Catalytic Polyelectrolyte Multilayers at the Bipolar Membrane Interface

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Ⓢ Supporting Information

ABSTRACT: Bipolar membranes are laminated anion and cation exchange membranes that split water at their interface very efficiently upon application of an electric field. This paper 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 were 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 were varied. Out of the investigated LbL assembly parameters, ionic strength and number of layers have shown 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, gave 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.

KEYWORDS: electrodialysis, ion exchange membrane, bipolar membrane, layer-by-layer, polyelectrolyte, electrochemistry

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.[1] The potential of the process in new industrial applications has been strongly extended by the development of bipolar membranes.[2] 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 1 shows a schematic of the structure and function of bipolar membranes.[3]

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.[4] The actual mechanism of water splitting is still controversial. There are, however, two theories to explain this phenomenon.
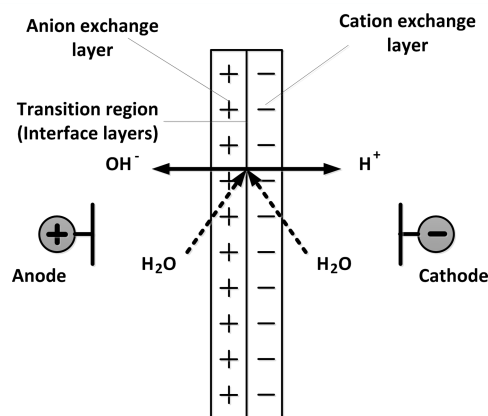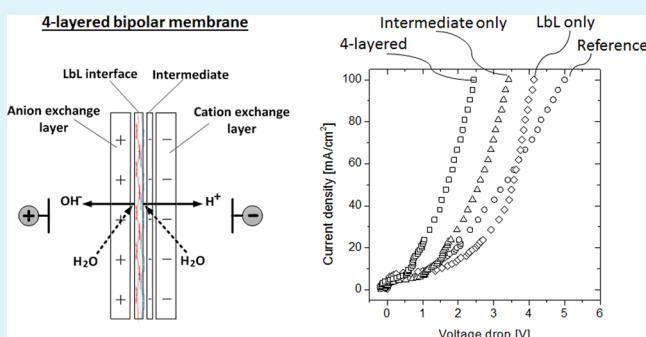
Figure 1. Schematic of the structure and function of bipolar membranes, adapted from ref 3.

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.[5] 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.[4] This led investigators to suggest the so-called proton transfer reaction mechanism, which is strongly supported by theory and experimental evidence.[6] 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[4,7,8]

$$B + H_2O \rightleftharpoons BH^+ + OH^- \tag{1}$$

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+ \tag{2}$$

$$A^- + H_2O \rightleftharpoons AH + OH^- \tag{3}$$

$$AH + H_2O \rightleftharpoons A^- + H_3O^+ \tag{4}$$

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.[9] Catalysts reduce the usually high activation energy of water dissociation, by providing alternative reaction paths, i.e., by forming reactive activated complexes.[7,9]

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,[10] such as suitable phosphoric acids,[11] carboxylic acids,[9] amino acids,[4] or pyridines.[12] As alternative catalyst types, immobilized heavy metal ion complexes like those of iron, chromium, zirconium, or others could be utilized.[13,14] They are immobilized by placing their insoluble salts in the intermediate layer or using a soluble salt with a subsequent treatment.[9] Hydroxides of the most suitable multivalent metal ions are immobilized due to their low solubility.[9] 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.[15]

To demonstrate the catalytic activity of different macromolecules, a series of fundamental studies have been carried out by Xu and co-workers[16−20] 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)[16] and polyvinyl alcohol (PVA),[17] polyamphoteric bovine serum albumin (BSA),[18] a dendrimer molecule polyamidoamine (PAMAM) which possesses higher amino groups,[19] and hyperbranched aliphatic polyesters of the Boltorn series.[20]

The catalysts can be immobilized before or after the film formation. There have been several methods applied: spray or dip-coating,[21] incorporating in the polymer material by even dispersion,[3] by electrochemical methods after formation of the layers or by in situ polymerization,[22] electrospray deposition,[23] etc. There exist also reports of some polymer materials which inherently contain the required catalytic functional groups in their repeating units.[3]

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.[24] 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 polycations, to form multilayers with properties controllable on the nanoscale. To the best of our knowledge, this is the first paper 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.

2. EXPERIMENTAL SECTION

2.1. Materials. The membranes used in the experiments were either the commercial membranes Fumasep (obtained from FuMA-Tech, Germany) or tailor-made membranes. The properties of the commercial membranes are shown in Table 1.

**Table 1. Properties of the Used Commercial Ion Exchange Membranes, As Provided by the Manufacturer**

name	type	IEC (meq/g)	thickness (mm)	area resistance (Ω cm²)	selectivity (%)
FBM	BPM, PEEK monofil reinforced	-	0.2−0.25	<3	
FKB	CEM, PEEK reinforced	0.9−1.0	0.08−0.10	<4	
FAA	AEM, PEEK reinforced	>1.2	0.13−0.15	<2	>92

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 PEEK powder (450PF, Victrex) to prepare the SPEEK 1.8 was carried out according to a method described elsewhere.[3] N-Methyl-2-pyrrolidone (NMP), obtained from Merck, Germany, was used to dissolve the polymers. The LbL interface layers were formed from different polyelectrolytes:poly(ethyleneimine) (PEI), MW = 750 000 g/mol, polydiallyldimethylammonium 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). The polyelectrolytes were all obtained from Sigma Aldrich.

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
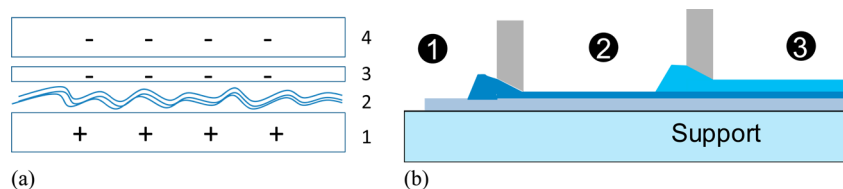
Figure 2. (a) Schematic of the composition of the four-layered tailor-made bipolar membrane. 1. Anion exchange layer. 2. LbL interface layer. 3. Intermediate layer. 4. Cation exchange layer. (b) Steps of preparing the tailor-made bipolar membrane by the casting/evaporation method: 1. Modification of anion exchange layer by LbL assembly. 2. Casting of intermediate layer. 3. Casting of cation exchange layer.
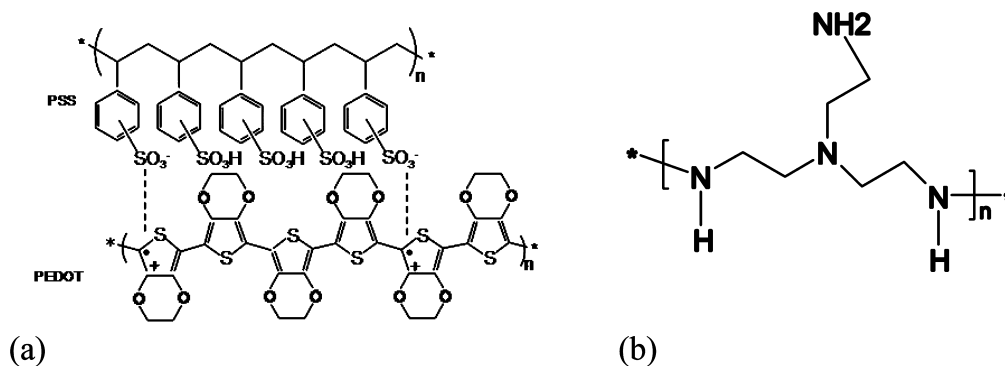
Figure 3. Chemical structures of (a) poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) and (b) hyperbranched poly(ethyleneimine) (PEI).

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 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 2(b).

The *cation exchange* layer was cast from a 20 wt % blend of SPEEK 1.4 and PES in 60:40 weight ratio.[25] 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 a water dissociation reaction. Their chemical structures are shown in Figure 3(a) and (b), respectively.

To introduce the polyelectrolyte interface layers, the FAA membrane was 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 by the LbL assembly method, by sequential dipping of the FAA membrane 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.

2.3. Characterization of the Monopolar Layers. The deposition of the polyelectrolyte layers was monitored by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Thermo Nicolet, Nexus 470) and X-ray photoelectron spectroscopy (XPS) (Kratos Analytical, Axis Ultra). Furthermore, permselectivity of the monopolar layers was checked by static permselectivity measurement, by measuring the potential drop across the monopolar layers placed between 0.1 and 0.5 M KCl solutions.

2.4. 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 a six-compartment electrodialytic cell shown schematically in Figure 4. The membrane to be measured is placed in the middle of the cell. The other membranes are auxiliary membranes, used to limit interference of the electrode reactions on the measurement.

The electrical resistance was measured using the four-point method: two working electrodes were used to apply the current while the potential drop across the membrane was measured using two reference electrodes. The reference electrodes were extended to a point as close to the membrane surface as possible using Haber−Luggin capillaries.

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. During the experiments the temperature was maintained at 25 °C, and the applied current density was increased stepwise,
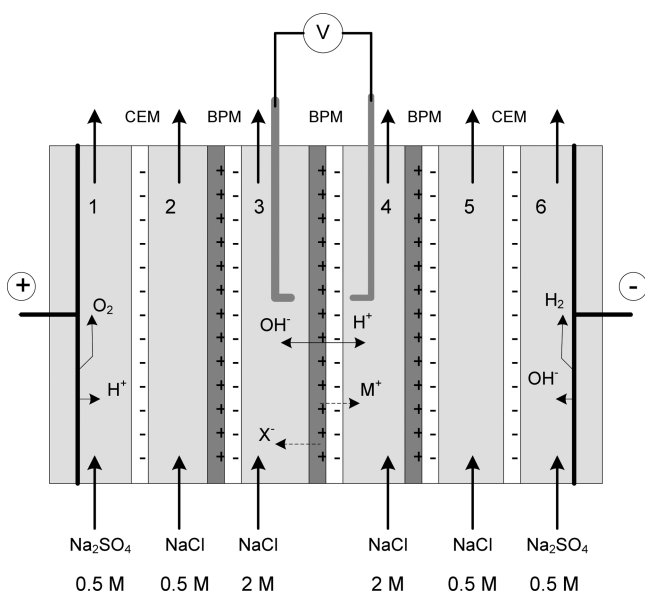
Figure 4. Schematic representation of a six-compartment measurement module for the measurement of electrical resistance of membranes.

every 30 s, to allow the membrane to reach a steady state. Most of the results are an average of three runs; the average standard deviation was observed to be within 5%.

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 5, with current density per unit active membrane area on the y-axis and the electrical potential drop across the membrane on the x-axis.
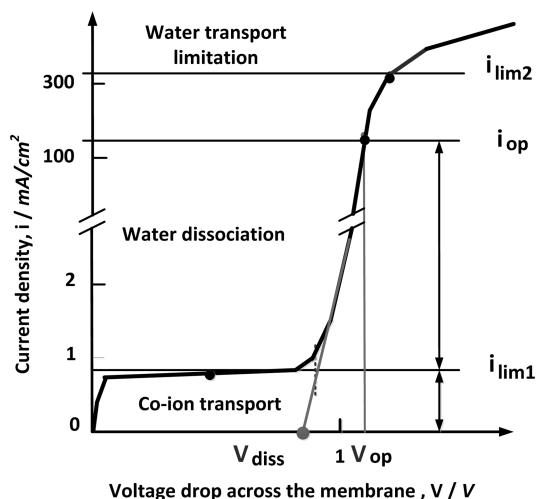
Figure 5. Typical steady-state current–voltage curve of bipolar membranes, adapted from refs 3 and 26.

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_{lim1}); 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 for 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[27,28]

$$J_{M^+}^{lim} = \frac{D_{M^+,AEL}(c^s)^2}{d_{wet,AEL}c_{char,AEL}}, \qquad J_{X^-}^{lim} = \frac{D_{X^-,CEL}(c^s)^2}{d_{wet,CEL}c_{char,CEL}} \qquad (5)$$

$$i_{lim\,1} = F\left(\frac{D_{M^+,AEL}(c^s)^2}{d_{wet,AEL}c_{char,AEL}} + \frac{D_{X^-,CEL}(c^s)^2}{d_{wet,CEL}c_{char,CEL}}\right) \qquad (6)$$

where J^{lim} is the flux of co-ions; i_{lim1} is the first limiting current density; C^s is the solution concentration; D is the diffusion coefficient; d_{wet} is the wet thickness of the ion exchange layers; C_{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_{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_{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_{lim2}),[29] 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.[30]

3. 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 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.

3.1. Monitoring the Deposition of Polyelectrolyte Layers. In Figure 6(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 6(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
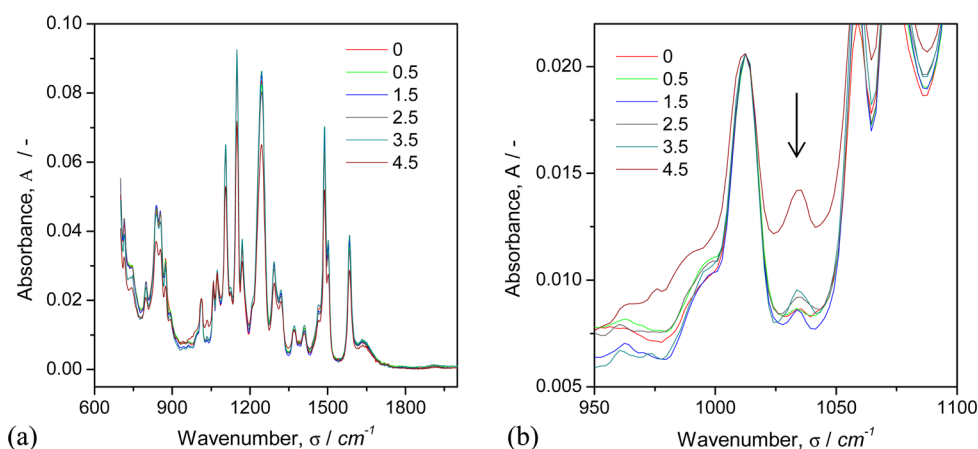
Figure 6. FTIR spectra of the FAA membrane coated with polyelectrolyte multilayers formed from PEDOT:PSS and PEI: (a) whole spectra and (b) zoomed to wavenumbers around 1033 cm^{-1}. Indicated in the legends are the number of bilayers, 0 being the pristine FAA membrane.

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 2), it can be seen that there is an increase in the O-

Table 2. Elemental Analysis of XPS Data of FAA Coated with PEDOT:PSS

			atomic conc. (%)	
peak		position BE (eV)	pristine FAA	FAA coated with PEDOT:PSS
O	1s	532.00	10.11	15.64
S	2p	168.50	2.25	3.77
C	1s	285.00	81.20	74.55

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.

3.2. Morphology Characterization of the Membranes. Morphology of the four-layered bipolar membranes was characterized using FE-SEM (Hitachi, S-4800). Figure 7(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 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 of the anion exchange layer, to visually confirm their deposition using FE-SEM (Figure 7(b)). In addition to the ATR-FTIR and XPS measurements, FE-SEM provided supplementary evidence of the presence of the LbL interface layers.

3.3. 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 8, which shows the comparison of the various membranes studied compared on their voltage drop at constant current density of 40 mA/cm^2. The membrane voltage drops were read off their respective $i-V$ curves. It can be seen from Figure 8 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
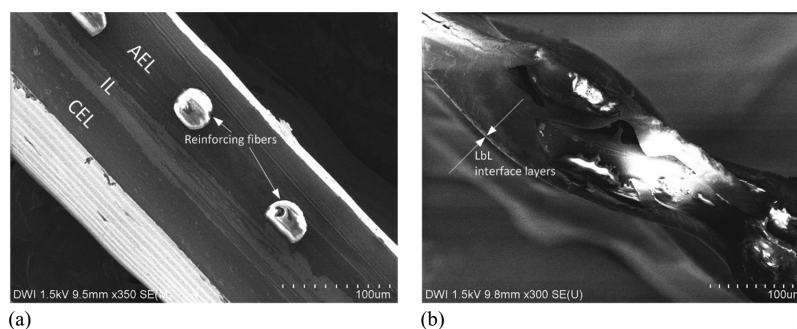
Figure 7. FE-SEM micrographs of a (a) four-layered bipolar membrane. Indicated on the micrograph: AEL, anion exchange layer; IL, intermediate layer; and CEL, cation exchange layer. (b) LbL interface layers atop of a reinforced FAA membrane without the cation exchange layer.
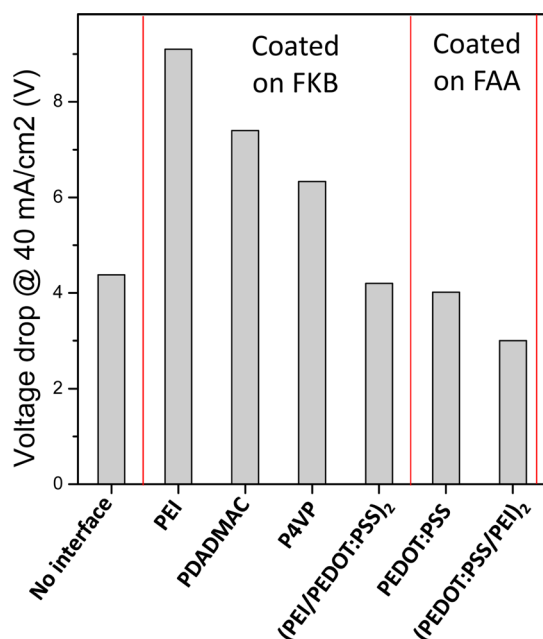
Figure 8. Bipolar membranes composed of two laminated commercial ion exchange membranes, FAA and FKB (FuMA-Tech, Germany), and a combination of a number of polyelectrolytes as interface layers.

slight decrease in the electrical resistance. PEDOT:PSS bears sulfonic acid groups, which in itself are not catalytic to water dissociation reaction.[31]

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 four single polyelectrolyte layers). It is noteworthy that coating the same bilayers on FKB (now (PEDOT:PSS/PEI)$_2$), however, showed increased electrical resistance.

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,[32,33] 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.

**3.4. 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.[34] From previous studies, particularly from the work of Balster et al.,[3] 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.[6] Hence, FAA was chosen for LbL modification for all the experiments, due to it being alkali stable and because it bears quaternary ammonium groups,[34] which are important factors when preparing high-performance bipolar membranes.

Figure 9 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_{lim1} plateau is flatter (Figure 9(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.[35] These functional groups facilitate the proton transfer between water molecules and the fixed ion
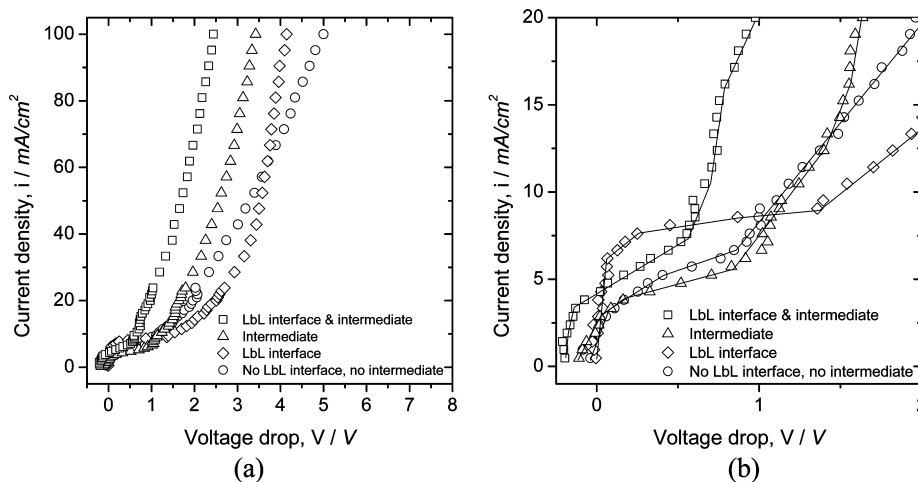
Figure 9. Effect of the addition of intermediate and interface layers and their combined effect on the electrical resistance of tailor-made bipolar membranes, characterized in 2 M NaCl solution. The LbL interface was made up of two bilayers of PEDOT:PSS/PEI coated on the FAA. (a) Complete curve. (b) Lower current density region; lines added to the data points to guide the eyes.
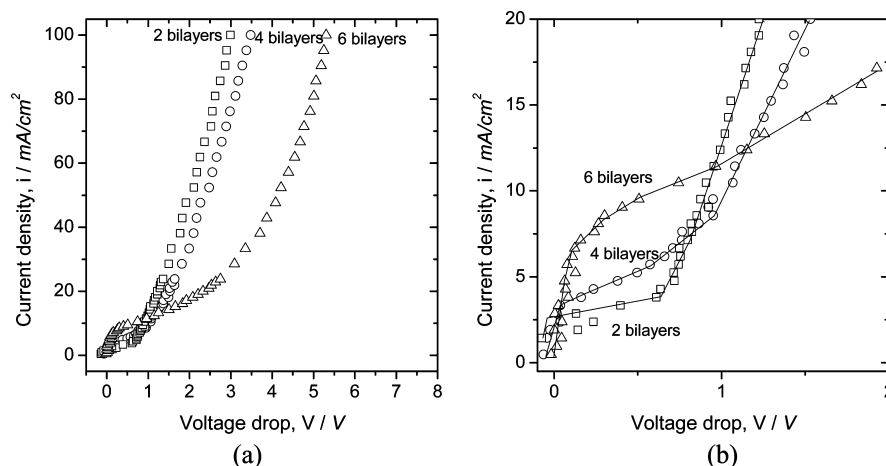
Figure 10. Effect of the number of the deposited polyelectrolyte layers on the electrical resistance of tailor-made bipolar membranes, characterized in 2 M NaCl solution. The LbL interface layers were made up of PEDOT:PSS and PEI. (a) Complete curve. (b) Lower current density regime; lines added to the data points to guide the eyes.

exchange groups of the anion exchange layer. These rapid protonation and deprotonation reactions proceed according to the reaction schemes in eqs 1 and 2 as proposed by Simons.[7] 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 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 1S of the Supporting Information).

3.5. Synergy of LbL Interface Layers with Highly Charged Intermediate Layer.
Balster et al.[3] 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 1.8 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 9. This is a clear indication that the thin 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.[13] 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.[13]

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/cm² 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 catalyzed 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.

3.6. 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.[22]

Figure 10 shows $i-V$ curves of the bipolar membranes with two, four, and six bilayers of PEDOT:PSS/PEI. From Figure 10(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_{diss}) as well as the lowest operating electrical resistance (R_{op}), approximated at a current density of 100 mA/cm². The trend observed was that increasing the number of layers will increase the electrical resistance of the bipolar membranes. The V_{diss} and R_{op} of the membranes are

summarized in Table 3. Furthermore, Table 3 shows that the relationship between the number of layers and the water

Table 3. Variation of Water Dissociation Potentials and R_{op} with the Number of Interface Layers[a]

	two bilayers	four bilayers	six bilayers
V_{diss} (V)	1.4	1.7	3.6
R_{op} ($\Omega \cdot cm^2$)	30	36	54

[a]Approximate values given here obtained from the i−V curves in Figure 10.

splitting potential (V_{diss}) does not correlate linearly. The difference in the water splitting potential (V_{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.

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 effective contact area (A_{eff}) and the bipolar junction thickness (2λ), a notion used by Alcaraz et al.[36] 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.[37]

In previous publications, scanning electron micrographs and X-ray spectrometry show that the typical thickness of the contact region is on the level of micrometers.[38,39] Nonetheless, this distance does not correspond to the space charge layer at the bipolar junction (2λ), which is believed to extend from the effective contact zone to some nanometers within the ion-exchange layers,[36] especially the anion exchange layer.[40]

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.[18] 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[40]

$$E = \left| \frac{|\varphi_{Don}^{tr}| + U_{bm}}{2\lambda} \right| \tag{7}$$

where E is the electric field strength; 2λ is the bipolar junction (transition) thickness; φ_{Don} 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.[5] According to Onsager's treatment of the second Wien effect, the increase in dissociation rate constant at high electric field (>10^9 V/m), can be approximated by[4,5]

$$\frac{K_d(E)}{K_d} = \sqrt{\frac{2}{\pi}} (8b)^{-3/4} e^{\sqrt{8b}} \tag{8}$$

For a monovalent electrolyte, b is given by

$$b = 0.096 \frac{E}{\varepsilon_r T^2} \tag{9}$$

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); ε_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 10^9 mol^{-1} s^{-1}.

Applying the Maxwell−Boltzmann and the Poisson equations to ion exchange membranes, by drawing 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.[41]

$$2\lambda = 2\sqrt{\frac{(2|\varphi_{Don}^{tr}| + U_{bm})\varepsilon_o \varepsilon_r}{XF}} \tag{10}$$

where 2λ is the bipolar junction (transition) thickness; φ_{Don}^{tr} is the Donnan potential across the transition region; U_{bm} is the externally applied voltage; ε_0 is the permittivity of free space; ε_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 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 10(a) were fitted according to a complete water dissociation model which incorporates the second Wien effect and the proton transfer reaction mechanisms.[40] 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 constant current density of 100 mA/cm^2. 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). It is likely that the presence of the LbL interface layers has

Table 4. Model Estimation of the Bipolar Junction Thickness without Taking into Account A_{eff} Increase by the Catalyst Groups

	two bilayers	four bilayers	six bilayers
computed apparent bipolar junction thickness (nm)	16.3	23	42.5

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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.[40] The used model parameters and initial conditions are listed in Table 1S of the Supporting Information.

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.[22] 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.[28] 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 10(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 5. Therefore, both in terms of electrical resistance and permselectivity, the membrane with the two bilayers of LbL interface was the optimal one.

Table 5. Variation of the First Limiting Current Density with the Number of Interface Layers[a]

	two bilayers	four bilayers	six bilayers
i_{lim1} (mA/cm^2)	~2.5	~3.5	~8

[a]Approximate values given here obtained from the $i-V$ curves in Figure 10.

3.7. 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 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 11(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.[42] 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 11(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.[43] 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,[44] which provides higher accessibility to the catalytic sites. It was demonstrated in the work of Wakamatsu et al.[23] 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 constant current density of 100 mA/cm^2, over a period of 2.5 h (Figure 11(b)). It was found that our bipolar membrane has an appreciable water splitting capacity close to 90% of the commercial membrane (average values of ~8.33 mmol/m^2 s vs ~9.43 mmol/m^2 s of the commercial membrane FBM).

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

4. 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 exchange 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
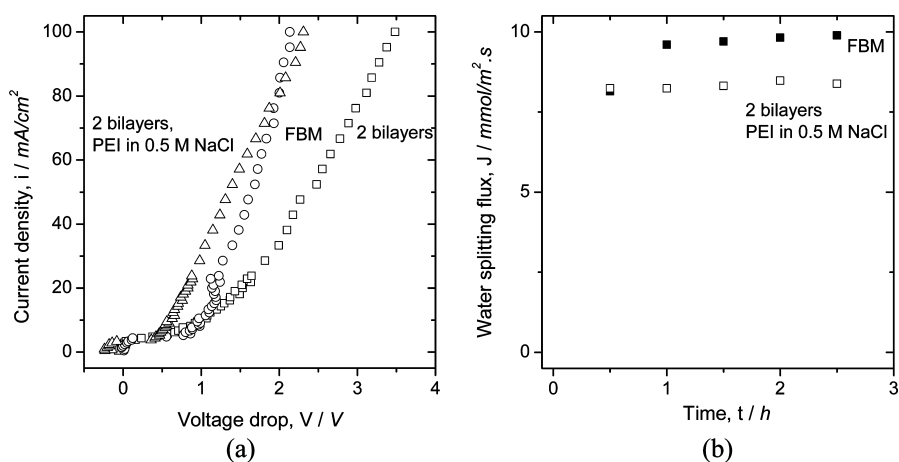
Figure 11. (a) Effect of the ionic strength of PEI on the electrical resistance of tailor-made bipolar membrane, characterized in 2 M NaCl solution. (b) Water splitting flux of the tailor-made membrane, in comparison to a commercial FBM, characterized in 2 M NaCl solution at constant current density of 100 mA/cm².

increased the co-ion leakage through the tailor-made membranes, characterized at the same concentration.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Effect of MW and concentration of PEI on the electrical resistance of the bipolar membranes; parameters of the used water dissociation model in bipolar membranes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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