case, the decreasing $C_2$ values could stem
from the decrease in the proportion of negative fixed charges on the membrane surface
as the number of bilayers is increased and the positively charged layers of the hyper-
branched PEI overlap. As the number of polyelectrolyte multilayers increases, the in-
crease in the proportion of positive charges at the surface of the membrane would re-
duce the Donnan potential, which is regarded in the literature as indicative for the re-
duction in the membrane permselectivity for counterions. However, in the present case,
the decrease in the Donnan potential may be interpreted as a consequence of the en-
hanced repulsive forces in the LbL film toward multicharged counterions, thus resulting in a decrease of the charging properties of the membrane/solution interface. In addition, the decrease of capacitance has also been attributed to the thickening of layers deposited on the surface of ion exchange membranes [134].

With regard to the other parameters, only slight changes can be observed. Minor variations in the values of \( R_1 \) are observed with the increase of the number of bilayers, thus confirming the moderate influence of the LbL films on the electrical resistance observed from the \( i-V \) curves. However, it is important to note that these slight variations observed in the \( R_1, R_2, \) and \( R_3 \) values for the different membranes may also be influenced by measurement inaccuracies, as it is usually reported for the through-plane measured impedance of ion exchange membranes [135].

Finally, it should be noted that the parameter \( \text{CPE}_{3-n} \) takes values close to 0.8. Park et al. reported values of the \( \text{CPE}_{3-n} \) between 0.7 and 0.8, which were attributed in that case to an insignificant development of diffusion boundary layers (typically associated with \( n \) values of 0.5) and the predominant role of convective transport [130].

### 5.3.3 Evaluation of Monovalent Ion Permselectivity

The monovalent ion permselectivity of the modified membranes was evaluated by measuring the evolution of \( \text{Ca}^{2+} \) relative to \( \text{Na}^+ \) ion concentrations in the diluate compartment. Typical concentration profiles for the unmodified CMX membrane and one modified membrane (with 11 bilayers of PEI/PSS) are shown in Figure 5.6. The performance of the modified membranes was compared against commercial benchmarks, i.e., the commercially available monovalent-ion-permselective membranes: Neosepta CMS (Astom, Japan) and Selemion CSO (AGC, Japan). The complete results of \( \text{Ca}^{2+}/\text{Na}^+ \) flux, monovalent ion permselectivity, and specific energy consumption of all the studied membranes are presented in Table 5.2 and Table 5.3.
Table 5.1: Best-fit estimates of the EEC parameters obtained from the impedance measurements for the unmodified and modified CMX membranes

<table>
<thead>
<tr>
<th>Number of (PEI/PSS) bilayers</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>1.5</th>
<th>6.5</th>
<th>7</th>
<th>10.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$ (Ω)</td>
<td>3.17 ± 0.00</td>
<td>3.23 ± 0.00</td>
<td>3.20 ± 0.00</td>
<td>3.41 ± 0.00</td>
<td>3.50 ± 0.00</td>
<td>3.37 ± 0.00</td>
<td>3.27 ± 0.00</td>
</tr>
<tr>
<td>$R_2$ (Ω)</td>
<td>0.018 ± 0.001</td>
<td>0.021 ± 0.000</td>
<td>0.031 ± 0.002</td>
<td>0.020 ± 0.000</td>
<td>0.049 ± 0.002</td>
<td>0.113 ± 0.003</td>
<td>0.111 ± 0.002</td>
</tr>
<tr>
<td>$R_3$ (Ω)</td>
<td>0.273 ± 0.003</td>
<td>0.298 ± 0.002</td>
<td>0.221 ± 0.003</td>
<td>0.256 ± 0.001</td>
<td>0.310 ± 0.004</td>
<td>0.345 ± 0.004</td>
<td>0.370 ± 0.005</td>
</tr>
<tr>
<td>$C_2$ (F)</td>
<td>14.14 ± 0.91</td>
<td>8.22 ± 0.59</td>
<td>10.19 ± 1.50</td>
<td>9.73 ± 0.59</td>
<td>6.34 ± 0.71</td>
<td>5.35 ± 0.29</td>
<td>4.89 ± 0.22</td>
</tr>
<tr>
<td>CPE$_3$-Q ($S \cdot s^n$)</td>
<td>22.74 ± 0.55</td>
<td>22.74</td>
<td>22.74</td>
<td>22.74</td>
<td>22.74</td>
<td>22.74</td>
<td>22.74</td>
</tr>
<tr>
<td>CPE$_3$-n (-)</td>
<td>0.77 ± 0.01</td>
<td>0.77 ± 0.00</td>
<td>0.80 ± 0.01</td>
<td>0.79 ± 0.00</td>
<td>0.85 ± 0.00</td>
<td>0.84 ± 0.01</td>
<td>0.87 ± 0.01</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>7.55x10^{-5}</td>
<td>1.28x10^{-4}</td>
<td>2.77x10^{-4}</td>
<td>8.12x10^{-5}</td>
<td>2.27x10^{-4}</td>
<td>1.70x10^{-4}</td>
<td>2.41x10^{-4}</td>
</tr>
</tbody>
</table>
Table 5.2: \( \text{Ca}^{2+}/\text{Na}^+ \) flux, monovalent ion permselectivity and specific energy consumption values of the commercial membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>CMX</th>
<th>CMS</th>
<th>CSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_{\text{Ca}^{2+}} ) ( \times 10^{-4} \text{ mol/}(\text{m}^2\text{s}) )</td>
<td>6.45</td>
<td>4.18</td>
<td>3.52</td>
</tr>
<tr>
<td>( J_{\text{Na}^+} ) ( \times 10^{-4} \text{ mol/}(\text{m}^2\text{s}) )</td>
<td>4.03</td>
<td>5.31</td>
<td>6.08</td>
</tr>
<tr>
<td>( P_{\text{Ca}}^{\text{Na}} )</td>
<td>0.64</td>
<td>1.23</td>
<td>1.72</td>
</tr>
<tr>
<td>( E_m ) (Wh/mol ( \text{Na}^+ ))</td>
<td>49.96</td>
<td>80.73</td>
<td>42.81</td>
</tr>
</tbody>
</table>

Table 5.3: \( \text{Ca}^{2+}/\text{Na}^+ \) flux, monovalent ion permselectivity and the specific energy consumption values of the LbL-modified membranes – effect of number of bilayers

<table>
<thead>
<tr>
<th>Number of PEI/PSS bilayers</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>1.5</th>
<th>2</th>
<th>2.5</th>
<th>3</th>
<th>6.5</th>
<th>7</th>
<th>10.5</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_{\text{Ca}^{2+}} ) ( \times 10^{-4} \text{ mol/}(\text{m}^2\text{s}) )</td>
<td>6.45</td>
<td>4.56</td>
<td>5.75</td>
<td>3.77</td>
<td>6.02</td>
<td>4.57</td>
<td>4.42</td>
<td>4.16</td>
<td>3.51</td>
<td>4.40</td>
<td>4.06</td>
</tr>
<tr>
<td>( J_{\text{Na}^+} ) ( \times 10^{-4} \text{ mol/}(\text{m}^2\text{s}) )</td>
<td>4.03</td>
<td>4.99</td>
<td>4.35</td>
<td>4.37</td>
<td>4.88</td>
<td>5.75</td>
<td>4.94</td>
<td>5.34</td>
<td>3.90</td>
<td>6.01</td>
<td>5.51</td>
</tr>
<tr>
<td>( P_{\text{Ca}}^{\text{Na}} )</td>
<td>0.64</td>
<td>1.09</td>
<td>0.76</td>
<td>1.15</td>
<td>0.83</td>
<td>1.20</td>
<td>1.08</td>
<td>1.24</td>
<td>1.17</td>
<td>1.35</td>
<td>1.31</td>
</tr>
<tr>
<td>( E_m ) (Wh/mol ( \text{Na}^+ ))</td>
<td>49.96</td>
<td>41.55</td>
<td>48.52</td>
<td>48.17</td>
<td>41.88</td>
<td>54.96</td>
<td>53.87</td>
<td>40.37</td>
<td>56.57</td>
<td>48.60</td>
<td>53.76</td>
</tr>
</tbody>
</table>
Layer-by-Layer Modification of Cation Exchange Membranes Controls Ion Selectivity and Water Splitting

Figure 5.6: Evolution of Ca$^{2+}$ and Na$^{+}$ ion concentrations in the diluate compartment, with the (a) unmodified CMX membrane and (b) CMX modified with LbL film of 11 bilayers. Values corrected for very slight differences in the initial concentrations.

Monovalent Ion Permselectivity of Commercial Membranes. The measured flux of Ca$^{2+}$ and Na$^{+}$ ions and the resulting permselectivities between calcium and sodium ions ($P_{Ca}^{Na}$) of the commercial membranes are presented in Table 5.2. The results show that for the CMX membrane the migration of divalent ions was higher than the monovalent ones, which leads to $P_{Ca}^{Na}$ values lower than one.

The results shown in Table 5.2 also reveal that the commercial monovalent-ion-permselective membranes CSO and CMS present higher $J_{Na+}$ values than $J_{Ca^{2+}}$, as expected. The monovalent ion permselectivity in CSO is probably imparted due to a thin positively charged coating on the surface of the membrane, which repels multivalent cations. On the CMS membrane, the monovalent ion permselectivity is partly related to an active layer on the surface, and it could also be due to the possible presence of a high degree of cross-linking on the membrane matrix (styrene-divinylbenzene) [136].

The voltage drop across the membranes was also measured during the permselectivity experiments and was then used to calculate the specific energy consumption of the membrane system per mole of transported Na$^{+}$ ions. While the standard CMX membrane requires ~50 Wh/mol Na$^{+}$, CMS requires significantly higher specific energy of ~80 Wh/mol Na$^{+}$. On the other hand, it is noteworthy that the CSO membrane exhibits rather low energy consumption, about half that of CMS. This striking difference in the energy consumption could be due to the fact that the CMS membrane possesses a dense membrane matrix.
**Monovalent Ion Permselectivity of the Modified membranes – Effect of Number of Bilayers.** The measured permselectivities between calcium and sodium ions ($P_{Ca}^{Na}$) of the modified membranes are depicted in Figure 5.7, showing the effect of the number of bilayers. The figure reveals that single layer formation of PEI (i.e., $(\mathrm{CMX})/(\mathrm{PEI/PSS})_0$) has not improved the monovalent ion permselectivity to the level of the commercial monovalent-permselective-ion-membranes. The strategy of single layer formation of PEI on the surface of cation exchange membranes was long investigated by Sata and Mizutani [137]. It was shown in their work that 1 g/L of PEI was optimal and a further increase in the polyelectrolyte concentration did not enhance the permselectivity. Accordingly, we have adopted this concentration for our LbL assembly. Unlike coating of a single layer of PEI, with the LbL approach, increased concentration of positive charges can be achieved on the surface of cation exchange membranes. Furthermore, the structures formed by LbL assembly are robust, as a result of the strong electrostatic bonding within the LbL layers.

![Figure 5.7: Measured permselectivities between sodium and calcium ions of the modified CMX membranes as a function of the number of (PEI/PSS)$_n$ bilayers.](image)

Figure 5.7, in addition, reveals that the permselectivity of the membranes modified by polyelectrolyte multilayers show different behavior depending on the number of deposited bilayers. The typical “odd–even” effect of the coated membranes can also be observed, whereby the permselectivity of the modified membrane is improved when the LbL coating is terminated with a layer of PEI. This “odd–even” effect is stronger at a lower number of deposited bilayers, and decreases with the number of deposited bilayers, eventually almost fading away at 10.5 and 11 bilayers. With respect to the PEI-
terminated layers, as mentioned before, with deposition of the first PEI layer, a steep increase in the permselectivity can be observed in comparison to the unmodified CMX membrane. Then the $P_{\text{Ca}}^{\text{Na}}$ values increase progressively with the number of deposited bilayers. At 6.5 bilayers already, a permselectivity (1.24) comparable to that of the CMS membrane was achieved.

The enhanced repulsion of divalent ions by the modified membranes is most likely the result of two effects: an increase of positive charges on the surface of cation exchange membranes as well as increased hydrophobicity on the same. The former effect increases with increasing number of bilayers due to the multibipolar structure of the polyelectrolyte multilayers. The multibipolar structure (shown schematically in Figure 5.8) enables fractionation of mono- and divalent ions because of a more pronounced Donnan exclusion towards the divalent ions, as discussed by Krasemann and Tieke [99]. In other words, the multivalent cations would experience a higher electrostatic repulsion by the positively charged layers of PEI deposited in the LbL film. Under the application of a constant current, the weaker repulsions of the LbL film toward monovalent ions would favor the fact that these ions can permeate easier through the membrane than multivalent ions.

The second effect is the concomitant hydrophobization of the membrane surface. This behavior can be correlated with the contact angle measurements (Figure 5.3(b)), where at a high number of bilayers the contact angle of the membranes increased in comparison to the contact angle of the unmodified membrane. This behavior, as noted above, is explained to be the result of a more or less complete coverage of the substrate mem-
brane by the polyelectrolyte layers. Therefore, the contact angles tend towards the real values of the PEI/PSS without the effect of the underlying substrate.

In electrodialysis, ions migrate with their hydration shells. To pass the solution/membrane interface, ions need to overcome an energy barrier, imposed by the requirement of their partial dehydration. Hence, the effect of this barrier is likely to be higher with monovalent-ion-permselective membranes or hydrophobized membrane surfaces [139]–[141]. Indeed, in the investigation of Firdaous et al. with monovalent-ion-permselective membranes [140], the ionic flux of chloride salts of three metal ions decreased in the sequence \( J_{\text{Na}^+} > J_{\text{Ca}^{2+}} > J_{\text{Mg}^{2+}} \). They followed the order of an increase in their hydration energy, as shown in Table 5.4. This observation was attributed to the above-discussed effect.

**Table 5.4:** Physico-chemical properties of sodium, calcium, and magnesium ions [taken from ref [142], [143]]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radius (nm)</th>
<th>Hydrated-ionic radius (nm)</th>
<th>Gibb’s hydration energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>0.102</td>
<td>0.218</td>
<td>365</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>0.100</td>
<td>0.271</td>
<td>1505</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.072</td>
<td>0.299</td>
<td>1830</td>
</tr>
</tbody>
</table>

Referring to the specific energy consumption data of the coated membranes in Table 5.3, no specific trend can be observed. The values vary between approximately 40 and 60 Wh/mol Na\(^+\) ions. The membrane with 6.5 bilayers coating had the lowest specific energy consumption for the passage of 1 mol of Na\(^+\) ions. For membranes coated with more than 6.5 bilayers, despite an improvement in the permselectivity, the specific energy consumption increases with the number of bilayers, due to the higher electric resistance of the membranes. Hence, in terms of ease of coating, the achieved permselectivity, and the specific energy consumption, the membrane with 6.5 bilayers seems optimal. This, of course, depends on the target industrial applications; i.e., the value of the metal ions to be recovered and the cost related to the electrical energy consumption have to be compromised. On the other hand, for the commercial membrane CMS, the monovalent ion permselectivity is achieved at the expense of energy
consumption; CMS requires twice as much specific energy demand of the membrane coated with 6.5 bilayers, for the passage of 1 mol of Na⁺ ions.

The above effect of the number of bilayers on the permselectivity was manifested for constant current density experiments in the ohmic region. Detailed data analysis of the polarization curves in the overlimiting current region reveals another remarkable effect. The polarization curves of the unmodified CMX and one modified CMX membrane (with 10.5 bilayers of PEI/PSS), with the simultaneously recorded pHs, are shown in Figure 5.9(a) and (b), respectively. For the unmodified CMX membrane, there is hardly any change in pH. Conversely, for some of the modified membranes (as exemplified in Figure 5.9(b)), there is a strong variation of pH caused by water splitting, starting from the limiting current density.

![Figure 5.9](image1.png)

**Figure 5.9:** Polarization curves along with pH measurements for (a) unmodified CMX and the (b) modified CMX membrane (with 10.5 bilayers of PEI/PSS).

The water splitting could originate from the catalytic activity of the LbL layers on the surface of cation exchange membranes, thus acting as quasibipolar membranes [119]. However, unlike bipolar membranes which reject all kinds of ions, these membranes still allow the passage of cations, when overlimiting currents are applied as shown schematically in Figure 5.10(a). A summary of the analysis of the water-splitting flux is depicted in Figure 5.10(b), which shows the ratio of the flux of protons across the cation exchange membranes to the total ion flux (i.e., Na⁺, Ca²⁺, and H⁺ ions) at a current density of 76 mA/cm². The graph clearly exhibits that the water splitting depends strongly on the nature of the last layer deposited. Water splitting is absent in those membranes terminated with PSS in the range up to 11 bilayers, whereas the water
splitting rate increases with the number of PEI-terminated layers. For instance, for the membrane with 10.5 bilayers of polyelectrolytes, the flux of protons is ~60% of the total ion flux at a current density of 76 mA/cm². There are some applications where ion permselectivity is needed, and at the same time, the pH should be regulated [144]. Our LbL-modified ion exchange membranes could be a key to such symbiosis.

In previous studies with pressure-driven membrane processes, it was shown that permselectivity of the modified membranes depends strongly on the selected polyelectrolyte pairs used to modify the membranes as well as on the LbL deposition parameters [99], [145]. To investigate the effect of LbL deposition parameters of the polyelectrolyte pairs, several LbL parameters were varied, with an optimal number of bilayers of this series, i.e., 6.5 bilayers. The membranes were coated, with the addition of salt and reversed molecular weight asymmetry of the PEI/PSS polyelectrolyte pairs. To prepare the membrane with the addition of salt, both polyelectrolytes were dissolved in 0.5 M NaCl. The multilayers with the reversed MW asymmetry were formed from 25 000 g/mol PEI and 1 000 000 g/mol PSS. Furthermore, PAH (pH = 3.0), along with PSS, was used instead of the PEI/PSS pair. The effect of the above variations was minimal on the permselectivity between Na⁺ and Ca²⁺ ions. Nonetheless, there was a significant difference in the specific energy consumption values. The results of these

Figure 5.10: (a) Schematic of competitive ion transport through the modified membranes in the overlimiting current regime in a state of water splitting. (b) The ratio of the flux of protons to the total ion flux as a function of the deposited number of bilayers.
variations on the permselectivity and the specific energy consumption can be found in Table A5.1 in the Appendix.

It is worth mentioning that the achieved monovalent ion permselectivity is also a strong function of the operating parameters, like stack design, feed concentrations and current density [107], [146]. In industrial stacks, cell configurations and hydrodynamic conditions could be optimized to achieve higher $P_{Ca}^{Na}$ values. These considerations, however, are clearly beyond the scope of this chapter.

5.4 Conclusions

In conclusion, competitive ion transport through LbL-modified cation exchange membranes was studied, with the main objective of inducing monovalent ion permselectivity on the membranes. It was demonstrated that the LbL assembly was successfully implemented on cation exchange membranes, without any pretreatment of the membranes as confirmed with FE-SEM, contact angle, and XPS measurements. Coating of the LbL layers caused only moderate variation of the ohmic resistance of the membrane systems. Nonetheless, the LbL layers had a substantial influence on the monovalent ion permselectivity of the membranes. A typical “odd–even” effect was present in the permselectivity, which was more prominent in the lower number of bilayers. As expected, the permselectivity was improved when the coating was terminated with PEI (positive) layers. Permselectivity comparable to that of a commercial monovalent-ion-permselective membrane was obtained with only six bilayers of polyelectrolytes, yet with significantly lower energy consumption per mole of transported Na$^+$ ions. The monovalent ion permselectivity was explained to be induced as a result of the synergy of two effects: increased Donnan exclusion for divalent ions and hydrophobization of the surface of the membranes that accompanies their modification. Furthermore, the double-layer capacitance obtained from impedance measurements was shown to be a qualitative indication of the divalent ion repulsion of the membranes, when the membranes are characterized in a mixture of mono- and divalent salts.

Yet another major finding was observed with regard to the water splitting behavior of the modified membranes. At current densities higher than the limiting current density, there was a strong change in the electrolyte pH of some of the modified membranes, which was insignificant for the unmodified CMX membrane. The flux of protons across the modified membranes increased with the number of PEI-terminated bilayers, while it was nearly absent for the PSS-terminated bilayers, up to a range of 11 bilayers.
There are applications in which ion permselectivity and pH regulation are needed at the same time; our LbL-modified ion exchange membranes could be a key to such symbiosis.
5.5 Appendix for Chapter 5

Table A5.1: Variation of LbL parameters for 6.5 coated bilayers and their resulting effect on Ca$^{2+}$/Na$^{+}$ flux, monovalent ion permselectivity and the specific energy consumption values

<table>
<thead>
<tr>
<th></th>
<th>Unmodified membrane</th>
<th>LbL-modified membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CMX</td>
<td>A</td>
</tr>
<tr>
<td>$J_{Ca^{2+}}$ (10$^{-4}$ mol/(m$^2$ s))</td>
<td>6.45</td>
<td>4.16</td>
</tr>
<tr>
<td>$J_{Na^+}$ (10$^{-4}$ mol/(m$^2$ s))</td>
<td>4.03</td>
<td>5.34</td>
</tr>
<tr>
<td>$P_{Na^+}$ Ca$^{2+}$</td>
<td>0.64</td>
<td>1.23</td>
</tr>
<tr>
<td>$E_m$ (Wh/mol Na$^+$)</td>
<td>49.96</td>
<td>40.37</td>
</tr>
</tbody>
</table>

(A) Modified with 1 g/L PEI (MW = 750 000 g/mol) and 1 g/L PSS (MW = 70 000 g/mol), both in water.

(B) Modified with 1 g/L PEI (MW = 750 000 g/mol) and 1 g/L PSS (MW = 70 000 g/mol), both in 0.5 M NaCl.

(C) Modified with 1 g/L PEI (MW = 25 000 g/mol) and 1 g/L PSS (MW = 1 000 000 g/mol), both in water.

(D) Modified with 1 g/L PEI (MW = 750 000 g/mol) pH 3.0 and 1 g/L PSS (MW = 70 000 g/mol), both in water.

(E) Modified with 1 g/L PAH (MW = 58 000 g/mol) pH 3.0 and 1 g/L PSS (MW = 70 000 g/mol), both in water.
Chapter 6

Overlimiting Ion Transport through Cation Exchange Membranes Modified with Polyelectrolyte Multilayers

6.1 Introduction

Similar to other membrane processes, concentration polarization is also encountered in electrodialysis, which is referred to as ion concentration polarization. The origin of this concentration polarization in electrodialysis is the difference in the transport number of counterions through the ion exchange membranes as compared with their transport number in the bulk solution. Consequently, diffusion boundary layers are formed in the vicinity of the ion exchange membranes, where the concentration of counterions increases at the surface of the membranes on the diluate side and increases on the concentrate side at the same time, as shown in Figure 6.1(a).

Typical current–voltage polarization curve of ion exchange membranes, shown schematically in Figure 6.1(b), exhibits three regions. In the first ohmic region the current increases linearly with the applied voltage. Further increase in voltage causes strong concentration polarization at the surface of the membrane. When the concentration of the counterions tends to zero on the diluate side of the membrane surface, limiting current density is reached, which leads to a drastic increase in the membrane resistance (region 2, plateau region). According to the theory of concentration polarization, any current higher than the limiting current density should not be expected. Whereas in

A modified version of this chapter has been published as:

reality overlimiting currents (region 3) can be realized as a result of the superposition
of other transport mechanisms that are discussed below. This severe ion concentration
polarization is also observed in other ion-selective solid surfaces, such as ion exchange
beads [147], nanochannels [148] and electrodes [149].

Electrodialysis processes for desalination are designed and operated on a simple rule of
thumb: the operating current is taken to be 80% of the limiting current to avoid comp-
lications associated with the overlimiting currents; two main reasons being (a) a dras-
tic increase in the electrical resistance, and (b) the detrimental water splitting which
causes irreversible metal hydroxide precipitation, and causes degradation of the mem-
branes not resistant to high acidic and alkaline media [15]. There are, however, rela-
tively new applications of electrodialysis that make use of the intense current transfer
and can even be operated in the overlimiting current, such as electrodialysis using bipo-
lar membranes (EDBM) [42], electro-deionization (EDI) [40] and pulsating current elec-
trodialysis [150]. Other emerging applications are in microfluidics. Several innovative
microfluidic devices were designed that utilize the concept of ion concentration polar-
ization, such as electroosmotic pumps [34], protein preconcentration devices [35], and
microfluidic chip for direct seawater desalination [36] etc.

The origin of the overlimiting current in ion exchange membranes has been a matter of
controversy for several decades. Five effects are discussed in the literature to explain
the overlimiting current phenomenon [39], [40]: two of which are related to the dissoci-
ation of water molecules at the surface of ion exchange membranes and the other three
effects due to salt ion transport (see Figure 6.2).
Figure 6.2: Physico-chemical phenomena discussed in the literature to contribute to the overlimiting current.

Overlimiting current has been for a long time mainly and often solely attributed to water dissociation producing protons and hydroxyl ions as additional current carriers [39], [151]. The generation of these ions also induces another secondary exaltation effect of salt counterions transport: protons and hydroxyl ions pull counterions towards the solution/membrane interface. Water splitting, which is more pronounced in anion exchange membranes than in cation exchange membranes was, however, shown in later studies not to be the main contributor to the overlimiting currents [152]. For a commercial anion exchange membrane, Krol et al. [152] reported that the hydroxyl ion transport number remains below 0.03.

The other two effects related to counterion transport are essentially current-induced convection: gravitational convection and electroconvection. These two forces lead to the agitation of the dilute boundary layer. Gravitational convection – Archimedean force in nature – arises due to a non-uniform density distribution as a result of concentration difference between the depleted solution near the membrane boundary and the bulk solution [153]. The density difference could also stem from a temperature difference: Joule heating increases the temperature of the depleted boundary layer, which has a high resistivity. The overall outcome is the lighter depleted solution ascending upwards and the heavier bulk solution descending downwards, thus creating macroscopic eddies around the membrane/solution interface. Gravitational convection is significant for electrodialysis cells with sufficiently large intermembrane distances and relatively higher salt concentrations [122].

Electroconvection, on the other hand, is an electroosmotic force in nature. It arises under the action of the external electric field on the space charge region near the membrane surface. A distinction between two types of electroosmoses is made. Electroosmo-
Overlimiting Ion Transport through Cation Exchange Membranes Modified with Polyelectrolyte Multilayers

sis of the 2nd-kind [154], [155], which is predominantly responsible for the electroconvection, is when the eddies are formed due to the interaction of the electric field with the non-equilibrium space charge on the membrane’s depleted side. This space charge, which is created under the intensive current transfer, is in the order of a few hundred nanometers away from the membrane surface. In contrast, electroosmosis of the 1st-kind is related to the space charge located in a quasi-equilibrium electrical double layer with a characteristic thickness in the order of the Debye length.

Quite recently a group of scientists suggested that one possible mechanism of the overlimiting current could be a loss in the ion selectivity of the membranes at high current densities, which they referred to as current-induced membrane discharge [156]. The membrane possibly loses its selectivity from the strong local pH shifts within the membrane because of the large electric field caused by the salt depletion near the membrane surface.

Depending on the membrane properties and operating conditions, the above-discussed physico-chemical forces can to a certain extent exist at the same time. However, electroconvection is now regarded to be the main driver of the overlimiting current in ion exchange membranes [39]. The existence of the convection rolls was visually proven in a quiescent cell by Rubinstein et al. [123] with fluorescent tracer particles using particle image velocimetry (see Figure 6.3). The electroconvective vortices were afterward visualized in micro-electrodialysis cells by Kwak et al. [157].

![Figure 6.3](image.png)

**Figure 6.3:** (a) Theoretical flow streamline patterns of electroconvective vortices. (b) Visualization of the electroconvective vortices in the vicinity of a cation exchange membrane. Images are taken from ref. [123].

Given the above-discussed mechanisms, it is by now generally believed that the membrane surface properties determine to a large extent onset of the overlimiting current rather than the bulk membrane properties [40]. Particularly, the degree of surface hydrophobicity [126], [127], electrical heterogeneity [158], geometrical heterogeneity, i.e., the creation of different kinds of reliefs on the surface [39], [159] and surface functional groups. Chemical nature of the surface has more to do with the water-splitting behavior of the membranes, but it was shown that it is possible to eliminate overlimiting cur-
rents with a coating of polyvinyl alcohol rendering the membrane surface homogeneous [160]. Other important operating factors are hydrodynamic conditions of the electrodialysis cell and Stokes radius of the treated ions [156].

In this study, we set to investigate whether polyelectrolytes can also be utilized to modulate overlimiting current phenomena in electrodialysis membranes. Layer-by-layer (LbL) assembly of polyelectrolytes was used to tailor the interface of the membranes: to alter the chemical nature of the surface and to increase the degree of membrane surface hydrophobicity. In addition, microcontact printing (µCP) was also applied to introduce uniform electrochemical heterogeneity on the surface of the membranes.

6.2 Experimental

6.2.1 Materials

The membrane studied was the commercial cation exchange membrane Neosepta CMX (Astom, Japan). It is a homogeneous membrane containing sulfonic acid groups as fixed charges.

The polyelectrolytes used to modify the CMX membrane were the polycations: poly(ethyleneimine) (PEI), poly(diallyldimethylammonium chloride) (PDADMAC), poly(allylamine hydrochloride) (PAH); and the polyanions: poly(sodium styrene sulfonate) (PSS) and poly(acrylic acid) (PAA). The chemical structures of the polyelectrolytes and their respective molecular weights (MW) are shown in Figure 3.1. All the polyelectrolytes were obtained from Sigma-Aldrich (Germany) and were used without any further purification. The polyelectrolyte solutions were prepared in ultrapure water with a concentration of 1 g/L. The pH of PAA (pH 3.0) and PAH (pH 10.0) solutions were adjusted with HCl and NaOH solutions, respectively.

6.2.2 Membrane Modification

LbL Assembly of Polyelectrolytes. To introduce the polyelectrolyte multilayers, the CMX membrane (stored priorly in 0.5 M NaCl solution) was first rinsed with ultrapure water and coated on only one side with the desired polyelectrolyte multilayers. Screening experiments were carried out to select one polyelectrolyte pair from among the polyelectrolytes listed in Figure 3.1. For the main experiments, the CMX was sequentially dipped in 1 g/L solution of PAH (pH 10.0) and 1 g/L PAA (pH 3.0) solutions. Except for the first layer, where the membrane was immersed in PAH for 45 min, the
rest of the layers were formed each for 22 min, PAH as well as PAA. In between the coating steps, the membranes were thoroughly rinsed with ultrapure water to remove any loosely-bound polyelectrolyte chains. The LbL layers were formed on the side that faces the anode (diluate side) in subsequent experiments.

**Stamp preparation.** Silicon molds, with circular holes (depth = 350 µm, diameter = 350 µm and an edge-to-edge spacing = 1200 µm) obtained from the University of Twente were used to prepare the PDMS stamps for µCP. To machine the microstructures in the silicon molds, standard photolithographic techniques were employed in combination with deep reactive ion etching (DRIE) in clean room facilities [161], [162]. Details of the preparation of PDMS stamps and the µCP procedure are mentioned in Section 3.2.2.

**6.2.3 Surface Characterization of the Membranes**

The deposition of the homogeneous polyelectrolyte layers was monitored by contact angle, ATR-FTIR, XPS and FE-SEM measurements. Whereas confocal- and fluorescence microscopy were employed to visualize the µCP-ed polyelectrolyte patterns (cf. Section 3.3).

The contact angle measurements were performed immediately after modification. The images for analysis of the contact angles were taken 1 min after the water droplet had settled on the membrane surface. For each membrane, an average of at least five measurements of the contact angle was taken, measured at different locations of the samples. The contact angle was evaluated by the sessile drop method.

**6.2.4 Electrochemical Characterization of the Membranes**

Polarization current–voltage ($i-V$) and chronopotentiometry measurements were performed to characterize the electrochemical behavior of the modified membranes. The measurements were carried out in a six-compartment electrodialytic cell shown schematically in Figure 6.4. The membranes, with an active membrane area of 10.5 cm$^2$, were characterized in 0.1 M NaCl. Prior to the experiments, the membranes were equilibrated in 0.1 M NaCl solution for about 24 h outside the membrane module.

The polarization and chronopotentiometry measurements were performed using the four-point method (cf. 3.4.2 and 3.4.3 for the details).
**Chronopotentiometry.** In chronopotentiometry, the evolution of the voltage drop of a sample is measured with time in response to a step input in current. The chronopotentiogram of an ion exchange membrane in response to an underlimiting current looks flat showing the regular ohmic response (Figure 6.5(a)). In contrast, if a current higher than the limiting current density is applied, the voltage drop response of ion exchange membranes looks like the graph shown schematically in Figure 6.5(b). The first jump is due to the combined ohmic potential losses of the membrane and the solution adjacent to it. Then the membrane voltage drop gradually increases with time, which is related to the concentration polarization losses. Eventually, the voltage drop reaches a plateau with a scatter resulting from the chaotic fluid instabilities caused by electroconvection – the higher the magnitudes of this scatter, the larger are the hydrodynamic instabilities. Further detailed description of the characterization of transient ion transport phenomena by chronopotentiometry can be found elsewhere [163], [164].
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Figure 6.5: Chronopotentiometric response of ion exchange membranes upon a sudden start of current with: (a) the regular ohmic response when underlimiting current is applied and (b) when overlimiting current is applied; the voltage fluctuations being a fingerprint of the chaotic disturbances in the diffusion boundary layer.

6.3 Results and Discussion

6.3.1 Effect of the Type of Polyelectrolytes

Six different polyelectrolyte combinations (Table 6.1) were screened to quickly preselect the best combination for subsequent investigations of the effect of the number of bilayers and the µCP. The desired criteria for the selection were a higher degree of hydrophobicity of the surface, lower plateau length, and the absence of water splitting. Contact angle and $i$–$V$ polarization experiments were performed for one-half and one bilayer of each of the polyelectrolyte combinations.

Table 6.1: Combination of polyelectrolytes used for the screening experiments

<table>
<thead>
<tr>
<th>#</th>
<th>Polycation</th>
<th>Polyanion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PAH (pH 10.0)</td>
<td>PSS</td>
</tr>
<tr>
<td>2</td>
<td>PDADMAC</td>
<td>PSS</td>
</tr>
<tr>
<td>3</td>
<td>PEI</td>
<td>PSS</td>
</tr>
<tr>
<td>4</td>
<td>PAH (pH 10.0)</td>
<td>PAA (pH 3.0)</td>
</tr>
<tr>
<td>5</td>
<td>PDADMAC</td>
<td>PAA (pH 3.0)</td>
</tr>
<tr>
<td>6</td>
<td>PEI</td>
<td>PAA (pH 3.0)</td>
</tr>
</tbody>
</table>
PAH and PAA are weak polyelectrolytes and, as such, their dissociation behavior depends on pH. Figure 6.6 shows the degree of dissociation of both polyelectrolytes as a function of pH. PAH has a pKₐ of ~7.5 and is completely dissociated at low pH values. PAA, on the other hand, has a pKₐ of ~4.5 and is completely dissociated at high pH values. For the experiments, the pH values of the solutions were selected to obtain a low degree of ionization of both polyelectrolytes. Thus, PAH solutions were prepared at pH 10.0 and PAA solutions at pH 3.0.

![Figure 6.6: Degree of dissociation of PAH and PAA polyelectrolytes as a function of pH (adapted from ref. [165]).](image)

**Hydrophobicity.** The first criterion for the selection of the polyelectrolytes was the ability to obtain a higher degree of hydrophobicity. Contact angle measurements were taken for the coated membranes after each half bilayer until three bilayers. Figure 6.7(a) shows the results for all membranes coated with the polycations in combination with the polyanion PSS. In general, the contact angle increases when the coating is terminated with the polycations and decreases when terminated with PSS, and this goes in a zigzag fashion with the number of bilayers indicating qualitatively the successful deposition of the polyelectrolytes. From among the polycations, PAH showed the highest contact angle. In combination with the polyanion PAA (Figure 6.7(b)), a similar alternating trend can be seen where PAH again shows the highest contact angle. Hence contact angle measurements indicate PAH/PSS or PAH/PAA pairs both as viable.

**Current–Voltage (i–V) Curves.** The other two selection criteria, i.e., plateau length and water splitting were obtained from the i–V curves of the membranes. Figure 6.8(a) shows a sample raw i–V curve of the membrane modified with one layer of PEI with the simultaneously recorded pH changes. It can be seen that this membrane splits wa-
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ter molecules strongly starting from the limiting current density. A strong scatter in the voltage drop readings of the overlimiting region was found in the raw data of all the experiments. Consequently, smoothing of the overlimiting region of the $i-V$ curves was necessary to clearly compare the results. Figure 6.8(b) shows a comparison of the $i-V$ curves (with the ohmic parts subtracted) of the unmodified CMX and the CMX membrane modified with a single layer of PAH.

Figure 6.7: Contact angle results as a function of the number of bilayers of the three polycations in combination with (a) the polyanion PSS, and (b) the polyanion PAA (pH 3.0).

Figure 6.8: (a) Sample $i-V$ curve with the simultaneously recorded pH of the CMX membrane modified with a single layer of PAH. (b) Sample comparison of $i-V$ curves for the commercial CMX membrane and the CMX membrane coated with a single layer of PEI (CMX/(PEI)$_{0.5}$).
**Plateau Length.** The second criterion was the ability to obtain shorter plateau lengths as a result of modifying the CMX membrane with the polyelectrolytes. An energy barrier equal to the plateau length must be overcome before the overlimiting current sets in. Thus, earlier onset of the overlimiting current, i.e., a shorter plateau length is more convenient for electrodialysis processes that can potentially make use of intense current densities.

A summary of the plateau length results of the screening experiments is shown in Figure 6.9. The unmodified CMX membrane (indicated with 0) shows the largest plateau length of ~0.85 V; thus, a reduction of the plateau length is obtained by applying single or double layers of the polyelectrolytes. From the single layers of polycations, PEI leads to the smallest plateau length value of ~0.55 V, followed by PAH ~0.68 V and PDADMAC ~0.7 V. The smallest plateau lengths were obtained for the combinations (PEI/PSS) and (PAH/PAA), with values of ~0.37 V and ~0.41 V, respectively.

![Figure 6.9: Plateau length results for all the polyelectrolyte combinations studied to modify the CMX membrane in the screening experiments.](image)

**Water Splitting.** pH changes may accompany electrodialysis processes in the overlimiting region because of water dissociation. Therefore, part of the current produced in the overlimiting region is sometimes carried by protons and hydroxyl ions. Although small in magnitude, this percentage of the current is occasionally, especially for anion exchange membranes, too high and it can cause appreciable losses of current efficiency. The pH changes can also lead to the precipitation of some multivalent ions on the membrane surface, thus impairing the electrodialysis process [1], [166], [167].
The CMX membrane shows no water splitting even in the overlimiting currents. Hence in our study, the presence of the polyelectrolytes or any of their combinations should not induce water splitting at the surface of the CMX membrane. Thus, the third criterion for selecting the polyelectrolytes: they should cause no pH changes as a result of water splitting. In other words, only electroconvection is desired as the main mechanism for the enhanced ion transport in the overlimiting region.

Figure 6.10 shows a summary of the water-splitting results of the studied membranes. It shows the percentage of the current carried by the hydroxyl ions from the total ion flux. The unmodified CMX (indicated with 0) shows no water splitting. From among the polycations, PEI clearly splits water molecules. This was indeed expected because the branched PEI consists in its repeating units a significant amount of secondary and tertiary amines, which were shown in a number of previous studies to be catalytic [119]. The highest water splitting was found for the polyelectrolyte combination (PEI/PSS) with a value reaching ~5%. Further, it is remarkable to see that none of the membranes coated with the polyanion PAA produced significant water splitting.

Figure 6.10: Water splitting results (percentage of the current carried by the hydroxyl ions from total ion flux) for all the polyelectrolyte combinations studied to modify the CMX membrane in the screening experiments.

Summarizing, based on the screening experiments, the combination PAH/PAA was selected for further study as the most viable combination based on the three selection criteria. First, PAH coating caused the highest increase in the degree of hydrophobicity of the CMX membrane compared with the other polycations. Then, although the combination (PEI/PSS) resulted in the lowest plateau length followed by (PAH/PAA), ex-
cept that the (PEI/PSS) produced the highest water splitting as can be seen in Figure 6.10. In contrast, no membrane coated with PAA produced any significant water splitting.

### 6.3.2 Surface Characterization of the Membranes

Before proceeding with the experiments of the selected polyelectrolyte combination, a successful deposition of the polyelectrolyte multilayers with this system needed to be monitored. To this end, several surface analysis experiments were carried out: contact angle, ATR-FTIR, XPS as well as FE-SEM.

**ATR-FTIR.** ATR-FTIR spectroscopy of the CMX membrane modified with a number of PAH/PAA layers was carried out. The spectra were obtained after each of the PAA layers since amine groups in the PAH can hardly be detected with FTIR spectroscopy. Figure 6.11(a) shows the entire FTIR spectra of the modified CMX membrane as a function of the number of deposited polyelectrolyte layers. The spectra zoomed in around the wave number in the range of 1200-1800 cm\(^{-1}\) are depicted in Figure 6.11(b). A growth of two signals can be seen with an increase in the number of layers that were absent in the unmodified CMX membrane. The peak at the wave number ~1710 cm\(^{-1}\) is attributed to the carboxylic acid (–COOH) groups present in PAA. The peak at ~1531 cm\(^{-1}\) could probably be due to an overlay of the signals of the carboxylate (–COO\(^-\)) and ammonium (–RNH\(_3^+\)) salts, arising from the presence of both PAA and PAH, respectively.

**XPS.** Until four bilayers, the deposition was also monitored with x-ray photoelectron spectroscopy (XPS) measurements. From the elemental analysis of the XPS spectra, Figure 6.12 shows the N/O ratio of the CMX membrane modified with a number of PAH/PAA layers. Here again, alternating trends of the N/O ratio can be seen, varying between ~0.5 when the coating is terminated with PAH and ~0.2 when the last layer is PAA. N-content increases when the coating is terminated with PAH due to the amine groups of the PAH, and O-content increases when the last layer is PAA due to the presence of the carboxylic acid group of the PAA. XPS results provided a roughly quantitative proof of the successful deposition of the multilayers.
Figure 6.11: ATR-FTIR spectroscopy of CMX membrane modified with different number of PAH (pH 10.0)/PAA (pH 3.0) bilayers (a) Entire spectra. (b) Spectra zoomed around the wave numbers in the range of 1200–1800 cm$^{-1}$.

Figure 6.12: N/O ratio obtained from the elemental analysis of XPS spectra of the CMX membrane modified with varying number of PAH (pH 10.0)/PAA (pH 3.0) bilayers.

**FE-SEM.** At a high number of deposited layers, FE-SEM brought about a visual proof of the successful deposition of the polyelectrolyte layers. Figure 6.13(a) and (b) show respectively, a cross-section FE-SEM images of the unmodified CMX membrane and the CMX membrane modified with ten bilayers of PAH (pH 10.0) and PAA (pH 3.0). In the image of the modified membrane, a thin stripe of the LbL film of 10 bilayers can be clearly distinguished, which has a thickness of about 1 µm. This amounts to an average polyelectrolyte layer thickness of about 50 nm. While this is thick as compared to
the thickness of layers on other very smooth and planar surfaces, this thickness analysis is very reproducible [168]. In addition, ellipsometry measurements also confirm thicker deposition of the polyelectrolyte layers on the surface of the highly-charged ion exchange membranes than the deposition on smooth planar surfaces [169].

Figure 6.13: Cross-section FE-SEM images of (a) an unmodified CMX membrane and (b) a CMX membrane modified with 10 bilayers of PAH (pH 10.0)/PAA (pH 3.0).

6.3.3 Effect of the Number of Homogeneous LbL Layers

We varied the number of subsequent deposition steps for the PAH/PAA polyelectrolyte pair from 1 to 11, the latter being indicated as 6.5 bilayers as shown in Figure 6.14. It is apparent from Figure 6.14(a) that the presence of the polyelectrolytes affects the plateau length significantly. It is also obvious from Figure 6.14(b) that the plateau length in general decreases with increasing number of polyelectrolyte layers. Superimposed onto this trend of shortening plateau length, a distinct switching pattern emerges between an upper bound for PAA-terminated surfaces as opposed to a lower bound for the PAH-terminated surfaces.

The shift of the plateau lengths between the upper and the lower bound, respectively for PAA and PAH layers, can be directly correlated to the contact angle results (Figure 6.15(a)). The PAH layers, which increase the membrane surface hydrophobicity, result in shorter plateau lengths. More hydrophobic surfaces intuitively lead to a higher slippage of the solutions on the surface of the membrane, thus facilitating the formation of the electroconvective vortices. A similar correlation between an increase in the contact angle and a decrease in the plateau length of ion exchange membranes can be cited in the literature [126], [127]. It was checked that no significant water splitting occurs on these membranes. Thus, much of the effect for the earlier onset of the overlimiting current must have originated from electroconvection effects, which in turn are enhanced by the slippage of the electrolyte solution by its interaction with the more hydrophobic surfaces.
Figure 6.14: (a) A typical current–voltage curve, corrected for the ohmic resistance of membrane and solution, for the reference (unmodified CMX) and the CMX membrane modified with an LbL coating comprising 6.5 bilayers. (b) Evolution of the plateau length with increasing number of LbL bilayers terminated with either PAH or PAA layer.

Figure 6.15: (a) Contact angle measurements for varying number of PAH (pH 10.0)/PAA (pH 3.0) bilayers deposited on the CMX membrane. (b) A picture showing the appearance of white flocs on the surface of CMX membrane, after being coated with 6.5 bilayers of PAH (pH 10.0)/PAA (pH 3.0).

A possible explanation of the effect of the homogeneous LbL layers is herein included. This interpretation can only be hypothetical and the inhomogeneity of the LbL layers can be suggested to be responsible for this shortening of the plateau length. In fact, after depositing 7 bilayers, the surface becomes very rough as if macroscopic coagulations
occur and the contact angles drop (Figure 6.15(a)). Figure 6.15(b) shows the vigorous precipitation (complexation) of the polyelectrolytes at the surface of the CMX membrane. Formation of white flocs on the surface of the membrane can be clearly seen. This precipitation starts occurring at an even fewer number of deposited layers if the polyelectrolytes are prepared in 0.5 M NaCl solution. The results shown in Figure 6.14(b) correspond until the apparition of the precipitation. The complete results including after the precipitation are in Appendix 6.5.1, showing the plateau length increasing after the precipitation.

With respect to the decrease of the plateau length, especially with an increase of the number of the first PAH layers could be, as a matter of speculation, due to the formation of voids within the LbL layers forming electrical heterogeneities of a probably larger scale than the scale of the electrical heterogeneities already present on the unmodified CMX. The CMX membrane is reported to have a degree of heterogeneity with the non-conducting domain making up about 7-8%, and the conducting domain having a pore size in the order of 0.156 nm [164]. The LbL layers, on the other hand, were formed from the weak polyelectrolytes PAH (pH 10.0) and PAA (pH 3.0), which when deposited in these pH values result in the polyelectrolyte chains adopting a coiled conformation, thus creating voids within the LbL layers [53]. Recent literature also indicates that electric fields can induce macroscopic morphological transitions in polyelectrolyte multilayers [170]. In addition, multilayers formed from PAH and PAA were shown to undergo irreversible phase transitions forming micro- and nanoporous structures in response to post-treatments with acidic or salt solutions [171], [172]. This can, in fact, be related to the results of Rubinstein et al. [173], where they showed that adding a porous heterogeneous layer on a highly permselective dense homogeneous layer increases the limiting current density; and suggested electroconvection to even occur in a liquid confined in the porosity.

Electroconvection arises because of the action of an electric field upon a space charge region – a region where electroneutrality is disrupted due to a non-uniform distribution of the conducting and non-conducting (less conducting) domains on the diluate side of the membrane surface. A distinction is made between electroosmosis of the 1st- and 2nd kind [154], [155]. Electroosmosis of the 1st kind is the electrolyte slip that occurs due to the action of the electric field on a quasi-equilibrium space charge region very close or at the diffuse part of the electric double layer, with a characteristic thickness in the order of the Debye length. In contrast, electroosmosis of the 2nd kind, which is more prominently responsible for the electroconvection, occurs on a non-equilibrium space
charge region, in the order of a few hundred nanometers up to 1 μm away from the membrane surface [39]. The size of surface electrical heterogeneities created by the LbL layers could be more relevant in initiating or enhancing the electroosmosis of the 2nd kind; thus, the plateau length of the membranes decreases with increasing number of the LbL layers.

To sum up, this experimental observation for the first time establishes a quantitative correlation between a rigorously-controlled and systematic surface modification with the induction of overlimiting currents at low polarization thresholds. The question whether lateral electrochemical surface heterogeneity can also influence the onset of electroconvective fluid motion will be answered below as well.

### 6.3.4 Introducing Surface Heterogeneities by Microcontact Printing of Polyelectrolytes

Soft lithography is known to enable the transfer of adsorbed macromolecules from a soft PDMS-based stamp to another surface [174]. The soft lithography-based µCP was used to apply a patterned electrochemical surface modification onto pristine CMX membrane or onto the membrane carrying already an LbL modification of 6 bilayers.

A light microscopic image of the used PDMS stamp with larger 350 μm circular patterns is shown in Figure 6.16(a). Confocal microscopy was employed to visualize the fluorescently-labeled PAH (PAH:Cy3) patterns directly printed on top of CMX with confocal microscopy. Figure 6.16(b) shows the confocal microscopic image of the membrane with the printed PAH patterns. Some difficulties associated with visualizing the polyelectrolyte patterns using fluorescence microscopy and improving the printing procedure are mentioned in Appendix 6.5.2.

![Figure 6.16](image-url)

**Figure 6.16:** (a) A light microscopic image of the PDMS stamp used to print the patterns (350 μm) atop the CMX membrane. (b) A confocal microscopic image of smaller circular (50 μm) PAH patterns applied directly onto the CMX membrane by µCP.
In terms of performance, the clear effect of the µCP on the plateau lengths can be seen in Table 6.2. Listed are the unmodified CMX membrane, and the two µCP-ed membranes and compared with their homogeneously-coated membrane counterparts. A detailed description of the modified membranes is commented on the footnote. Table 6.2 shows that applying the PAH micropatterns decreased the plateau length of the membranes. These results indicate that introducing surface micro-heterogeneities by µCP is even more effective in diminishing the plateau lengths than increasing the number of homogeneous LbL layers – comparing the results of the single PAH micropatterns (CMX/µCP-(PAH)$_{0.5}$) with the 6.5 homogeneous bilayers (CMX/(PAH/PAA)$_{6.5}$). In general, a shortening in the plateau length was obtained by introducing electrochemical heterogeneity on the membrane surface by means of LbL assembly or µCP. This result is supported by several studies [159], [175]–[177], which demonstrated the strong effect of the (surface) heterogeneity of ion exchange membranes on their limiting and overlimiting ion transport properties.

Table 6.2: Plateau lengths of the unmodified CMX membrane, and the CMX membrane modified by LbL assembly and µCP (membrane symbols indicated on the footnote)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Plateau length [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMX</td>
<td>0.82</td>
</tr>
<tr>
<td>CMX/(PAH)$_{0.5}$</td>
<td>0.52</td>
</tr>
<tr>
<td>CMX/(PAH/PAA)$_{6.5}$</td>
<td>0.36</td>
</tr>
<tr>
<td>CMX/µCP-(PAH)$_{0.5}$</td>
<td>0.25</td>
</tr>
<tr>
<td>CMX/µCP-(PAH/PAA)$_{6.5}$</td>
<td>0.24</td>
</tr>
</tbody>
</table>

To gain a deeper insight into the magnitude of the electroconvective instabilities, chronopotentiometry experiments were carried out for the above membranes. Figure 6.17 shows the dynamic signal of the voltage drop over the membranes at a current above the limiting current density (30 mA/cm$^2$) of the membranes. To focus on the fluid instability only, the voltage drop is corrected for the ohmic resistance of the mem-

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The membrane symbols: (CMX): the unmodified CMX membrane; (CMX/(PAH)$_{6.5}$): CMX modified with a single homogenous layer of PAH; (CMX/µCP-(PAH)$_{0.5}$): CMX modified with a µCP-ed PAH layer on the original CMX; (CMX/(PAH/PAA)$_{6.5}$): CMX modified by applying 6.5 homogenous bilayers of PAH/PAA; (CMX/µCP-(PAH/PAA)$_{6.5}$): CMX modified with a µCP-ed PAH layer on top of the CMX membrane already carrying a 6 LbL homogenous layers of PAH/PAA.
Overlimiting Ion Transport through Cation Exchange Membranes Modified with Polyelectrolyte Multilayers

branes and the unpolarized solutions, by subtracting it from the total voltage. Hence
the only contribution to the signal stems from the polarization in the diffusion bounda-
ry layer and the dynamic fluctuations associated with the fluid flow instabilities.

Figure 6.17: Dynamic polarization signal obtained for (a) the unmodified CMX membrane, and modi-
fied by applying a single homogeneous PAH layer (CMX/PAH) or modified with a µCP-
ed PAH layer (CMX/µCP-PAH) on the original CMX (b) the unmodified CMX mem-
brane, and modified by applying 6.5 homogeneous double layers of PAH/PAA
(CMX/(PAH/PAA)) or modified with a µCP-ed PAH layer on top of a 6 LbL double
layer-modified CMX membrane (CMX/µCP-(PAH/PAA)).

It can be observed that the overlimiting region of ion exchange membranes is generally
characterized by a scatter in the voltage drop readings [163] – in agreement with the
theory that electroconvective instabilities and hydrodynamic chaos are created near the
surface of ion exchange membranes at overlimiting currents [124], and that electrocon-
vection is the main cause of the apparition of overlimiting currents [123]. Furthermore,
in comparison with the unmodified membrane, the magnitude of these voltage fluctua-
tions is higher in the modified membranes – the micropatterned membranes more so
than the homogeneously-coated membranes. The hydrodynamic instabilities are higher
in the modified membrane due to more intensive electroconvection effects. From among
the investigated membranes, Figure 6.17(b) presents that the highest fluctuation was
observed for the CMX membrane modified with six homogeneous bilayers and termi-
nated with micropatterns of PAH (CMX/µCP-(PAH/PAA)). Intriguing is the fact
that the nanometer-thick lateral polyelectrolyte PAH micropatterns cause these vigorous electroconvective fluid stabilities, which are electroosmotic in nature. Power spectral analysis of the fluctuations have been suggested in the past [178], but they only give a broad distribution of fluctuation frequencies with little to no extra information to be extracted from the chaotic signal.

According to Rubinstein and Zaltzman [158], introducing slight periodic distortions of the flat membrane surface (geometrical heterogeneities), of size in the order of the diffusion boundary layer would likely give rise to an earlier onset of the overlimiting current. Based on our experimental conditions, the diffusion boundary layer thickness is in the order of 100 µm, calculated according to Equation 2.6. The electrochemical heterogeneity, and to some extent geometrical heterogeneity introduced by the lateral polyelectrolyte patterns, is in the order of the diffusion boundary layer; thus, reducing the plateau lengths and causing increased fluid instabilities.

The effect could also be physically related to the so-called “funneling effect” depicted schematically in Figure 6.18 [40], [179]. Here in contrast to a homogeneous membrane, the presence of (at least on the surface) electrical heterogeneity in a membrane (when part of the membrane is poorly-conducting or non-conducting) leads to two effects. The electrical heterogeneity facilitates the formation of a tangential electric field, which more readily sets the charged solution volume in motion. The “focusing” of the current lines through the conducting areas also leads to higher local current densities in those areas in comparison with homogeneous membranes subjected to the same average current density. In our case, the less-conducting domains are presumably created by the lateral polyelectrolyte micropatterns. This, of course, is in addition to the intrinsic microscopic electrical heterogeneity present in homogeneous membranes, such as the CMX membrane here.

This observation in the chronopotentiometric experiments leads to the hypothesis that the combination of LbL layers and micropatterns is the most effective method to eliminate the detrimental effect of concentration polarization. Yet it poses the next question whether optimizing the geometric features of the molecularly printed polyelectrolytes can further attenuate this destabilization effect. Systematic variations in stamp pattern architecture are required in the future; however, they go beyond the scope of this chapter.
Figure 6.18: Schematic representation of the so-called “funneling effect” showing the formation of electroconvective vortices at the surface of an ion exchange membrane with surface electrical inhomogeneities, with presumably less-conducting domains formed by the µCP-ed polyelectrolytes and high-conducting domains formed by the uncoated membrane surface. The scheme adapted from ref. [39].

6.4 Conclusions

This study aimed at investigating whether modifying ion exchange membranes with polyelectrolyte multilayers can modulate their overlimiting mass transfer behavior. The commercial cation exchange membrane CMX was modified by the LbL assembly of polyelectrolytes as well as by the µCP technique. In the first part of this study, different polyelectrolytes were screened to preselect the best combination to further study the effect of the number of polyelectrolyte layers as well as µCP. The selection criteria for the polyelectrolytes were the ability of the polyelectrolytes to (a) increase the degree of hydrophobicity of the membrane surface, (b) lower the plateau length of the membrane, and (c) cause no water splitting at the surface of the membrane. The polyelectrolyte pair poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) was selected as the best combination. Among the polycations, PAH resulted in the highest contact angle of the membrane surface. When PAH/PAA combination was applied, no water splitting was observed, and lower plateau length was obtained in comparison to the other combinations of polyelectrolytes.

As for the effect of the number of PAH/PAA layers, the plateau length decreased significantly with increasing number of the polyelectrolyte layers. Lower values of the plateau length were obtained for the PAH-terminated membranes than the PAA-terminated membranes, directly correlating with their contact angles – PAH layers being more hydrophobic. The lowest plateau length was obtained when 6.5 bilayers of polyelectrolytes were coated, where the PAH was the last layer applied. Coating of more than 6.5 bilayers caused conspicuous precipitation of the polyelectrolytes to ap-
pear on the membrane surface and the plateau lengths increase but do not fall into a specific pattern.

µCP was also employed to print micropatterned PAH layers onto the unmodified CMX membrane and onto the CMX membrane modified beforehand with 6 bilayers of PAH/PAA polyelectrolytes. The plateau length decreased by applying the PAH micropatterns. The results further indicate that introducing polyelectrolyte micropatterns was more effective in diminishing the plateau length than increasing the number of homogeneous polyelectrolyte layers. The dynamic voltage response from the chronopotentiometry measurements of the modified membranes showed higher fluctuations in response to a step input in overlimiting current than the unmodified commercial membrane. Much higher fluctuations appeared in the case of µCP-ed membranes. Of the investigated membranes, the highest fluctuation was observed for the CMX membrane modified with 6 homogeneous PAH/PAA bilayers and terminated with a µCP-ed PAH layer. These results lead to the conclusion that electroconvection effects are so far most effectively enhanced by applying LbL layers of polyelectrolytes in combination with introducing micropatterns.

Along the line of the findings in this study, it is worthwhile investigating the influence of the size and spacing of the circular micropatterns. Furthermore, applying multi-layered micropatterns rather than only applying a single layer of micropatterns could as well prove to be promising. In terms of geometry, some theoretical considerations of the optimal conditions for the appearance of electroosmosis of the 2nd kind near flat surfaces can be cited in the literature [180], indicating that stripes or squares, with identical sites of conducting and non-conducting domains, are optimal.
6.5 Appendix for Chapter 6

6.5.1 Plateau Length as a Function of Number of Bilayers

![Plateau Length Graph]

**Figure A6.1:** Evolution of the plateau length with increasing number of LbL bilayers terminated with either PAH or PAA layer, before and after the appearance of the white precipitated flocs on the membrane surface.

6.5.2 Improving Protocol for Microcontact Printing of Polyelectrolytes

**Hindered Visualization using Fluorescence Microscopy.** Figure A6.2 demonstrates successful loading of the PAH onto the PDMS stamp and successful printing of the PAH patterns on a glass substrate. Here the fluorescence micrographs were obtained using a fluorescein-labeled PAH.

![Fluorescence Micrographs]

**Figure A6.2:** (a) A scanning electron micrograph of the PDMS with smaller circular patterns of 50 µm diameter and 25 µm apart (edge-to-edge). Fluorescence micrographs of (b) a sample inked PDMS stamp and (c) PAH micropatterns printed on a glass substrate.

The fluorescence micrograph of the printed CMX membrane is shown in Figure A6.3. The printed patterns of the fluorescein-labeled PAH could not be clearly identified. The
fluorescent light emitted in the image can also be observed in the unmodified CMX membrane.

The reason why the patterns could not be clearly identified could be due to the strong background fluorescence from the CMX, and could also be due to the chemical interaction of the fluorescein dye with the membrane material leading to a “quenching” effect. Another reason could be related to the pH sensitivity of the fluorescein dye. Though the printing was conducted at pH 10.0, the fluorescence of the fluorescein marker could be hindered if, for some reason, the pH decreases locally at the membrane surface to below pH 4.

Figure A6.3: Fluorescence micrographs of (a) CMX membrane modified with a single µCP-ed PAH patterns and (b) the CMX membrane modified beforehand with 6 homogeneous bilayers of PAH/PAA, and terminated with a µCP-ed PAH:FITC layer. In both cases, the printed PAH patterns could not be identified on the CMX membrane; the fluorescence light emitted from the CMX is from the base membrane matrix.

**Improved µCP Procedure.** Subsequent to the experiments performed above, a series of µCP experiments were performed to improve the µCP procedure. The “optimized” procedure is shown in Figure A6.4(b).

Figure A6.4: Confocal microscopic image of PAH patterns directly µCP-ed onto the CMX membrane using (a) the standard procedure and (b) the “optimized” procedure, i.e., the PDMS stamp treated using a 50 W O₂ plasma for 2 min, and the patterns printed by applying a pressure of ~200 g/cm² for 20 min.
Chapter 7

Tuning Ion Transport through Ion Exchange Membranes with Patterned Microgels

7.1 Introduction

Surface properties of membranes play decisive roles in the overall membrane separation processes. Membrane surfaces are elaborately altered during membrane formation or in a separate step afterward with the objective of enhancing some desired performances or mitigating drawbacks that are inherent to membrane separation processes [3], [4].

Over the last years, several surface modification methods have been developed. The use of particulate materials such as nanoparticles to modify the surface of membranes are recently gaining increased interest [181]. For instance, Luo et al. [182] modified the surface of poly(ether sulfone) ultrafiltration membranes with TiO$_2$ nanoparticles resulting in an increased hydrophilicity of the membranes, consequently reduced fouling. Recently Escobar-ferrand et al. [183] demonstrated an all-nanoparticle layer-by-layer surface modification of micro- and ultrafiltration membranes using charged-SiO$_2$ nanoparticles yielding composite membranes with nanofiltration membrane properties. Chan et al. [184] tailored the surface of a commercial nanofiltration membrane with multilayers of SiO$_2$ nanoparticles to enhance permselectivity for mono- and divalent ions.

Part of this chapter has been published as:

Nanoparticles can also be incorporated into thin polymeric films for the surface modification of membranes. For instance, Kochan et al. [185] prepared ultrafiltration membranes with promising antibacterial properties by modifying the surface of poly(ether sulfone) membranes with metallic Ag nanoparticles incorporated within a polyelectrolyte multilayer film. Belashova et al. [127] enhanced the overlimiting mass transfer through cation exchange membranes by modifying their surface with a thin film of Nafion comprising evenly-dispersed carbon nanotubes.

In view of the successful application of nanoparticles, highly-functionalized microgels, as particulate materials, may augment the functionality of membranes. Microgels are particulate cross-linked polymer networks in a typical size range of about 50 nm–5 µm [6]. They differ from rigid colloidal particles, in that microgels are soft and can be swollen in suitable solvents, have a diffuse boundary and can be penetrated by smaller molecules [63], [64]. Depending on their type, microgels also exhibit stimuli-responsive behavior, i.e., they undergo swelling and de-swelling transitions (change in dimensions and structure) and variation in their interactions in response to external stimuli, such as temperature, pH, ionic strength etc. [7], [8]. They are thus, as smart materials, candidate for a number of different applications, such as drug delivery, sensing, separation and purification technologies, catalysis etc. [7], [65].

Of particular interest to the combination of microgels with membranes is that presynthesized microgels also retain their responsiveness in the adsorbed state as shown in a number of previous publications [9], [10], [66]. Menne et al. for the first time reported a reversible thermoresponsive flux and retention behavior of hollow fiber membranes that were modified with presynthesized poly(N-vinylcaprolactam)-based microgels [9]. Surface modification of ion exchange membranes, which are the object of this study, was by and large carried out using polymeric thin films [21].

In summary, surface modification using presynthesized microgels (also applies to polyelectrolytes) entail a number of advantages: The surface modification is a relatively easy physical process requiring no pretreatment of most membranes [11]. With microgels, a rigorous control of the membrane surface properties at the nanometer-scale can be achieved [12]. Other advantages include stimuli-responsiveness, the applicability to different membrane geometries etc. [9].

This study aims to explore the potential application of functional microgels to modify the surface of ion exchange membranes. Both highly-charged aqueous polyelectrolyte microgels and their uncharged precursor latex particles were used to modify the surface
of ion exchange membranes. Within the scope of this study, methods to form dense confluent- and micropatterned microgel monolayers on top of ion exchange membranes are developed. The study is rounded off with preliminary performance tests of the membranes modified with the above-mentioned methods. Polarization behavior and monovalent ion permselectivity of the modified membranes were characterized. In addition, application of the microgels as catalysts for water dissociation at the interface of bipolar membranes was also investigated.

7.2 Experimental

7.2.1 Materials

The commercial ion exchange membranes CMX, CMS, FKB or FAA were used, and their respective properties are shown in Table 3.1. The microgels poly(methacrylic acid) (PMAA) and quaternized poly(2-vinylpyridine) (qP2VP), and the latex precursor of qP2VP, i.e., P2VP were used in this study to modify the membranes. Synthesis of the particles, their physical properties, and chemical structures are given in Section 3.1.3.

The polyelectrolytes used to modify PDMS stamps for microcontact printing (µCP) were the polycations poly(ethyleneimine) (PEI) and poly(allylamine hydrochloride) (PAH), and the polyanions poly(sodium styrene sulfonate) (PSS) and poly(acrylic acid) (PAA) (cf. Section 3.1.2). The polyelectrolyte solutions were prepared in ultrapure water with a concentration of 1 g/L. The pH of PAA (pH 3.0) and PAH (pH 10.0) solutions were adjusted with 1 M HCl and 1 M NaOH, respectively.

7.2.2 Membrane Modification

The membranes were modified with either confluent monolayers of microgels or their micropatterned monolayers – formed by a method similar to dip-coating (henceforth referred to as slip-coating method) and by microcontact printing (µCP) technique, respectively. Further details about the methods developed to pattern the microgels on top of ion exchange membranes are presented in the Results Section.

7.2.3 Membrane Characterization

The modified membranes were visualized using field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi, Japan) and scanning electron microscopy (SEM) (S-3000N, Hitachi, Japan). The polarization current–voltage ($i–V$) curves and monovalent
ion permselectivity of the membranes were characterized using the six-compartment cell described in Chapters 4, 5 and 6, with the setup described in Section 3.4.1.

7.3 Results and Discussion

7.3.1 Developing Membrane Modification Methods

Forming a Confluent Monolayer of Microgels. The method employed at first to form a confluent monolayer of microgels was evaporative self-assembly using a confining rubber [186]. The following requirements, nonetheless, led to the development of the slip-coating (inverse dip-coating) method. First, the self-assembly method should be reproducible, faster and should cover a relatively large area of the membranes (5x5 cm) for electrochemical characterization. In addition, our desired end membrane surface properties are also anisotropic, thus dictating the fourth requirement: the modification should be carried out on only one side of the membrane.

With the slip-coating method developed and pursued in this study, the microgels were deposited using an in-house-built setup shown schematically in Figure 7.1. The setup comprises a PHD ULTRA syringe pump (Harvard Apparatus, USA) connected via a small capillary tube to a needle tip reaching to the bottom of a coating cell that fastens the membrane. The needle or capillary tube is held about 0.05 mm above the membrane. The particles are infused in uphill and withdrawn from the coating cell to “slip-coat” the membrane on only one side.

Figure 7.1: An in-house-built setup to “slip-coat” latex particles or microgels on one side of ion exchange membranes.

Evaporation-driven convective self-assembly of monodisperse colloids into 2D (i.e., monolayer) or 3D colloidal crystals is widely studied; they represent a new class of self-assembled materials with diverse potential technological applications [187]–[192]. In convective self-assembly, an ordered array of colloidal nanospheres is generated in a process, whereby dispersed particles are convectively transported to the meniscus of a
wetting substrate and locked in place by the lateral capillary forces at the contact line of a drying front (see Figure 7.2). Several forces influence the self-assembly of fine particles in a dip-coating process, such as electrostatic forces, Van der Waals forces, capillary forces and hydrodynamic forces.

Consequently, precise control on the thickness and order of the crystal can only be achieved by fine-tuning a number of physico-chemical and process parameters. These parameters include the choice of substrate material, slanting angle of the substrate with respect to the liquid-air interface, ambient temperature, relative humidity, the concentration of colloids and evaporation rate [187], [192], [193]. Additionally, a polydispersity of the particles influences the quality of the obtained monolayer particle array films [194]. For further reading on the convective self-assembly by dip-coating, akin to our slip-coating method here, refer to the pioneering work of Dimitrov and Nagayama [187].

![Figure 7.2: Schematic representation of the convective self-assembly by dip-coating, showing the drying front of a thin wetting film. $v_w$ is the substrate withdrawal rate; $v_c$ is the array growth rate; $j_w$ is the water influx; $j_p$ is the respective particle influx; $j_e$ is the water evaporation flux; and $h$ is the thickness of the array (adapted from ref. [187]).](image)

For a continuous uniform particle deposition on the substrate, Dimitrov and Nagayama [187] suggested a steady-state volumetric flux of the drying front, assuming the withdrawal rate of the substrate to be equal to the particle array growth. Based on the material balance, they derived a simpler expression for the rate of array growth $v_c$ given
by Equation (7.1), from which the rate of withdrawal of the substrate needed to obtain a specific packing texture can be derived.

\[ v_c = \frac{\beta J_e \varphi}{h(1 - \epsilon)(1 - \varphi)} \]  

(7.1)

where \( v_c \) is the rate of withdrawal; \( l \) is the length of the drying substrate; \( J_e \) is the rate of evaporation of the solvent; \( \varphi \) is the particle volume fraction; \( \beta \) is a proportionality constant between the mean solvent and particle velocity dependent on the extent of interaction of the particles with the solvent; \( \epsilon \) is the porosity of the array; and \( h \) is the height of the deposited colloidal crystals.

Recently Yan et al. [194], in addition, found that strong Coulombic interactions between substrates and colloidal spheres of opposite charge hinder the mobility of the particles during convective self-assembly. Conversely, ordered packing of the particles was observed on substrates of the same charge as the particles. In our case, we similarly observed that it was more difficult to form ordered colloidal arrays from the positively-charged qP2VP microgels on the negatively-charged membrane CMX. Hence, the strategy pursued here is to assemble a dense layer of uncharged P2VP latex particles and introduce charges by post-deposition quaternization in the gas phase. The functionalization was carried out using methyl iodide vapor according to the scheme shown in Figure 7.3.

**Figure 7.3:** Schematic of the post-modification of self-assembled P2VP spheres in the gas phase using methyl iodide vapor to obtain positively-charged qP2VP microgels (scheme by Rahul Tiwari).

For the deposition of the P2VP particles, the parameters shown in Table 7.1 were varied, which were in the range reported in the literature for self-assembly of colloidal par-
articles by dip-coating [191]. As a result, the best confluent monolayer was obtained for
the following conditions: sol concentration of 0.5 wt%, sonicated for 40 min and depos-
ited at 10° slanting angle of the stage holding the coating cell, with a hold time of
4 min, and a withdrawal rate equivalent to 0.1 mm/s. This result was fairly reproducible.
As mentioned before, one of the main factors that strongly influence the self-
assembly process is the stability of the dispersion. Hence to ensure reproducibility, son-
ication of the latex particles immediately before the deposition is a must. As an addi-
tional measure, cautious slow filtration of the dispersion to remove large aggregates is
also possible.

Table 7.1: Physico-chemical and process parameters varied to deposit P2VP latex nanoparticles on the
commercial cation exchange membrane CMX.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
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<td>Sol concentration</td>
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</tr>
<tr>
<td>Sonication time</td>
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</tr>
<tr>
<td>Withdrawal rate</td>
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</tr>
<tr>
<td>Slanting angle</td>
<td>10°</td>
</tr>
<tr>
<td>Hold time</td>
<td>0 min</td>
</tr>
</tbody>
</table>

Figure 7.4(a) and (b) show FE-SEM surface image of the unmodified CMX membrane
and the membrane modified with the P2VP particles, respectively. Figure 7.4(c) zooms
into 10kx magnification displaying arrangement of the particles on the membrane sur-
face, and a Fast Fourier Transform (FFT) analysis of the image (on the inset) reveals
hexagonal packing of the particles. The body of literature on colloidal crystallization is
on smooth planar surfaces. But interestingly, here the particles faithfully adapt to the
somewhat rugged surface of the CMX membrane. The CMX membrane has a rugged
(wavy) surface due to the intertwining fine reinforcing fibers. Finally, and importantly,
a cross-section image (Figure 7.4(d)) reveals the formation of only a monolayer of the
particles.

**Micropatterning a Monolayer of Microgels.** Within the scope of this study, micro-
patterning of polyelectrolytes and microgels on top of ion exchange membranes were
also systematically studied. At first, some experiments were conducted to find more or
less optimal conditions to µCP polyelectrolytes with PDMS stamps. The optimal condi-
tions to print polyelectrolytes (PAH) are illustrated in Chapter 6. To the best of our
knowledge, our previous study [195] reported the first µCP-ed micropatterns on a membrane surface as a substrate.

**Figure 7.4**: Monolayer formation of P2VP nanoparticles on top of the cation exchange membrane CMX using the slip-coating setup. FE-SEM image of (a) the surface of the unmodified CMX membrane; (b) the surface of the CMX membrane modified with a monolayer of P2VP particles; (c) higher magnification of the surface of the modified membrane revealing hexagonal packing of the particles (FFT analysis on the inset) and (d) cross-section of the modified membrane showing formation of only a monolayer of the particles. The image Figure 6.5(d) was taken by Rahul Tiwari.

Based on the experiments with polyelectrolytes, the PDMS stamps were at first treated with a 50 W O₂ plasma for 2 min. Then coated with the first polyelectrolyte layer for 1 h, and then coated with the second polyelectrolyte layer for 30 min, after which the PDMS stamps were soaked with the 1 wt% sol of P2VP particles for 30 min. Afterwards, the stamps were rinsed very briefly with ultrapure water and dried. Finally, the particles were transferred onto the CMX membrane by pressing at 200 g/cm² for 30 min. A schematic representation of the µCP of the P2VP particles is shown in Figure 7.5. It is not clear at this stage whether the polyelectrolytes also get transferred with the particles. For polyelectrolytes only, multilayer transfer printing is possible [62], i.e., an entire polyelectrolyte multilayer assembled on a PDMS stamp can be transferred onto a substrate provided that the interaction of the first polyelectrolyte layer with the PDMS is finely tuned and conducive conditions are maintained for the printing.
Three different experiments were performed. Figure 7.6 shows that a decent amount of P2VP particles are taken up by the PDMS stamp or transferred onto the CMX when the PDMS is inked beforehand with one bilayer of PEI/PSS. The P2VP particles are transferred in an aggregated state when the PDMS is primed with one bilayer of PAH/PAA, and few particles are transferred when not using polyelectrolytes to prime the PDMS (see Figure A7.2 and Figure A7.3 in the Appendix, respectively). It might be possible to obtain micropatterns each with denser (higher number of) microgels by µCP using porous stamps prepared by a method called phase separation micromolding (PSµM) [196], [197], details of which can be found in the Appendix 7.5.1.

Figure 7.5: Schematic of µCP of P2VP particles on CMX membranes using PDMS stamp primed with one bilayer of PEI/PSS.

Figure 7.6: FE-SEM image of (a) micropatterns of P2VP particles printed on the CMX membrane using PDMS stamp primed with one bilayer of PEI/PSS; (b) a higher magnification of one of the micropatterns with the primary particles visible; (c) the PDMS stamp and (d) a higher magnification of the one of the pillars of the stamp showing the adsorbed P2VP particles.
In the following sections, preliminary electrochemical characterization of some membranes will be presented, which were modified with the modification methods developed in this study.

### 7.3.2 Polarization Behavior and Monovalent Ion Permselectivity

**Polarization Behavior.** We demonstrated in a previous study [195] that judiciously-selected homogeneous layers of polyelectrolytes and particularly their lateral micropatterns hasten the onset of the overlimiting current by electroconvection. As an extension, this preliminary work also attempts at studying the influence of patterned microgels on the polarization behavior of cation exchange membranes. Four different membranes were compared: the unmodified CMX membrane, the CMX membrane modified with a confluent monolayer of P2VP and qP2VP particles, as well as the CMX membrane modified with micropatterned P2VP particles – circular patterns 50 µm in diameter and 25 µm apart (edge-to-edge). The confluent monolayers and the micropatterns were formed according to the methods described in Section 7.3.1. Figure 7.7 shows *i*–*V* curves of the membranes corrected for their ohmic resistances and with the scatter of the overlimiting values averaged out. Their characteristic polarization values are listed in Table 7.2.

![Figure 7.7: *i*–*V* performance of the unmodified CMX membrane, and the CMX membrane modified with a confluent monolayer of P2VP particles (Conf. P2VP) and a confluent monolayer of qP2VP microgels (Conf. qP2VP) and micropatterned monolayer of P2VP particles (µCP P2VP). The *i*–*V* curves were obtained in 0.1 M NaCl solution.](image-url)
Table 7.2: Polarization characteristics of the unmodified CMX membrane and the CMX membrane modified with the microgel qP2VP and its precursor P2VP

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$R_{\text{Ohmic}}$ [Ω·cm$^2$]</th>
<th>$i_{\text{lim}}$ [mA/cm$^2$]</th>
<th>Plateau length [V]</th>
<th>% of current carried by OH$^-$ ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified CMX</td>
<td>66</td>
<td>16.2</td>
<td>0.75</td>
<td>1.57x10$^{-4}$</td>
</tr>
<tr>
<td>Confluent P2VP</td>
<td>62.5</td>
<td>15.8</td>
<td>0.92</td>
<td>1.7x10$^{-3}$</td>
</tr>
<tr>
<td>Confluent qP2VP</td>
<td>55.2</td>
<td>17.6</td>
<td>2.4</td>
<td>4.65</td>
</tr>
<tr>
<td>µCP P2VP</td>
<td>48.5</td>
<td>25.6</td>
<td>0.77</td>
<td>6.63x10$^{-5}$</td>
</tr>
</tbody>
</table>

$^a$ The unmodified CMX membrane, and the CMX membrane modified with a confluent monolayer of P2VP particles (Conf. P2VP) and a confluent monolayer of qP2VP microgels (Confl. qP2VP) and micropatterned monolayer of P2VP particles (µCP P2VP).

$^b$ Ohmic resistance of the membrane/electrolyte systems.

$^c$ Limiting current density.

In comparison with the unmodified CMX membrane, the membrane modified with micropatterns of P2VP particles (µCP P2VP) stands out having significantly reduced the ohmic resistance of the membrane systems and resulting in a significantly higher limiting current density. Here, the ohmic resistance of the membrane systems decreased by ~27% and the limiting current density increased by ~60%.

To determine the plateau length of the membranes, the transition from the limiting to the overlimiting current was defined according to a mathematical sigmoid method recently reported by Doyen et al. [198], which offers a less-subjective and less-ambiguous alternative to the conventional methods.

In terms of the plateau length, the membrane modified with the micropatterned P2VP particles (µCP P2VP) had a plateau length similar to the unmodified membrane. The confluent qP2VP membrane shows a rather unusually large plateau length of 2.4 V. This large plateau length may have been caused by the high degree of swelling of the qP2VP microgels film (3.5 folds for qP2VP in comparison with 1.5 folds for P2VP [199]). The swollen microgels could potentially narrow the interstices in the hexagonal packing rendering the membrane surface more homogeneous. One important factor that contributes to the overlimiting conductance by electroconvection is the surface heterogeneity, which facilitates electroconvection by creating a non-uniform distribution of the space charge region [39]. Therefore, masking of the original surface heterogeneity of the unmodified CMX membrane by the thin layer of qP2VP microgels partially impairs the initiation of the electroconvective vortices. Similar results of broadening of the
plateau length or even a complete elimination of the overlimiting conductance were reported by Rubinstein et al. [160] for cation exchange membranes modified with a thin layer of poly(vinyl alcohol).

Whereas all the other membranes showed insignificantly low water dissociation, for the membrane modified with a confluent layer of qP2VP microgels (Conf. qP2VP), the percentage of the current carried by water dissociation products amounted to 4.65% during the course of the \( i-V \) experiment. This may provide an indirect proof of the successful quaternization of the assembled P2VP particles in the gas phase. Normally, cation exchange membranes cause hardly any water splitting while anion exchange membranes do at overlimiting currents due to the interaction of water molecules with the quaternary ammonium groups of the anion exchange membranes [71], [152], [166]. The water dissociation was suggested to be brought about by an electric field-enhanced catalytic protonation and deprotonation reaction of weakly basic groups, such as tertiary and secondary amines. Quaternary ammonium groups can at high electric fields degrade to tertiary and secondary amines to become more reactive [70], [71]. In monopolar membranes, this water dissociation is thought to take place within a thin catalytic interface layer with a thickness of about 2 nm at the depleted solution/membrane interface [39].

The fact that the membrane modified with the micropatterned P2VP (µCP P2VP) particles did not cause any water dissociation may also indicate that the PEI polyelectrolytes are possibly not transferred along with the particles. The hyperbranched PEI polyelectrolyte comprises plenty of tertiary and secondary amines, with a single homogeneous layer of the polyelectrolyte sufficient to result in a noticeable water splitting [195].

**Monovalent Ion Permselectivity.** Polyelectrolytes were demonstrated as promising materials to induce monovalent ion permselectivity in standard cation exchange membranes [168]. Six bilayers of polyelectrolytes were required on CMX to achieve monovalent ion selectivity comparable to that of a commercial monovalent-ion-permselective membrane CMS (see Table 7.3). The decisive advantage being the lower energy consumption required with polyelectrolyte-modified CMX membrane – about half as much. The use of microgels, on the other hand, may offer the comparative advantage of forming a relatively thicker active separation layer on the surface of ion exchange membranes per deposition step.
The monovalent ion permselectivity was determined according to the method described in Chapter 3. In terms of performance, Table 7.3 shows that the monovalent ion permselectivity of the CMX membrane is improved by applying a single monolayer coating of qP2VP microgels, although not to the degree of the six bilayers of polyelectrolytes. The assembled monolayer was the densest which could be achieved, albeit the presence of interstitial spaces in the hexagonal packing. Due to the high degree of swelling of the quaternized microgels film (as noted above), it is likely that the neighboring particles narrow the interparticle spaces and forming some kind of wrinkled thin film. A logical follow-up to improve this performance is thus to form multilayers of the microgels with polyelectrolytes as “glue” layers in between [200]. Or in spite of the interparticle spaces, electrostatic repulsion towards divalent ions may be ensured by highly charged qP2VP microgels. Therefore, it is as well necessary to test the permselectivity performance at different quaternization reaction times. Conversions of up to 90% were demonstrated in this project for microgels prepared by click-type chemistry [64]. Conversions of the microgels prepared by quaternizing in the gas phase have to, however, be yet determined.

Table 7.3: Monovalent ion permselectivity of the CMX cation exchange membrane modified with microgels compared versus with polyelectrolyte multilayers, for a feed solution comprising a mixture of 0.05 M NaCl and 0.05 M CaCl₂

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( \frac{p_{Na}^{Na}}{p_{Ca}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMX</td>
<td>0.64</td>
</tr>
<tr>
<td>CMS</td>
<td>1.23</td>
</tr>
<tr>
<td>CMX(/PEI/PSS)₆ᵃ</td>
<td>1.24</td>
</tr>
<tr>
<td>CMX/qP2VPᵇ</td>
<td>0.9</td>
</tr>
</tbody>
</table>

ᵃCMX modified with 6.5 bilayers of PEI/PSS polyelectrolytes  
ᵇCMX modified with a confluent monolayer of qP2VP microgels

### 7.3.3 Water Dissociation Behavior in Bipolar Membranes

Some preliminary experiments were also conducted with bipolar membranes whose interface layers were modified with microgels. The bipolar membranes were assembled by hot-pressing two commercial monopolar ion exchange membranes: the anion exchange membrane FAA and the cation exchange membrane FKB. The membranes were pressed at 90 bar and 120 °C for 10 min using a hot press (Agila, Belgium). The microgels were beforehand adsorbed onto the surface of the monopolar membranes on only one side using the slip-coating setup. The anionic microgel PMAA was used to modify
the FAA and the cationic microgel qP2VP to modify FKB. For the latter, P2VP was first deposited and quaternized to qP2VP in the gas phase.

Figure 7.8 presents the $i$–$V$ performance of the membranes characterized in 2 M NaCl. The membranes were characterized using the six-compartment setup with the arrangement of the membranes in the module as shown in Chapter 4. The membrane prepared from only the anion- and the cation exchange layer without the microgels shows the typical $i$–$V$ response of a bipolar membrane. It shows a small linear ohmic region, followed by a plateau and subsequent steep rise in the current representing the area of active water dissociation in the curve. This membrane has a relatively high electrical resistance compared with commercial benchmarks. At 100 mA/cm$^2$ current density, this membrane has a voltage drop of ~6.3 V versus ~2.3 V for the commercial bipolar membrane FBM (FuMA-Tech, Germany) [119].

Adding the anionic microgel deposited on the anionic layer slightly decreases the electrical resistance of the bipolar membrane. The PMAA microgels could not be identified on the membrane surface with FE-SEM. If any, the decrease in the electrical resistance is probably because of the weak carboxylic acid groups of the microgel catalytic to water splitting [24].

The bipolar membrane composed by depositing the cationic microgel on the cation exchange layer still exhibits the typical $i$–$V$ profile of a bipolar membrane but with pro-
hibitively high electrical resistance. At moderately-high current densities, the curve even shows a second plateau indicating the drying out of the membrane, i.e., not enough water is reaching the interface to replenish the water consumed in the water dissociation reaction, presumably caused by the thick dense microgel layers. This probably goes to show that not only the anion- and the cation exchange layers determine the diffusive water transport to the bipolar interface, but also the intermediate layer indirectly influences the water supply, because it affects the electric field present at the bipolar interface [16].

Therefore these preliminary experiments, supported by the separate study with polyelectrolytes [119] clearly indicate that it is reasonable to focus the efforts on modifying the anion exchange layer of bipolar membranes. In the study with the polyelectrolytes, it was shown that coating the anion exchange layer of a bipolar membrane rather than the cation exchange layer yields better performance. In this regard, adhesion of the anionic microgel to the anion exchange membrane should be improved. Tuning the size and charge density of the microgels and the possibility of introducing transition or noble metal salts as counterions of the microgel may enhance the performance.

7.4 Conclusions

This work explored the potential application of aqueous polyelectrolyte microgels to modify the surface/interface of ion exchange membranes. Methods were developed to modify the surface of the ion exchange membranes with patterned monolayers of microgels – both confluent dense and micropatterned. A two-step procedure was employed to form the confluent monolayers of microgels: convective self-assembly of microgel precursor latex particles by a method similar to dip-coating and introducing the charges post-deposition in the gas phase by quaternization to obtain the charged polyelectrolyte microgels. The micropatterns were formed by microcontact printing with PDMS stamps primed with polyelectrolytes.

Preliminary experiments were performed to characterize the performance of the modified membranes. Particularly promising is that a 60% increase in the limiting current density of the commercial cation exchange membrane CMX was obtained by modifying its surface with micropatterned monolayers of P2VP nanospheres, and the same cation exchange membrane modified with a dense confluent monolayer of positively-charged qP2VP microgels showed an increased monovalent ion permselectivity. The potential of
the polyelectrolyte microgels to catalyze water dissociation at the interface of bipolar membranes has to be thoroughly studied further.

These preliminary performance tests show promising results. The possibility of synthesizing the microgels in various sizes, charge density and with different counterions along with the precise control over the state of their deposition will enable the rational optimization of the performances. Further outlook is also testing the performance of the membranes in response to external stimuli.
7.5 Appendix for Chapter 7

7.5.1 Micropatterning a Monolayer of Microgels

Figure A7.1: FE-SEM image of (a) micropatterns of P2VP particles printed on the CMX membrane using PDMS stamp not coated with polyelectrolytes; (b) a higher magnification of one of the micropatterns with the primary particles visible; (c) the PDMS stamp and (d) a higher magnification of one of the pillars of the stamp showing the adsorbed P2VP particles.

Figure A7.2: FE-SEM image of (a) micropatterns of P2VP particles printed on the CMX membrane using PDMS stamp primed with one bilayer of PAH/PAA; (b) a higher magnification of one of the micropatterns with the primary particles visible; (c) the PDMS stamp and (d) a higher magnification of one of the pillars of the stamp showing the adsorbed P2VP particles.
7.5.2 Microcontact Printing using Porous Stamps

It might be possible to obtain micropatterns each with denser microgels by microcontact printing (µCP) using porous stamps prepared by a method called phase separation micromolding (PSµM) [196], [197]. For µCP, unlike the widely-used standard PDMS stamps, porous stamps enable (easier) printing of larger nanoparticles. In addition, porous stamps can be fabricated to have permanent hydrophilicity, and can also act as “ink reservoirs” allowing several prints without the need to reink [197].

Some experiments were performed toward this goal. The porous stamps were prepared from a polymer dope solution comprising 19% polyetherimide (PEI), 11% polyvinylpyrrolidone – both dissolved in NMP and using water as a non-solvent for phase separation [197]. Figure A7.3(a) shows a cross-section FE-SEM image of one such porous stamps with uniform interconnected pores of about 2 µm. A proof of principle of µCP of a relatively dense monolayer of P2VP particles was also demonstrated on a glass substrate using one of the porous stamps (Figure A7.3(b)).

The challenge here was obtaining porous stamps with solid pillars to be able to imprint the micropatterns. Collapsed pillars are known to be formed as a result of the entrapment of air bubbles in the wells of the silicon molds during casting [162]. Therefore, some parameters were varied to counteract this effect and the resulting stamps are shown in Figure A6.4. Though not reproducible, solid pillars could be formed by casting the polymer at room temperature, and by subsequently allowing the cast film to degas at 90 mbar for 1 h in N₂ atmosphere before the phase separation, then drying it at room temperature (see Figure A7.5).

Figure A7.3: FE-SEM image of (a) cross-section of a porous stamp with uniform interconnected pores (b) relatively dense monolayer of P2VP particles printed on a glass substrate using a porous stamp.
7.5.3 Preparation of Porous Stamps with Solid Pillars

(a) Effect of casting temperature (5 min waiting time before phase separation)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temp</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>50 °C</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>100 °C</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
</tbody>
</table>

(b) Effect of waiting before phase separation (casting at room temperature)

<table>
<thead>
<tr>
<th>Waiting Time</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>1 h</td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>24 h</td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure A7.4: Effect of (a) casting temperature and (b) waiting time before phase separation on the preparation of porous stamps using PSpM. Minimal effect of casting temperature and waiting time before phase separation was observed in forming solid pillars.

Figure A7.5: SEM image of a porous stamp with solid pillars.
Chapter 8

Summary and Conclusions

The work at hand investigated the surface/interface modification of both monopolar and bipolar ion exchange membranes for electrodialysis applications. The ion transport phenomena investigated in this thesis are particularly influenced by the state of the membrane surface/interface. The phenomena studied are overlimiting mass transfer through electrodialysis membranes, monovalent ion permselectivity of cation exchange membranes and water dissociation catalysis at the interface of bipolar membranes. For the non-covalent surface modification of the membranes, two classes of materials are applied: polyelectrolyte multilayers and microgels.

Chapter 1 gives a general introduction and outlines the need for surface modification of ion exchange membranes. Chapter 2 discusses briefly ion exchange membranes – their structure, properties, preparation methods and applications; and about polyelectrolyte multilayers and microgels.

In the Results part of the thesis, polyelectrolyte multilayers, and microgels are successfully implemented – as homogeneous- and micropatterned layers – to tailor the interface of ion exchange membranes without any prior treatment of the membranes. Their depositions are subsequently characterized with several surface analytical techniques.

Chapter 4 investigates the layer-by-layer (LbL) deposition of polyelectrolyte multilayers as a tool to introduce molecularly thin catalyst groups at this interface of bipolar membranes. The bipolar membranes are prepared by first modifying an anion exchange membrane by consecutive dipping LbL assembly, then casting a thin highly charged intermediate layer followed by casting a cation exchange layer. The results reveal that polyelectrolytes of higher charge density coated on the anion exchange layer yield better performance. Several parameters of the LbL interface deposition are varied. Out of the investigated LbL assembly parameters, ionic strength and number of layers show the largest influence on catalytic activity as well as ionic selectivity. The membrane
with two bilayers of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and poly(ethyleneimine) (PEI), where the PEI was prepared in 0.5 M NaCl, gives rise to the best performance. Surprisingly, detailed data analysis at low electrical potential suggests that the interface layers of a bipolar membrane play a major role in its permselectivity. Previously, only the bulk thickness of the anion and cation exchange membrane was assumed to influence the bipolar membrane selectivity.

**Chapter 5** studies the possibility of inducing monovalent ion permselectivity on standard cation exchange membranes by the layer-by-layer (LbL) assembly of poly(ethyleneimine) (PEI)/poly(styrenesulfonate) (PSS) polyelectrolyte multilayers. Coating of the (PEI/PSS)$_N$ LbL multilayers on the commercial CMX membrane cause only moderate variation of the ohmic resistance of the membrane systems. Nonetheless, the polyelectrolyte multilayers have a substantial influence on the monovalent ion permselectivity of the membranes. Permselectivity comparable to that of a commercial monovalent-ion-permselective membrane is obtained with only six bilayers of polyelectrolytes, yet with significantly lower energy consumption per mole of Na$^+$ ions transported through the membranes. The monovalent ion permselectivity stems from an increased Donnan exclusion for divalent ions and hydrophobization of the surface of the membranes concomitant to their modification. Double-layer capacitance obtained from impedance measurements shows a qualitative indication of the divalent ion repulsion of the membranes.

At overlimiting current densities, water dissociation occurs at membranes with PEI-terminated layers and increases with the number of layers, while it is nearly absent for the PSS-terminated layers. Hence, LbL layers allow switching on and turning off water splitting at the surface of ion exchange membranes. There are applications in which ion permselectivity and pH regulation are needed at the same time; our LbL-modified ion exchange membranes could be a key to such symbiosis.

**Chapter 6** deals with overlimiting mass transfer through electrodialysis membranes that sets in beyond the theoretical limitation of concentration polarization. Overlimiting current is mainly driven by the formation of electroconvective vortices destabilizing the stable boundary layer (depleted of ions) in the vicinity of ion exchange membranes. Little is known whether these instabilities can be induced and affected by chemical topological heterogeneity in surface properties. This chapter attempts to answer the question whether polyelectrolytes can also be utilized to modulate overlimiting current phenomena in electrodialysis membranes.
This study proves that controlled adsorption of polyelectrolyte multilayers (with well-defined ionic macromolecular properties) at the interface between the ionic solution and membrane surface triggers a significantly earlier onset of electroconvection at lower polarization potential. It further proves that their uniform regio-selective adsorption imposed by microcontact printing is even more effective, and enhances macroscopic electro-osmotic chaotic fluid instabilities. These surface manipulations will have significant implications for the operational opportunities of electrodialysis desalination and microfluidic processes.

Chapter 7 is on an exploratory study of the potential application of aqueous particulate microgels to modify the surface/interface of ion exchange membranes. Within the scope of the study, methods are developed to modify the surface of ion exchange membranes both with confluent- and micropatterned monolayers of microgels. A two-step procedure is employed to form the confluent monolayers of microgels: convective self-assembly of microgel precursor latex particles by a method similar to dip-coating and introducing the charges post-deposition in the gas phase by quaternization to obtain the charged polyelectrolyte microgels. The micropatterns are formed by microcontact printing with PDMS stamps that are primed with polyelectrolytes.

Thorough performance tests of the modified membranes are necessary. Some preliminary tests, however, show promising results. Most promising of the results is a 60% increase in the limiting current density of the commercial cation exchange membrane CMX modified with micropatterns of poly (2-vinylpyridine) latex nanoparticles (~200 nm in size), and an increased monovalent ion permselectivity of the same membrane modified with a confluent monolayer of quaternized poly(2-vinylpyridine) microgels. The preliminary results thus demonstrate aqueous microgels as viable materials for the rigorous surface manipulation of ion exchange membranes at the nanometer-scale. The possibility of synthesizing the microgels at various sizes, charge density and with different counterions, along with the precise control over the state of their deposition will enable further optimization of the performances.

Apart from electrodialysis, the findings of this thesis may provide equally valuable insights in other areas of applications of ion exchange membranes, which require membranes with tailored surface properties.
References

Limitations,” University of Twente, Enschede, 1997.


[59] G. Ladam, P. Schaaf, J. C. Voegel, P. Schaaf, G. Decher, and F. Cuisinier, “In Situ Determination of the Structural Properties of Initially Deposited...
References


References


References


R. Kwak, G. Guan, W. K. Peng, and J. Han, “Microscale electrodialysis: Concentration profiling and vortex visualization,” Desalination, no. 0.


