



NOVEL ION SELECTIVE MEMBRANES

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1. Introduction

The ion exchange membrane (IEM) can be defined as a membrane that carries electrical charges and its importance can be understood by its application in electrodialysis, diffusion dialysis, facilitated transport etc. An IEM has inherent properties, such as ion conductivity, hydrophilicity and a fixed career charge within the membrane matrix. These properties make it enormously significant for further development in ion separation [1]. There are two types of IEM namely the cation exchange membrane (CEM) that carries a fixed negative charge on the polymer backbone and the anion exchange membrane (AEM) that has a fixed positive charge [1,2]. These properties of an ion exchange membrane draw the attention to involve it in harvesting valuable ions. In this consideration we particularly focus on IEM to separate novel ions such as Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} etc.

Ion exchange membranes are the key component for two most important state of the art technologies: electrodialysis (ED) and diffusion dialysis (DD). In ED, an electric potential difference is the driving force whereas DD is based on concentration gradient for separation. Diffusion dialysis is advantageous because of its characteristic low energy consumption, low operating and installation cost and environment friendly technology [3]. Brackish water desalination using DD is a good example and also largest application of this separation technique [4-8]. However, so far selective separation of monovalent ions by IEM with considerable efficiency is not achieved yet. Therefore improving monovalent ion selectivity such as such as Li^+ separation from a Li^+/K^+ or Li^+/Na^+ by IEM could be an interesting aspect.

We particularly focus on the selective transport of Li^+ in the cation exchange membrane. The demand of lithium is remarkably increasing in the area of large capacity rechargeable battery, future nuclear fusion fuel and electronic devices [9]. Therefore our future vision is to develop an efficient IEM process to harvest Li^+ from sea water. And present objective is to investigate selective transport of Li^+ in the ion exchange membrane by the diffusion dialysis to understand the monovalent ion transport behaviour. In sea water, presence of lithium (0.178 ppm or in between 0.14-0.25ppm) is very low compare to the sodium (10, 800ppm). Nevertheless the total amount present is quite high (roughly 230 billion ton) [10-11]. Hence harvesting lithium from seawater could be a potential area to explore.

To obtain the properties of monovalent ion selectivity (Li^+) in ion exchange membrane, one considerable approach is to modify the ion exchange membrane surface by polyelectrolyte. Polyelectrolytes (PE's) are the polymers with ionisable groups. In presence of a solvent these polymer dissociates leaving charges on the polymer chain and releasing counterions in solution [12]. Polyelectrolyte multilayers (PEM) are formed by exposing a substrate to solutions of oppositely charged polyelectrolytes. Hence, one of the methods for such multilayer preparation is the layer by layer (LbL) technique in which adsorption of ionised polyelectrolyte occurs by dipping the substrate in PE solutions i.e. dip coating method. The requirement for this adsorption is to have alternative charges between substrate and polyelectrolyte. Thus the PEM can be formed by the LbL dip coating with different combination of oppositely charged polyelectrolytes. The LbL is reported as a versatile technique that can influence the surface and the overall performance of the membrane[13-15].

Here we argue that the surface modification of ion exchange membrane by polyelectrolyte multilayer is able to influence the monovalent ion selectivity. The modified membrane can be employed in the diffusion dialysis for selective separation of the Li^+ . For our research a commercial cation exchange membrane (FUMASEP- FKB) was used. Membranes with polyelectrolyte multilayers (PEM) were prepared with adopting the layer by layer (LbL) dip coating technique. For this purpose PDADMAC (polydiallyldimethylammonium chloride), PSS (polystyrenesulfonate) and a zwitterionic polymer, PSBMA (polysulfobetaine poly (N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine) were considered. PDADMAC is a cationic polymer, widely used in the portable water purification. It is chlorine resistant and can be operated over a wide pH range [16]. Other polyelectrolyte PSS is anionic. It has ion exchange characteristics and also applies in the water softening application [17]. Therefore PDADMAC-PSS polyelectrolyte pair could be a good choice for the polyelectrolyte multilayer. We particularly focus to achieve an effective layer growth and apply it in the monovalent ion separation.

1.1 Aim of the project

The aim of the project is to grow PEM multilayers on cation exchange membranes by dip coating to obtain a better understanding of the PEM modified membrane and its performance. The project focuses on the formation of different multilayers on the membrane, an investigation of the membrane properties and the performance in diffusion dialysis. The characteristic change of cation exchange membrane due to the multilayer growth and an investigation of the monovalent ion selectivity is the integrated part of the research.

The aim of the project can be summarised as:

1. Improving the monovalent ion selectivity of the cation exchange membrane by LbL self-assembly of polycation and polyanion multilayer.
2. Evaluation of the membrane performance in diffusion dialysis keeping a focus on a K^+/Li^+ system.

2. Theory

2.1 Ion exchange membrane

The ion exchange membrane (IEM) can be a porous and/or non-porous membrane composed of functional polymers that have ionic groups. The backbone materials are mainly organic polymer with covalently bonded functional groups which also determines the acidic or basic nature of the membrane (Table 1). These functional groups are able to interact selectively with various ions and can conduct electrical charge via ions. Therefore ion exchange membrane is ion conductive in nature. It favours selective ion permeation through the membrane together with water molecules which results a selective transport of ions. A potential difference accelerates such transport, refers to the basis of electrodialysis and a concentration gradient between two solution separated by the ion exchange membrane is the key principle of diffusion dialysis [2,5]. The basic classification of ion exchange membrane is given in Table 1.

Table 1: The ion exchange membranes (IEM) and its basic nature.

Ion exchange membrane (IEM)	
Cation exchange membrane (CEM)	Anion exchange membrane(AEM)
1. Carries fixed negative charge in the polymer matrix.	1. Carries fixed positive charge in the polymer matrix.
2. Can be strongly acidic $-\text{SO}_3^-$, medium acidic $-\text{PO}(\text{OH})_2$, weakly acidic, $-\text{COO}^-$.	2. Can be strongly basic, $-\text{N}^+(\text{CH}_3)_3$ and weakly basic, $-\text{N}(\text{CH}_3)_2$.

In the IEM, fixed charges (either negative or positive) are in electrical equilibrium in the interstitial space; results the stable surface charge whether exposed in the solution or stored. Any discrete charge in the electrolyte solution which is opposite to the fixed membrane charge is called counterions whereas the charge similar to the fixed membrane charge is called co-ions. Figure 1 shows a schematic diagram of a CEM which has a matrix of fixed negative charge. In electrolyte solution counterion which is positively charged (cation) can pass through the cation exchange membrane and the anion which is negatively charged (co-ion) is retained. The electrical charge of the membrane creates the affinity towards the

positive charge (for CEM). Similarly exclusion of the negatively charged ions occurs due to the repulsion by the membrane charge. The exclusion of co-ions is called Donnan exclusion [1, 2-4].

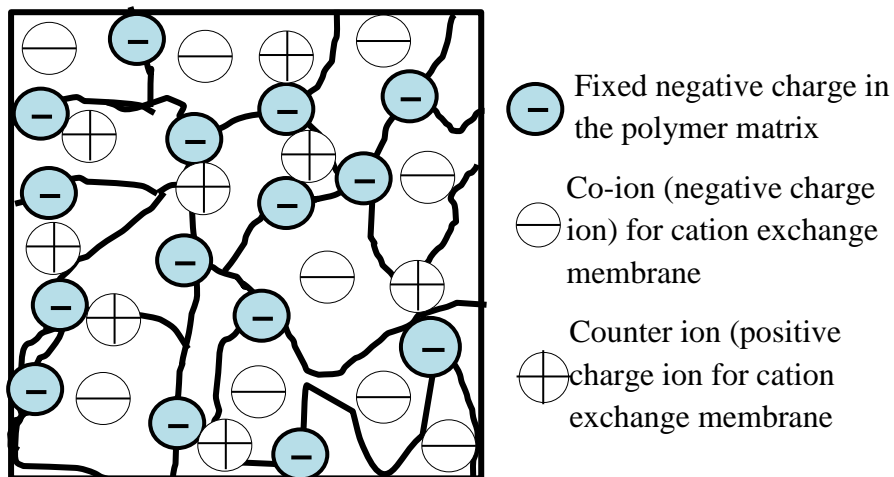


Figure 1: A Scheme of a cation exchange membrane.

In application, a high conductivity at low degree of swelling is often expected to obtain high selectivity of ions. Other important factors are ion exchange capacities, kinetics, permeability under current load and electrochemical cell characteristics [8, 18-21].

2.2 Modification of ion exchange membrane

The ion exchange membrane state of the art expresses that it can separate cation from anion and vice versa. The challenge is the selective separation of monovalent ions. Therefore the modification of the membrane came under consideration involving the IEM in separating specific ions. Also the affinity differences among ions and the ion mobility in membrane phase are important factors for the IEM.

As a first approach an increase of the cross linking of a cation exchange membrane is one of the ideas because the hydrated ionic radii of cations differ (Table 2) to sieving them with a dense polymer matrix. Ionic radii, Stokes radii and Gibbs hydration energies of various ions are given in Table 2. Stokes radii is defined as the radius of a hard sphere that diffuses at the same rate as that solute synonymous to the effective hydrated radius in solution.

Table 2: Crystal radii (r_c), Stokes radii (r_s) and Gibbs hydration energy ($-\Delta G_h$) in water of various ions [22].

Ions	$r_c(\text{\AA})^{11}$	$r_s(\text{\AA})^{12}$	$-\Delta G_h(\text{kJmol}^{-1})^{12}$
Li^+	0.73	2.40	510.4
Na^+	1.16	1.80	410
K^+	1.52	1.30	337
Ca^{2+}	1.14	3.10	1592
Cl^-	1.67	1.21	317

Because the hydrated ionic radii of the cation differs from each other and a cross linking make the membrane denser, therefore increasing the cross linking can influence the sieving of cation permeation. For instance increasing phenol content in m-phenolsulfonate and formaldehyde changes the cross linking of the membrane therefore permeation of the calcium ions greatly reduces than the sodium ions [22].

A second approach is to produce a bilayer membrane for example a cationic polyelectrolyte layer on the membrane surface. This modification often makes a rod-like spherical structure [23] and can affect the ionic mobility. The intrinsic structure of the polymer and the thin cationic layer alternate the electrostatic repulsion towards different cations. Different ionic radii of cations play an important role to influence the selectivity (Table 2). Thus cation with lower valence and higher ionic radius receives stronger electrostatic repulsion on the membrane surface [22,23].

Other modifications of the cation exchange membrane are reported as the formation of hybrid membranes by the sol-gel method, the cation exchange membrane with a conducting polymer. However the modification by a sol-gel or conducting polymer is rather sensitive to achieve the desired membrane, nevertheless can influence the membrane. In recent years the molecular imprinting techniques have been actively studied to prepare resins and membranes with high selectivity for specific molecules and inorganic ions. Comparing the above mentioned modification techniques, a thin cationic charged layer on the top of the cation exchange membrane favours to selectively permeate cations with lower valence and larger hydrated radius. Thus separation based on the different ionic and hydration radii, valence and size selectivity come to the consideration. As a consequence, permselectivity study for monovalent cations is reported as an effective approach to understand the separation behaviour of monovalent cations [22-24].

2.3 Layer by layer (LbL) self-assembly

There are many ion exchange membranes modification techniques are reported however, layer by layer (LbL) can be a promising alternative for the ion exchange membrane modification. In principle it can be defined as the alternating exposure of a charged substrate to solutions contains positive or negative polyelectrolytes, respectively [25,26]. The basic idea is that the sequential exposure leads to the adsorption on the surface due to the electrostatic interaction between the polyelectrolyte and the charged surface, therefore the surface either need to have charge or the neutral surface need to be modified for the adsorption. A charge inversion occurs for such self-assembly method. A charge inversion is the reversal of polarity due to an excess adsorption of oppositely charged polymer. The stability of such film depends on the electrostatic interactions [27,28]. Figure 2 shows a layer by layer (LbL) by dip coating where alternating exposure of the polyelectrolyte results in layer formation.

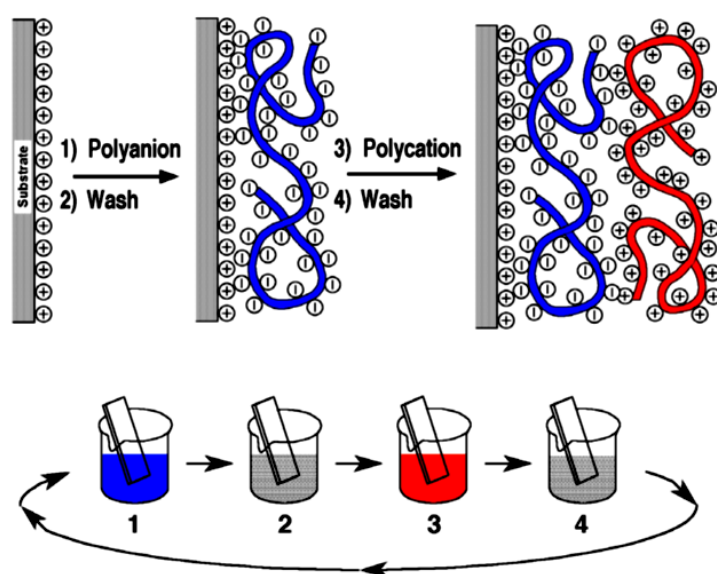


Figure 2: LbL deposition scheme via dip coating [26].

The deposition cycle showed in the figure 2 repeats to achieve the desired multilayer on the substrate. A positively charged substrate is dipped in the solution that contains negatively charged polyelectrolyte. After an interval of time of adsorption, a washing step is followed to remove the excess polyelectrolyte from the surface. Then deposition of positively charged polyelectrolyte and a washing step completes one cycle of deposition and results one bilayer of polyelectrolyte multilayer (PEM) on the substrate surface [26].

Apart from the LbL by dip coating two other layer deposition techniques are the dip coating and the spray coating and the spin coating. Figure 3 shows a schematic diagram for the spray and spin coating. Comparing among these techniques spray coating is faster but wastage of polyelectrolyte occurs due to the excess drainage during the coating. A spin coating is unable to coat a bigger surface area. In contrast the dip coating is a slower process than the other two but advantageous in coating a larger surface area with a small amount of electrolyte [29]. Therefore the layer by layer (LbL) by a dip coating technique is preferred.

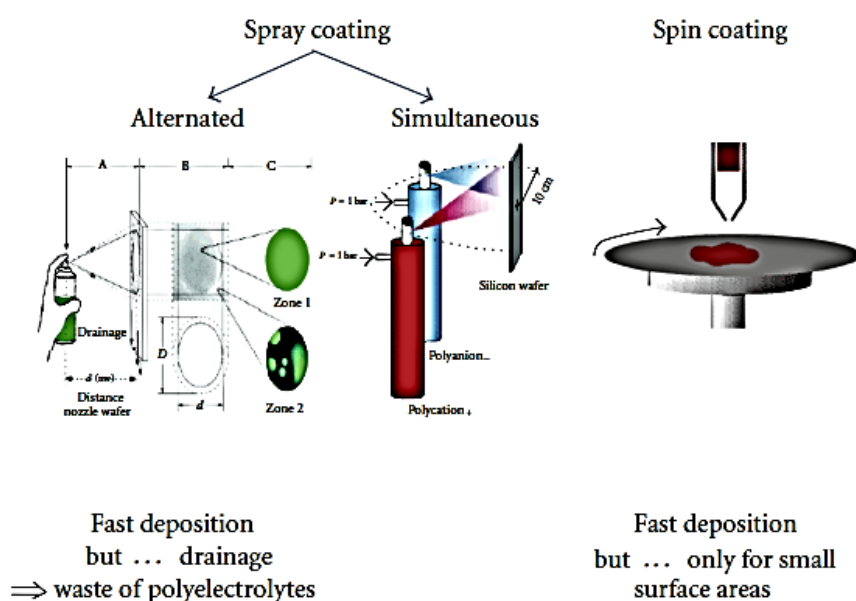


Figure 3: The LbL deposition by spray and spin coating [29].

2.3.1 General features of polyelectrolyte multilayers (PEM) by LbL dip coating

The remarkable feature of polyelectrolyte multilayer by LbL dip coating is- a small amount of polyelectrolyte molecule can alter the surface as well as its properties. However, the multilayer by LbL dip coating propagates because of the reversal of charge. Each deposition step (Figure 2, step 1 & 3) leaves the surface primed for the next deposition step thus the PEM formation propagates with each immersion step in polyelectrolyte solution. Charge over compensation is the partial complexation of the second layer with the loops of the first layer and 1:1 polyelectrolyte stoichiometry is a general assumption for such association [30,31]. However, the polyelectrolytes multilayer by LbL dip coating gives unique features (Table 3) which also can be termed as the competitive advantage over bulk chemistry i.e. chemistry in general. For example a PEM by LbL dip coating allows achieving a vast surface coverage

with a tiny amount of PE material. In each deposition step it produces a thin, stable layer on the substrate but influence the surface properties significantly. A charge overcompensation and a charge reversal gives even more options for the surface properties tuning for example incorporating a targeted amount of charge by varying substrate, electrolyte types, deposition condition etc. As a consequence specific property like a monovalent ion selectivity and enhanced ion transport in the membrane are assumed to be achievable.

Table 3: General features of the polyelectrolyte by LbL dip coating [31].

Variable	Brief description
Surface functional groups	Accessible only from the solution side.
Monolayer thickness	0.5 nm to 5 nm
Typical surface area	0.20 nm ² per molecule, 5x10 ¹⁴ molecules per cm ² .
Mass density	At a mass of 400 g/mol, 1 cm ² of a densely packed monolayer corresponds to 0.33 μg of material.
Area coverage	5g (semi-preparative scale) covers 1500 m ² .
Monomolecular layers of polymer	May be thinner and less dense and typically consist of 0.1 to 1.5 mg/m ² .

2.3.2 PEM phenomena by LbL

The formation of the layer is the combination of two consecutive steps; adsorption of polyelectrolyte on the substrate surface and the stability of this layer due to the electrostatic interaction. When a substrate is exposed in the polyelectrolyte solution, redistribution of the electrolyte particles occurs between the solution and the substrate interface which creates an interfacial potential difference [32]. Therefore the interface differs from the substrate and the bulk solution phase and ultimately leads to the adsorption. The electrostatic interaction between the polyelectrolyte chain and substrate surface results a stable layer. The PEM formation is highly dependent on the surface charge density (substrate) and polyelectrolyte chain in the solution. When surface charge density increases, the dilute chain of polyelectrolyte on the surface transforms into the semi dilute. As a result a thin layer forms on the substrate. These polyelectrolyte layers differ from the bulk polymer by leaving behind

an overcharged surface i.e. overcompensation of the surface charge by polyelectrolyte chain which results a molecularly layered multicomposite film with high degree of complexity on the substrate [33-38]. A fast adsorption is followed by slow rearrangement and transport of the chains to the surface occurs by diffusion so that electrostatic force can take place. A slow rearrangement enables the diffusion again into the inner region of previously deposited layer. By mixing positive and negative segments, irreversible complexation of the charges occurs. In each monolayer deposition we obtain the oppositely charged surface which is the charge reversal of the surface [37, 38].

The basic structure of a polyelectrolyte multilayered film can be divided into three regions as shown in the figure 4.

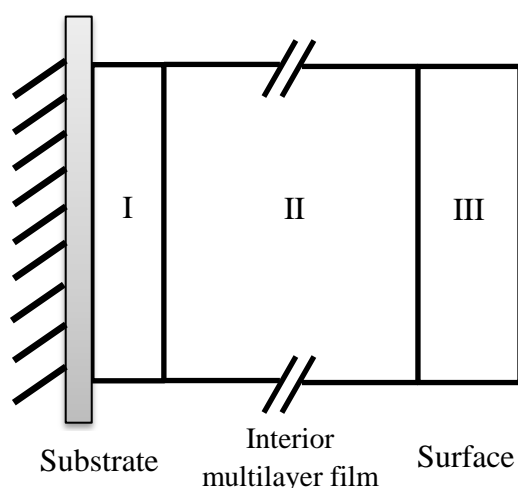


Figure 4: A Scheme of PEM multilayer [40].

The PEM can be divided into three zones. The first zone is near to the surface, zone II is the bulk zone and zone III is the transition zone. Zone I is composed of few multilayers and the number of layer depends on the type of substrate. When a new layer is absorbed after having the arrangement shown in Figure 4, thickness of zone I and zone III stays the same and the zone II grows one layer more. However the thickness of each individual layer of zone I is smaller than the thickness of each layer of zone II. On the other hand all layers of zone II are composed of equal thickness of polyanion and polycation. Polyelectrolyte of the zone II mainly follows a 1:1 stoichiometry. It worth to mention that the transition between the layers are not as sharp as it is shown in the Figure 3.

When PEM layer is fabricated, zone I completes first, then zone II and zone III. After forming zone III, each new layer addition increases the zone II by transiting one layer from

zone III, but the overall thickness of zone I and zone III stays the same [40]. While conventional multilayer growth suggests a symmetric trend, an asymmetric growth model is proposed for PDADMAC/PSS polyelectrolyte on the silicon surface [41].

One possibility of asymmetric growth could be the absence of the surface ions. In this case the charge reversal cannot occur symmetrically with each deposition step and thus an asymmetric growth originates. Whenever the charge is not balanced by ion pairing between polyelectrolyte repeat units counterions are found whether in the bulk or at the surface of the polyelectrolyte multilayer. In polyelectrolyte multilayer polymer and counterion charge balance is often termed as extrinsic and intrinsic charge balance. Extrinsic charge is defined as the charge by the polymer and counterion interaction and intrinsic charge occurs when polymer ions interact. In Figure 5, extrinsic and intrinsic charge balance is schematically shown.

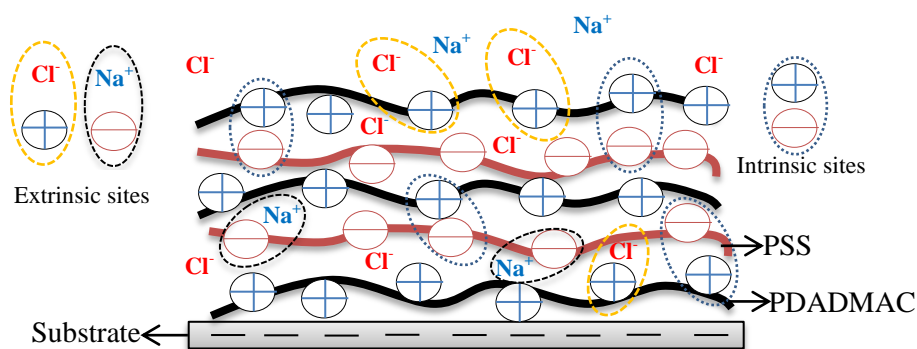


Figure 5: Scheme of intrinsic and extrinsic charge balance in the PEM [41]

However the overall charge is balanced by the combination of extrinsic and intrinsic charges which also gives a stable multilayer on the substrate.

After forming a number of layers it is observed that the alteration of the charge does not follow symmetric order rather complete alternation of the charge occurs only near the surface. Figure 6 shows that after forming a dozen layers, excess positive sites begin to accrue in the multilayer.

Treating the surface as a reaction-diffusion region for pairing of polymer charges, a model profile was shown in figure 6. Different reaction-diffusion ranges of positive and negative polyelectrolyte charge lead to a coverage of glassy, stoichiometric complex growing on the top of a layer of rubbery, PDADMAC-rich complex [41]

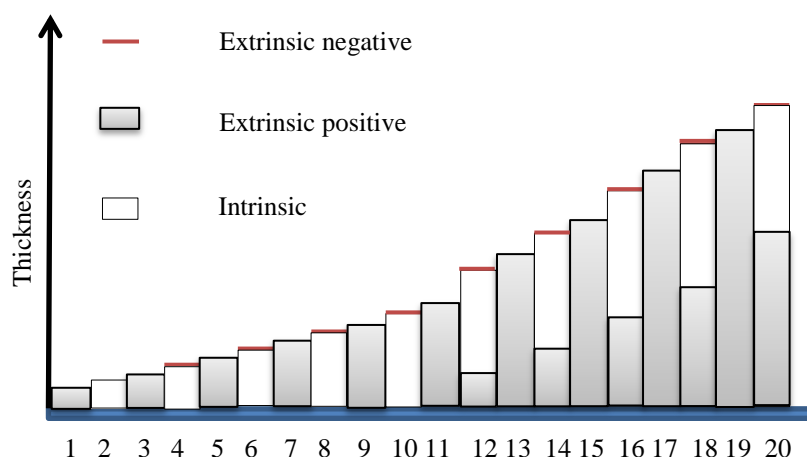


Figure 6: Asymmetric growth phenomena of PSS/PDADMAC layer build-up. Layer number represents the PSS/PDADMAC alternatively [41].

It is reported that the complete alternation of the charge occurs only near the surface and an intrinsic negative thin layer forms with almost all PDADMAC deposition steps. Also after 10-12 layers, PSS no longer compensates all the PDADMAC charges therefore PEM contains anions all the time which is the crucial point for asymmetric growth. The phenomenon can be explained as when PDADMAC is on the top layer, many positive sites are found and in addition PSS all positive sites are consumed.

After deposited the PSS, a stoichiometric film produces but with PDADMAC multilayer forms with excess PDADMAC. Thus, the growth becomes asymmetric; however the salt concentration and the substrate are important in such system.

In general, it worth to mention that that for PDADMAC/PSS system after a sufficient number of layers, a persistent layer of PDADMAC remains within the bulk of the film, and the alternation of charge occurs only near the surface. However polyelectrolyte repeat unit is a part of long chain, for this reason a thin layer has a strong dependence on polyelectrolyte molecular weight. The adsorption of PSS is rate limiting therefore PSS molecular weight has a stronger dependence on layer [41].

Nevertheless the layer formation is a complex method with a diverse dependency on the multiple variables which need to be considered for the desired surface structure. A number of parameters and their effect on layer growth are explained in the following section.

2.4 Variables for PEM by LbL

A successful LbL growth is primarily guided by longer adsorption time, rinsing volume of water and surface coverage. Longer adsorption time favours to the reproducibility because the plateau of the adsorption depends on polyelectrolyte concentration and adsorption time. The polyelectrolyte (PE) concentration is easy to reproduce but at the initial phase of adsorption small difference of time causes large difference in the adsorbed mass. And close to the adsorption plateau even large difference of time lead only a small difference of adsorbed mass. [42].

The volume of rinsing water is important because of the possibility of cross contamination. Whenever the substrate is removed from one polyelectrolyte solution, it adhere some excess of polyelectrolytes and can create cross contamination with the next PE deposition step. Therefore a dilution factor needs to be considered to avoid cross contamination. Dilution factor is calculated by dividing the volume of the first rinsing bath by the estimated volume of the adhering liquid. The number and the rinsing bath are normally chosen so that the overall dilution factor is maintained at least $1:10^6$.

The surface coverage of the functional groups is one of the most important key parameters for reproducibility. Most of the LbL shows linear growth which is associated with the functional group densities on the surface. Increasing or decreasing the surface coverage of the functional groups or the molecule diffusing in the whole surface able to influence the polyelectrolyte multilayer (PEM) linear growth. However for PDADMAC/PSS system, the growth can be different then a linear which is explained by figure 5 and figure 6. The substrates with few functional groups permit a molecular orientation towards the surface when absorbed. The polyelectrolyte with a high degree of polymerization gives a large number of functional groups, thus the orientation become less. Therefore, reproducible result for successful polyelectrolyte multilayer growth on any substrate is highly dependent on surface coverage, deposition condition and molecular weight of the polyelectrolyte [43-45].

Nevertheless, polyelectrolyte multilayer formation depends on a wide range of parameters. Table 4 gives a list of different variable which shows that polyelectrolyte multilayer dependency is a function of not only different parameters but also different possible interactions. Therefore a careful consideration of parameter (Table 4) control needs to consider for a successful layer growth with a reproducible standard.

Table 4: A List of different variables for PEM by LbL dip coating [45].

Different interactions for LbL	Important parameters (Primary)	Other important parameters
1. Electrostatic interaction.	1. Individual layer & its thickness	1. Solvent
2. Donor/acceptor interactions	2. Type of surface, salt & PE concentration,	2. Concentration of adsorbing species
3. Hydrogen bridging	3. Surface properties such as nature and density of the charged groups,	3. Adsorption time
4. Adsorption/drying cycles	local mobility (in case of a polymeric surface)	4. Temperature
5. Covalent bonds		5. Nature and concentration of added salt
6. Stereocomplex formation or specific recognition		6. Rinsing time
		7. Humidity
		8. Drying
		9. Agitation or rinsing
		10. dipping speed etc.

The deposition condition is a vast aspect for PEM as the target thickness with functionalities and desired properties are often expected; however the type of polymer, salt concentration and the deposition time are often considered as most important.

It also worth to mention that- the structure and the properties of each layer is governed by the respective polyanion/polycation pair and the deposition conditions. Therefore the choices of parameters are also different for different polyelectrolytes. As an example, the layer deposition for PSS/PAH is strongly pH dependent whereas PDADMAC/PSS is mostly not [45].

After several layer formation the properties of the substrate are hindered by the polyelectrolyte which means the properties of thin polyelectrolyte multilayer becomes dominant over the properties of the substrate. Therefore it is often said that polyelectrolyte multilayer films are independent of the underlying substrate.

2.4.1 Effect of temperature

The layer thickness increases with increasing temperature and relative humidity. Even small differences in temperature can easily account for changes in film thickness of the order of 5–

10% depending on the swellability of the film, however can be overlooked with the standard laboratory conditions. A film thickness vs. temperature for a (PDADMAC/PSS) 10 is shown in figure 7.

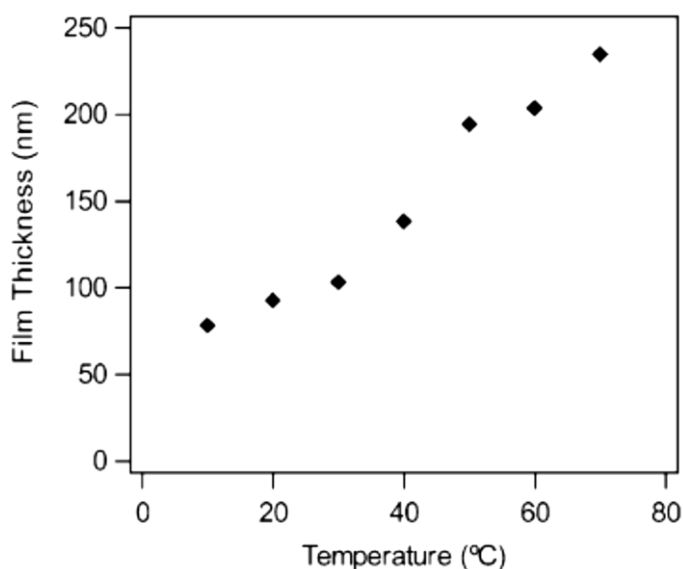


Figure 7: Effect of deposition temperature on the thickness of a (PDADMAC/PSS) 10 multilayer on Si wafer and deposited at 1M NaCl. [46]

The thickness of layers increases with the increasing temperature. The possible explanation is the change of interaction with temperature. At elevated temperature the solubility of PSS in water decreases which can be related with the solvent quality i.e. water. Thus solvent quality is reduced when temperature is increases and results a thicker film [30,47]. In addition to that another argument is about the possibility of the hydrophobic effect. The solubility of hydrophobic materials decreases at high temperature. The reduced solubility is assumed to drive the polymer to the surface and increase the thickness of adsorbed layers. It seems that at high temperature both localized dissociation and conformational dynamics of polyelectrolyte molecules tend to increase which results an increased tendency to send the loops on the surface and tail to the solution [30, 46]

2.4.2 Effect of salt concentration

The polyelectrolyte multilayer formed at different salt concentration shows different fluorescence emission intensity shown in figure 8. The measurement was performed by the fluorescence emission spectrometer on a solid sample holder. The incident angle was 45° to the film surface. The emission intensity was taken at 396 nm as the characteristics of pyrene

and evaluated after subtracting the intensity of a cleaned quartz slide (as a blank) to eliminate the substrate emission and scattering. It was shown that the salt concentration increases as the intensity increases. A second example is shown in figure 8(b), as the layer number increases the thickness increases. Thicknesses were determined using an ellipsometer with 632.8 nm radiation at 70° incident angle. [48,49].

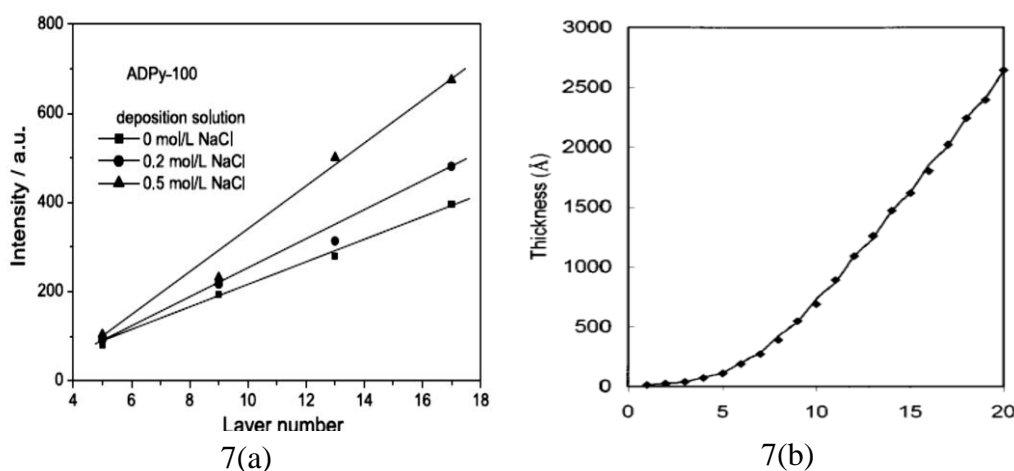


Figure 8: 8(a) Fluorescence intensity varying with the layer number of the multilayer film made of ADPy-100 (The pyrene labeled polyanion) and PDADMAC deposited in NaCl solutions [42]. 8(b) Thickness vs. layer number for PSS/PDADMAC deposited from 1.0 M NaCl [49].

While increasing the ionic strength of the medium, the layer becomes thicker. At a higher salt concentration, the polyelectrolyte tends to be coiled more and increases the thickness which can be explained by the intrinsic charge compensation, schematically shown in figure 9 [48]. Compensation via polycation–polyanion complexation is called intrinsic charge compensation. However, increasing the salt concentration will increase the extrinsic charge compensation, which reduces the number of complexation points between two polyelectrolytes, allowing the more possibilities to coil or to move through the film which gives rougher and thicker structures.

It worth to mention that, at a very high salt concentration the layer can be de-structured due to the high number of counterion interactions [50-53]. Therefore salt concentration effect is obvious on polyelectrolyte multilayer which indicates a careful choice of salt concentration; necessary to obtain the desired thickness.

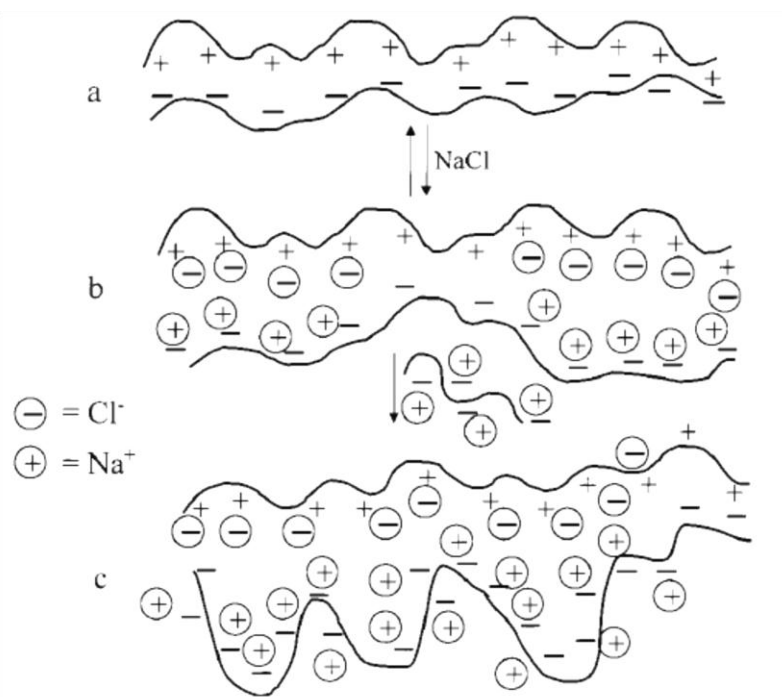


Figure 9: Interior of a multilayer, scheme with two oppositely charged polymer strands (a) fully intrinsic. (b) Ion swells the multilayer and competes for polymer charge in the presence of polyelectrolyte. (c) Overcompensation from the surface into the film [48].

Figure 9 shows the hypothesis of adding a salt and therefore the transformation from intrinsic to extrinsic with the phenomenon of charge overcompensation. When two polymer chains are fully intrinsic, an addition of the NaCl makes the previously intrinsic polymer chain to be swelled and also more water is brought by the salt. If one of the polyelectrolytes, either positive or negative is added; the overcompensation extends further because it decreases the segment-segment repulsion. As a result, more coiled complex structure forms. However the swelling of multilayer by salt is reversible but by polyelectrolyte addition is irreversible. Since a deposition cycle terminates with the rinsing step therefore increase in film thickness with additional salt is not expected. If the polymer were adsorbed in the thermodynamically reversible limit, the polymer would desorb in pure water. Thus the thickness increment in the polyelectrolyte deposition in a time scale can be considered as irreversible. The irreversibility is checked by preparing a radiolabeled positive layer (14C labeled PM2VP) on the top of 10 layer of PSS/PDADMAC and immersed it to 10 mM PDADMAC in 0.1 and 1M salt solutions. No evidence of desorption was found on a time scale of hours, and a small exchange was observed after several days [49,54].

2.4.3 Effect of ion type

The effect of salt concentration, type of salt and water content relation during the formation of a polyelectrolyte multilayer is shown in the figure 10. The polyelectrolyte of oppositely charged layers creates voids in the multilayer. In vacuum these voids are empty but upon swelling filled with water which is called void water. Void water does not contribute to the swelling of the multilayers but exclusively change the scattering length density.

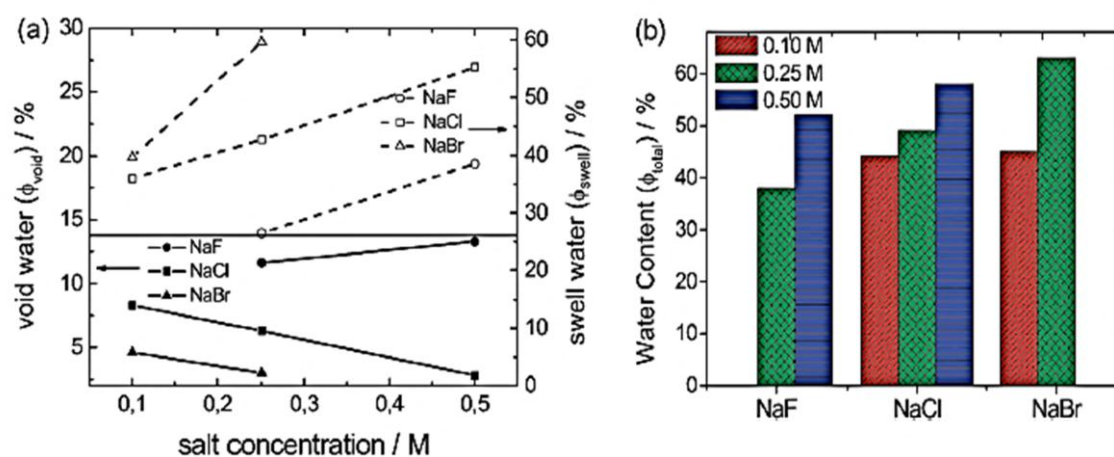


Figure 10: For a PDADMAC/PSS system on Si substrate (a) Salt concentration vs. void water and swelling water and type of salt. (b) Salt concentration, type of salt and total water content [55].

An increasing the ionic concentration increases the amount of swell water and decreases the amount of void water. Also higher the ionic strength the total amount of the water content is larger. At 0.5 M NaBr multilayer are unstable therefore not shown in the figure 10.

Since swell water and void water behaves opposite to each other which means two water species partially compensate each other. The presence of different salt can create variable electrostatic screening of the charge on the polyelectrolyte layer and also influence both the dynamics of polyanion/polycation complexes.

The different dynamics are the result of the hydration behaviour of the salt and the solubility behaviour when different salt is used. The solubility behaviour and the complex formation often referred partially to the Hofmeister Series that gives the consistent effect of solubility as $F^- > Cl^- > Br^-$ and hydrophobic effect. Thus in PDADMAC/PSS, both thickness and water

content of the multilayers increases with increasing ionic strength and ion size. The amount of void water decreases with the increasing salt concentration and anion radius while the amount of swelling water increases with salt concentration and anion radius. This can be interpreted as a denser structure in the dry state and larger ability to swell in water for multilayers, prepared from high ionic strengths and/or salt solution of large anions [55]. In other explanation says that the smaller ion has a relatively small polarizability, high electric fields at short distances, and keep their water of hydration which can affect the structure of the PEM [56,57]. The anion effect on PSS/PDADMAC films is much higher than the cation [58]. At the same time the trend of the thickness and the roughness is a function of the type of the counter ion; the larger the anion, the thicker and rougher the film. The larger ion has higher polarizability, and therefore interacts more strongly with polyelectrolytes which increases more coiled structures. The stronger interaction of the ions/polyions will also increase the polymer mobility inside the PEM by decreasing the complexation points between polyanions and polycations. In reality, the effect of increasing anion size (F^- , Cl^- and Br^- used as counteranions) is qualitatively the same as increasing ionic strength (0.1, 0.25 and 0.5M NaCl) [55-58].

2.4.4 Effect of pH

The pH of weak polyelectrolyte solutions dramatically affects the film thickness and makes a strong effect on permeability behaviour whereas for strong polyelectrolyte pH does not have any effect on the polyelectrolyte multilayer [59-63]

The reason of this behaviour is because the weak polyelectrolytes are not fully charged in solution, and moreover their fractional charge can be modified by changing the solution pH, counterion concentration, or ionic strength. A weaker polyelectrolyte has a lower dissociation constant that means it will be partially dissociated at intermediate pH. On the other hand a strong polyelectrolyte such as PDADMAC/PSS dissociates completely in solution for most reasonable pH values [62,63]. Thus in weak polyelectrolyte polymer charge density is a strong function of pH but for strong polyelectrolyte it is normally expected to be pH independent. However figure 11 does not agree with the statement and shows an increase of layer thickness increases when pH is high [64].

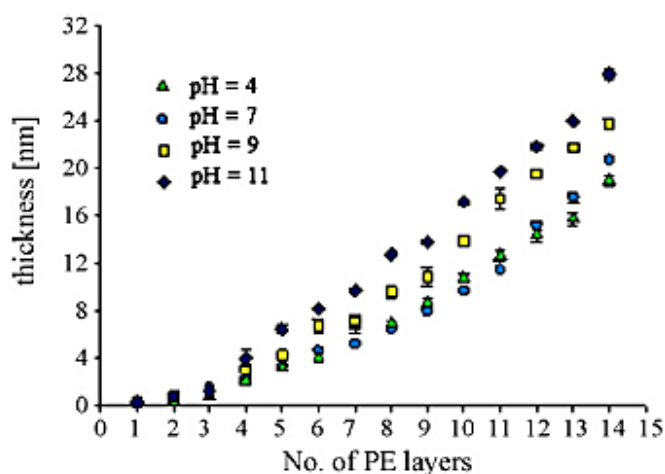


Figure 11: Effect of pH vs. layer thickness for PDADMAC/PSS multilayers on Si/SiO₂ surface [64].

It is usually expected that thickness of PDADMAC/PSS should be identical irrespective to the pH condition. Since the negative surface charge of Si/SiO₂ support increases strongly with pH [65] therefore the increase of thickness of PDADMAC/PSS with pH has occurred [64,66]. A substrate effect also can be understood from figure 11.

2.5 LbL polyelectrolyte membrane

The LbL assembly of different polyelectrolytes on the various types of membrane results a composite membrane which allows high separation capability [50-57]. Selective transport of the ions and molecules across the polyelectrolyte multilayer membranes are reported as potential for water softening and desalination [70]. The LbL assembly is conducted by the conjugation of two types of oppositely charged polyelectrolytes; therefore can give a highly cross-linked structure. Therefore, it can act as a molecular sieve for separating small and large molecule from each other [71]. Using the different type of polyelectrolytes with different charge density, the network can be controlled and application of it can be forecasted in the controlled release, water purification, separation and the purification of organic compounds [72]. As for example, PDADMAC/PSS gives a comparably more porous structure and size selective transport has been reported for mono and polyfunctional alcohol derivatives [73]. Transport of the differently charged aromatic compounds of similar size was also investigated which indicates that the organic ions with the highest charge density receive the strongest electrostatic (Donnan) rejection from the membrane, quite similar to the

inorganic ions [72,73]. A rejection model scheme is shown in figure 12 where multi-bipolar structure of the polyelectrolyte membranes favours the separation of mono- and divalent ions by Donnan exclusion [74]

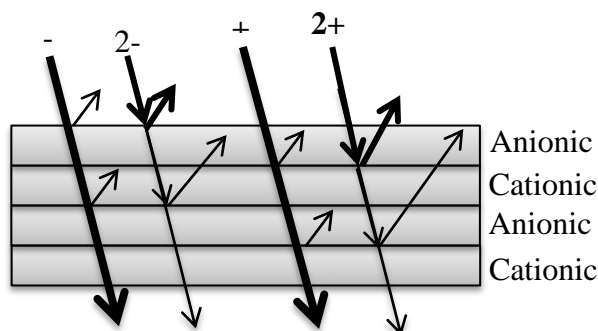


Figure 12: Rejection model of multi-bipolar membrane by polyelectrolyte. [74]

The architecture of multi-bipolar film rejects the ions by electrostatic repulsive forces, also called Donnan exclusion. Divalent ions receive a much stronger repulsive force from the positively charged layer than monovalent ones. Thus divalent ions are more strongly rejected and a good selectivity is obtained. Similarly divalent anions are rejected by the negatively charged layers. However the model shows that the difference in the permeation of mono- and divalent ions becomes effective when the number of adsorbed layers is increased. When membranes containing polyallylamine (PAH) as the cationic polyelectrolyte, a 60 layer pairs of PAH/polystyrenesulfonate shows the separation factor for $\text{Na}^+/\text{Mg}^{2+}$ up to 112.5 and for $\text{Cl}^-/\text{SO}_4^{2-}$ up to 45.0 [74,75] However, permeation also depends on the concentration of excess charges, addition of salt to the polyelectrolyte solution or increasing the pH. Salt addition leads to additional incorporation of charged chain segment and thus improves the ion separation and the increase of the pH value may lead to deprotonation of the cationic polyelectrolyte so that chain segments (without charge) are incorporated, which deteriorate the ion separation. Another important factor influencing the ion transport is the molecular structure of the polyelectrolyte. A high charge density favours a dense, less permeable membrane exhibiting improved rejection of divalent ions [75]

A single polymer adsorption makes significant affect in the polymer morphology. Also different combination of the weak and strong polyelectrolyte gives even more change in the polymer morphology. Therefore it is an interesting phenomenon to study the permeability of a membrane with a blend formation and the morphology as well for ion separation [76]. To improve the separation behaviour and the surface properties, one of the ideas is to engage

macrocyclic compounds such as calixarenes and crown ethers. It has been reported that the modification with such compounds make the membrane more permeable for monovalent than for divalent ions because the divalent and the trivalent ion receive stronger repulsion from the membrane bound charges. Therefore permeation rates of alkali metal ions increase in the direction of lower charge density of the ions ($\text{Li}^+ < \text{Na}^+ < \text{K}^+$). The effect also can be correlating with the ring size of the compounds. As the ring size increases the permeation value for different ions differs therefore can be considered for monovalent ion selectivity [77-81].

A careful controlling of the LbL and the polyelectrolyte deposition is able to give confined pore geometry on the surface which enhances the volume density of ionisable groups in the membrane phase. Such high density allows the permeation control upon Donnan exclusion of ionic species. For example the LbL films of PAH and PAA on a glass filter can remove the environmentally-unfriendly gasses (Basic odorant) [80]. A PDADMAC/PSS multilayer on porous substrate shows a high flux ($\text{Cl}^-/\text{SO}_4^{2-}$). As a best case (PSS/PDADMAC)₃PSS on a porous alumina support showed a 96% rejection of SO_4^{2-} , a chloride/sulfate selectivity of 26 [83]. Also recently found that the Cl^-/F^- nanofiltration selectivities of PSS/PDADMAC films on porous alumina membranes reach a maximum value of 3.4 for (PSS/PDADMAC)₄PSS films [84]. Nevertheless, ion transport through polyelectrolyte multilayers depends on ion-exchange sites. And the ion-exchange capacity of PSS/PDADMAC films is a function of the number of deposited layers. Therefore at higher number of layers it is expected to have better monovalent ion selectivity [85].

2.6 Diffusion dialysis and LbL

Diffusion dialysis is an ion-exchange membrane separation process which is driven by concentration gradient and also known as concentration or natural dialysis. Since the driving force for the separation process is mainly concentration gradient, dialysis is known as a spontaneous separation process [86]. If there is a concentration difference of solutes across an ion exchange membrane, solute diffuses through the membrane. Thus, diffusion potential corresponding to the concentration gradient is generated across the membrane [2]. Due to the attractive force inside the membrane (Ion exchange membrane), the transport of counter-ions through the membrane is more facilitated. However, electrical neutrality needs to be preserved in the whole process. Co-ions with small hydration radius and little charge can always have high mobility and transport through the membrane [87,88]. The characteristic of low energy consumption, low installation and operating cost, make it attractive however, it

has the limitation to the low processing capability and low efficiency [89]. The applications of diffusion dialysis are recover acids and valuable metals from industrial waste solution [90]

The principle of the diffusion dialysis process is shown in the figure 13 (recovery of base) considering a cation exchange membrane.

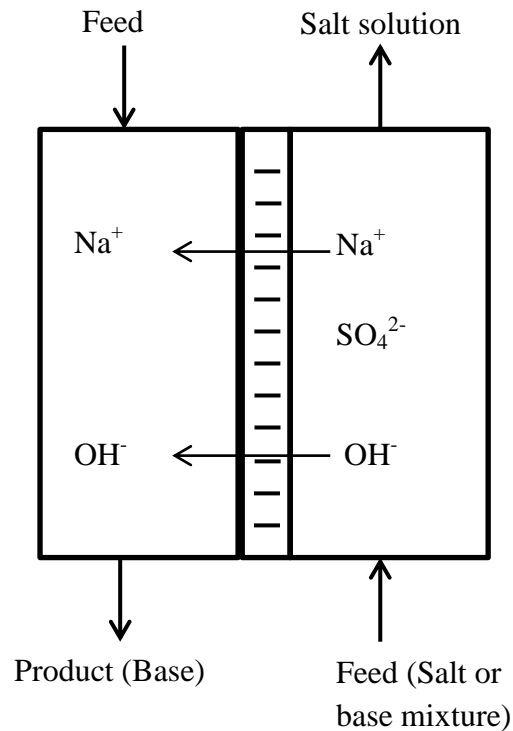


Figure 13: Schematic drawing illustrating the principle of diffusion dialysis utilizing a cation exchange membrane to recover a base [4].

The mass transport in diffusion dialysis is determined by the transport of ions through the membrane. The feed and the product solutions are separated by the membrane. In order to promote the process efficiency a practical consideration is to decrease membrane thickness and increase the membrane area. [7]. The electro dialysis is an electromembrane separation technique uses ion exchange membrane arrangement and also a difference in electrical potential to separate ions from solution and from each other [91].

Ion transport by the diffusion dialysis and electro dialysis, in general, is described by the Nernst-Planck's equation (Equation 1). The equation illustrates three forces diffusion, migration and convection. The simplified expression is as-

$$J = -D \frac{dc}{dx} - cDZ \frac{F}{RT} \frac{d\phi}{dx} + cV \quad (1)$$

Here J is ionic flux [$\text{molm}^{-2}\text{s}^{-1}$], v is convection velocity in [ms^{-1}] c is concentration of component [molm^{-3}] D is diffusion co-efficient of the component [m^2s^{-1}], x is direction co-ordinator [m] z is valence number of component I [-], F is Faraday constant [Cmol^{-1}], R is gas constant [$\text{Jmol}^{-1}\text{K}^{-1}$] T is temperature [K] and ϕ is electric potential [V]

In the equation first term represents the diffusion which is first Fick law; second term is the migration force and third is the convection. Since for the dense membrane no convection occurs the equation can be rewrite as equation (2)

$$J = -D \frac{dc}{dx} - cDz \frac{F}{RT} \frac{d\phi}{dx} \quad (2)$$

In the following paragraph, definition of important parameters such as membrane degree of swelling, resistance and flux are given which often considered to describe diffusion dialysis and/or electro dialysis.

2.6.1 PEM and diffusion dialysis

The modification of the cation exchange membrane and applying it in diffusion dialysis could give specific cation selectivity. The nanoscopic PEM allows significant changes in morphology and/or surface properties like surface charge density. These changes can effectively contribute to improve on cation separation, recovery of ions, water purification, acid and base separation or recovery. [92,93].

The LbL deposition by the electrostatic interaction affects the ion exchange sites [94], size of the ion and their mobility. Under the influence of diffusion dialysis condition these parameters could give monovalent ion selectivity by diffusion.

A diffusion dialysis with the high cross linked dense membrane (by PEM) may be able to hinder the larger size ions and gives size exclusion. Positive layer on the cation exchange membrane can make higher repulsion to the multivalent ions which also affect the monovalent ion selectivity [2, 33, 94-99].

3. Experimental

3.1 Materials

The polyelectrolyte multilayer (PEM) samples were prepared on FKB Fumatech cation exchange membranes which were purchased from FuMA-Tech GmbH, Germany. The layer by layer technique was followed by using polycation PDADMAC^{*}, polyanion PSS^{**} and poly zwitterion PSBMA^{***}. Polyelectrolyte multilayer deposition was conducted in a salt medium prepared by sodium chloride, NaCl ($\geq 99.5\%$). Different inorganic salts including sodium chloride, NaCl ($\geq 99.5\%$), potassium chloride, KCl ($\geq 99\%$), and sodium sulphate, Na₂SO₄ ($\geq 98\%$) were purchased from Sigma Aldrich. Lithium chloride, LiCl ($\geq 98\%$) was obtained from Fluka analytical and hydrochloric acid, HCl (37%) from Merck, Germany. MiliQ milipore demiwater was used for other auxiliary purpose. All chemicals were laboratory grade standard.

*Poly (diallyldimethylammonium chloride), Mw = 150 kDa, 20 wt % in water from Kemira, Finland). ** Polystyrene sulfonic acid, Mw = 100 kDa, 20 wt % in water from Tosoh Organic Chemical Co., LTD (Japan). *** Poly- N-(3-Sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (SBMA) from Sigma Aldrich (The Netherlands) .

3.2 Methods

3.2.1 Preparation of polyelectrolyte multilayer by PDADMAC and PSS

The polyelectrolyte multilayer sample was prepared on the fumasep® FKB cation exchange membrane. The membrane was preconditioned in demineralized water for six hours to obtain the optimal performance, minimal wrinkling and lowest electrical resistance. Since the membrane was already in H⁺ form therefore further acid treatment was avoided.

In the following step, a PDADMAC and a PSS bath was prepared by mixing 1g/l of each polyelectrolyte in 0.2 M NaCl solution. Both the solution was vigorously stirred for approximately 30 minute in room temperature for proper mixing of the polyelectrolyte in the

salt solution. Another two baths were prepared by the demiwater for rinsing purpose. The volume water in each bath was kept as same as the polyelectrolyte baths.

Preconditioned FKB membrane was then cut into approximate 3.5x 3.5 cm and taped over a square shaped glass support. Each four side of the square shaped membrane was taped on the glass support keeping approximately 3x3 cm membrane area to be exposed in the solution. The sample was vertically dipped in the PDADMAC solution bath and then rinsed in water bath. At this step a monolayer i.e.0.5 bilayer was formed. The next successive step sample was dipped in the PSS bath and then rinsed in the water. At this stage 1 bilayer was formed. The duration of the layer deposition and rinsing was followed as 30 min/bath.

A scheme of LbL formation on FKB membrane.by dip coating is shown in figure 14.

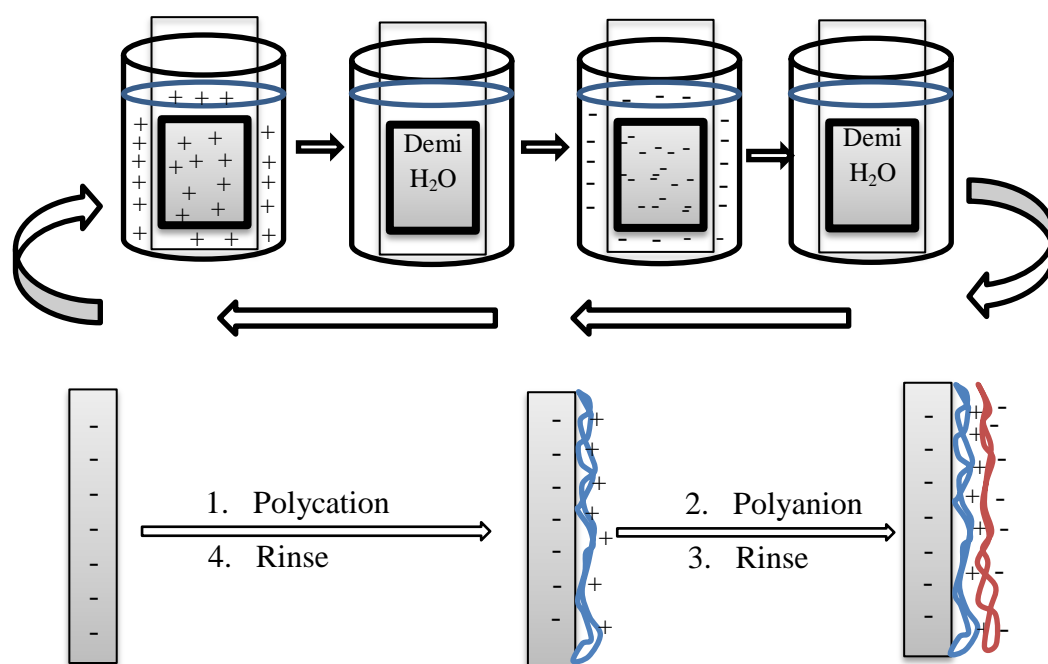


Figure 14: A Scheme of polyelectrolyte multilayer by LbL via dip coating.

The cycle of deposition steps were repeated to obtain desired bilayers on the FKB membrane. All samples were prepared at room temperature and the duration of each deposition step was considered as 30 minute. In each deposition step membrane sample kept as vertical and rinsing water was replaced by new after two times rinsing. Several sets of sample were prepared up to 7th bilayer. The prepared sample was stored in 0.5M NaCl solution.

3.2.2 Preparation of the polyelectrolyte multilayer by PDADMAC- PSBMA-PSS

The preparation method was same as described in the section 3.2.1. The difference is an additional deposition step was employed in between the PDADMAC and PSS; deposition of PSBMA which is a zwitterionic polymer, exhibits both positive and negative charge in the molecule. To prepare the solution 1g/L polymer was dissolved in the 0.2M NaCl solution. Vigorous stirring was done until the polymer completely dissolves. Dissolving PSBMA took longer time than PDADMAC and PSS. The other condition of the deposition such as salt type and its concentration, deposition time kept as constant. After PDADMAC-PSBMA-PSS deposition, the sample considered as one trilayer. In this PEM sample preparation, PSBMA layer is sandwiched in between the PDADMAC-PSS layers.

Figure 15 shows a scheme of the polyelectrolyte multilayer with zwitterion polymer PSBMA where at first step PDADMAC is deposited and successively PSBMA and PSS deposition was performed. Sample considered as PDADMAC terminated and PSS terminated layers. Sample was prepared up to seven trilayers.

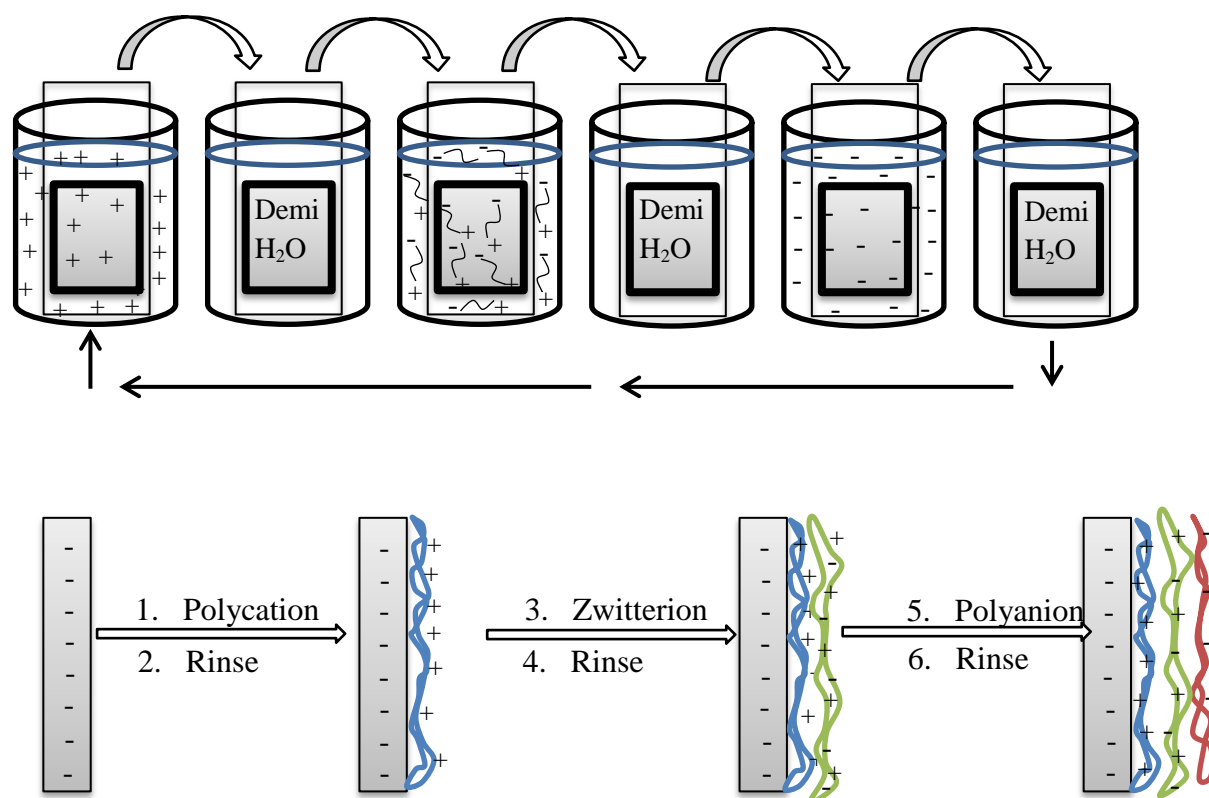


Figure 15: Scheme of polyelectrolyte multilayer (PDADMAC-PSBMA-PSS) by LbL by dip coating.

Deposition of PEM on the FKB membrane was conducted at the salt concentration 0.2M NaCl because at salt concentration 0.2M, PDADMAC/PSBMA the layer deposition is observed as most stable [104]

3.2.3 UV-Vis measurement

The UV-Vis was measured by the spec: USB 2000+Miniature fiber optics from Ocean Optics, Inc, USA.

The UV-Vis set up consist a UV source (Deuterium light), optical fiber connections, membrane holding cell, detector and recorder (Ocean plus software). Absorption occurred in the membrane holding cell where the membrane was placed. During measurement UV light was allowed to passes through the optical fiber line to the membrane holding cell. Another optical fiber was connected from the membrane holding cell to the detector. After absorption in the cell the detector responses are recorded by the Ocean plus software that gives a UV-Vis profile with a characteristic peak. UV-Vis measurement was conducted for several sets of membranes.

First of all PDADMAC/PSS polyelectrolyte multilayers (PEM) were deposited on the negatively charged quartz glass surface. Before layer deposition, quartz glass was cleaned by the acid piranha solution. Acid piranha is a 3:1 mixture of concentrated sulphuric acid (H₂SO₄) with hydrogen peroxide (H₂O₂). The methodology adopted from http://www.lamp.umd.edu/Sop/Piranha_SOP.htm. Each bilayer formation on the quartz glass was conducted by following the same procedure as described in section 3.2.1. After each bilayer deposition, the sample was dried under a stream of N₂ and then UV absorbance was measured. Up to seven bilayers UV-Vis profile were measured and recorded.

Referring to the section 3.2.1 and 3.2.2, two other sets of sample (FKB modified by PDADMAC/PSS and PDADMAC/PSBMA/PSS) up to seven bilayers were prepared and dried under N₂ stream before the experiment.

Ultraviolet visible spectroscopy is a quantitative measurement technique of characterization based on the Beer-Lambert law (Equation 4).

$$A = \log_{10} (I_0/I) = \epsilon cL \quad (4)$$

Where A is absorbance in AU, I_0 is the intensity of the incident light at the given intensity and I is the transmitted intensity, ϵ is the molar absorptivity i.e. often called extinction coefficient, c is the absorbed species concentration and L is the path length through the sample. An example of UV-Vis absorption spectra is shown in figure 16.

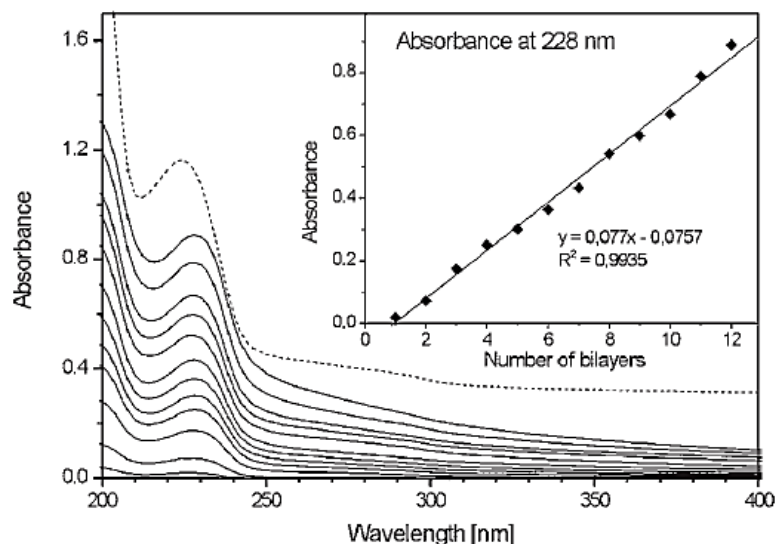


Figure 16: UV-Vis absorption spectra of PDADMAC/PSS block- VN multilayer [78].

It was reported that PSS gives absorption band at 228 nm and PDADMAC absorption is negligible in the spectroscopic region. Nevertheless there is no distinct maximum for PSS and one can observe in the range of 280-320 nm [102].

3.2.4 Contact angle measurement

The contact angle (CA) was measured by the Data Physics OCA20, Germany.

The equipment is a telescope-goniometer in which a horizontal stage is used to mount a solid sample; a micrometre syringe was used to form a water liquid drop (ultrapure water as a probe liquid), an illumination source, and a telescope with camera.

Before CA measurement, the membrane sample was dried overnight in the vacuum oven at 30°C to get a dry membrane surface. Then the membrane was placed as flat as possible on the horizontal stage. The micrometre syringe (filled with ultrapure water) was in vertical position on the membrane. The illumination source and the camera focus were adjusted to

have the vision of the membrane surface. OCA 20 software allows making a precise water droplet of 1 μ l and dispenses it on the membrane surface. Then a snapshot was taken and CA was measured. For a single sample, three to five droplet were dispensed in different position of the surface and corresponding snapshot were recorded which were used to measure contact angle. taken for each sample and in different place of the membrane and corresponding contact angle was measured.

After dispensing water droplet (1 μ l) on the membrane, five second waiting time was considered for the consistency.

Contact angle measurement gives the information of the hydrophilicity/hydrophobicity and surface energy of PEM. Small contact angles ($\ll 90^\circ$) correspond to high wettability, while large contact angles ($\gg 90^\circ$) correspond to low wettability. An example of water contact angle vs. number of PDADMAC/PSS multilayer on Si substrate is shown in figure 17. [64]

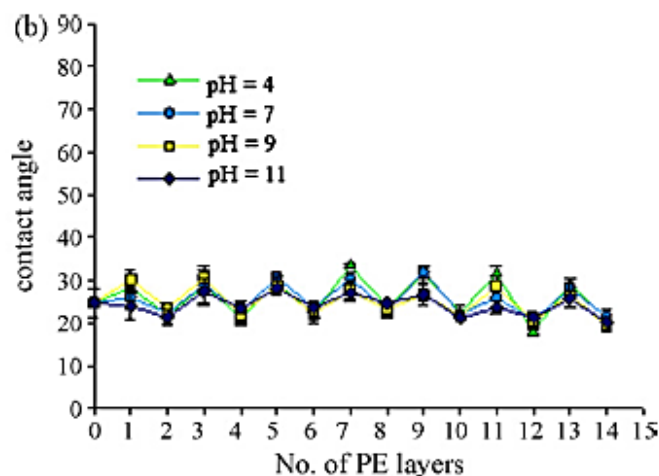


Figure 17: Dependence of PDADMAC/PSS films formed at various pH of solution on Si. [64]

It was reported that PDADMAC/PSS multilayer on Si substrate does not show any pH dependency however PDADMAC terminated layers give higher contact angle than PSS terminated. Nevertheless CA value differs significantly from substrate to substrate which gives the information of surface dominated characteristic of PEM [64,103]. Films terminated by polycation layers are more hydrophobic. Also amplitude of layer-to-layer contact angle oscillations and average hydrophobicity depends on the polyelectrolyte adsorption conditions.

3.2.5 Measurement of electrical resistance and current voltage curve

The electrical resistance was measured in a six cell electro dialysis unit (Figure 18).in which two outer compartments contain two working electrodes; the anode and the cathode. These electrodes were used to apply an electric field though the membrane. In the middle there were two central compartments with Haber-Luggin capillaries. A shielding compartment in between each electrode and main compartment was used. The membrane under investigation was placed in between Haber-Luggin capillaries.

Other cell membranes (often called principle auxiliary membranes) of the figure 18 were used to prevent transport of water dissociation product from electrode to main compartment. The Haber-Luggin capillaries were filled with 1 M KCl solution which was connected to calomel reference electrode (Schott B2810) by silicon tubing. The reference electrode was connected with Autolab potentiostats/galvanostats, which allowed controlling the current level and measures corresponding voltage drop in the test cell.

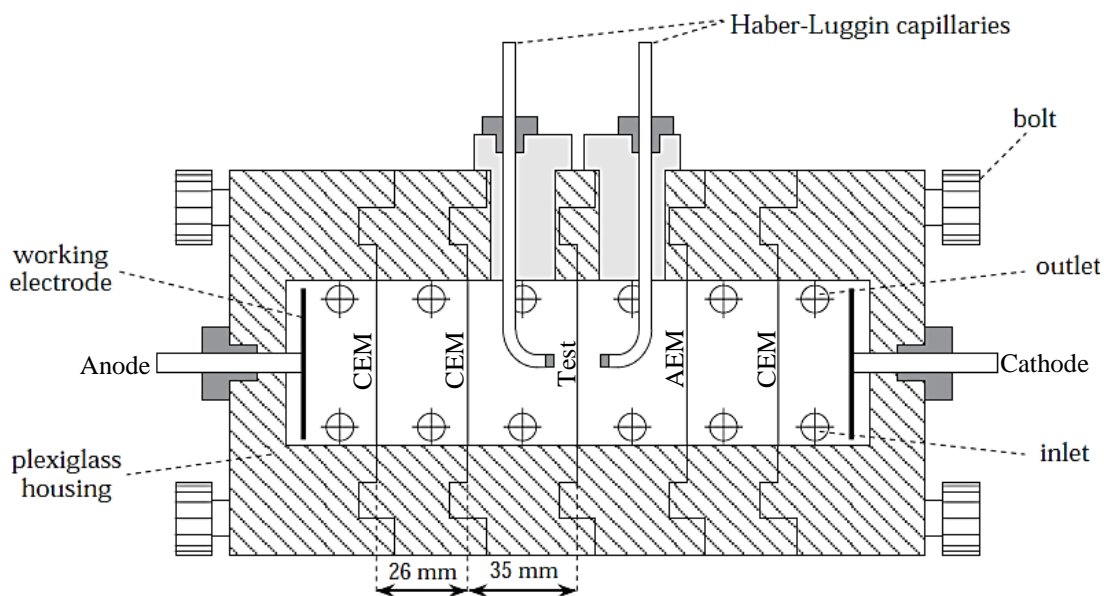


Figure 18: Schematic drawing of the six cell setup. [1]

In electrode compartments 0.5 M Na₂SO₄ (2L) and in other compartments 0.5 M NaCl (2L for shielding and 2L for central compartment) were pumped at a rate of 450ml/min and temperature was maintained as 25°C. The Haber-Luggin capillary tip of each electrode was placed as close as possible to the membrane but not in contact with the test membrane to

avoid the interference of the electric field. All salt solutions were allowed to circulate for 10-15 minutes to obtain a stable condition for electrical resistance measurement.

Current was applied in the range of zero to 135 mA with stepwise increase (15mA/step). For each step of current increase, corresponding voltage were measured and recorded. Current-voltage data were further calculated and plotted as current density (mA/cm^2) vs. voltage drop (mV). A linear relation was found and the slope was calculated which eventually gave the electrical resistance, R ($\Omega \cdot \text{cm}^2$).

Before the measurement, the membrane sample was preconditioned overnight in 0.5M NaCl solution to be stabilized. The measurement with the sample membrane gives a total resistance of membrane and solution. Therefore a blank run (without any membrane sample) was conducted to measure the resistance contribution of the salt solution.

$$R_{\text{membrane}} = R_{\text{membrane+solution}} - R_{\text{solution}}$$

The electrical resistance of an electrical conductor is the opposition to the passage of an electric current through that conductor. The electrical resistance of ion-exchange membranes is one of the factors which determine the energy requirements of electro dialysis processes. The resistance (R) of an object is defined as the ratio of voltage across it (V) to current through it (I),

$$\text{Thus } R = V/I \tag{3}$$

The specific membrane resistance is usually reported as [$\Omega \text{ cm}^2$] or [$\Omega \text{ m}^2$]

3.2.6 Limiting current density

The limiting current density (i_{lim}) was measured with the same set up as described in section 3.2.5 however higher level of current was used to determine i_{lim} so that ohmic, limiting and over limiting region can be obtained

From the experiment current (mA) and corresponding voltage drop (V) data was obtained which further calculated and plotted to obtain a current density (mA/cm^2) vs. voltage (V) curve. For each measurement, two fresh samples were considered to confirm the reproducibility of the results.

An example of current-voltage graph is shown in figure 19. In the first region resistance of the cell is fairly constant, i.e. the current density is increasing linearly with the applied voltage according to Ohm's law. When a certain current density is reached, the cell resistance increases drastically which is the plateau region. This transition point is called as the limiting current density (i_{lim}). Further increase of current density lead to over limiting region though over limiting current density is not yet completely understood. A certain amount of the current in the over limiting current density region is transported by the protons and hydroxyl ions generated by electroalytic water dissociation at the ion-exchange membrane. [1,4-7,100,101].

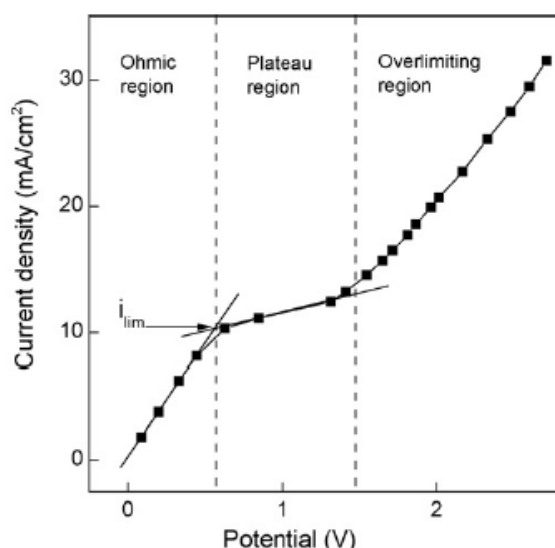


Figure 19: Experimentally determined current vs. voltage curve measured in a laboratory electrolysis stack with a 0.05 M NaCl-solution [101].

The current- voltage behaviour is related with the concentration polarization. In ion exchange membrane feed mixture components permeate at different rates and thus results a concentration gradient in the fluids and on the both side of the membrane which is termed as the concentration polarization. In the feed side depletion of the permeating solute and in the permeate side enrichment of the permeating solute occurs. At a current load salt concentration on a desalting surface of the membrane is decreased and reduced to zero at limiting current density. This leads to a drastic increase of the voltage drop across the boundary layer and results high energy consumption as well as water dissociation [1, 4-7].

3.2.7 Ion flux measurement by diffusion experiment

The ion flux was measured by a standard glass diffusion cell as shown in figure 20

The standard glass diffusion cell consists a feed compartment and a receive compartment separated by the test membrane. The membrane area was 3cm^2 and polyelectrolyte membrane surface was faced to the feed compartment. Polymeric gaskets with two teflon plate were used around the membrane to prevents leakage during the measurement. Both feed and receiving compartment had equal volume (70ml) and magnetic stirrer was used for vigorous mixing. The test membrane was kept in the salt solution overnight to be stabilized for the diffusion dialysis experiment (same as the experimental salt concentration).

Prior to the experiment both the feed and the receiving compartment was washed several times by demiwater and homogenized by the salt solution.

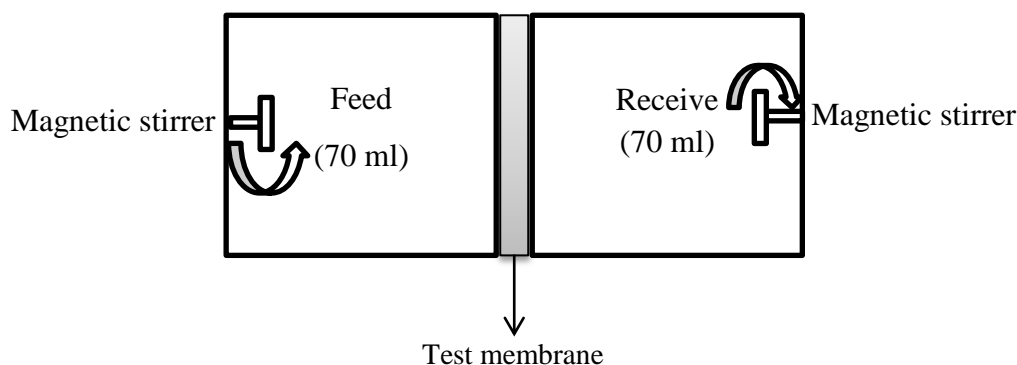


Figure 20: Schematic standard glass diffusion cell.

The feed compartment was used for the salt solution (KCl or LiCl or the mixture of both) and receive compartment for the equal concentration and amount of the acid (HCl). Thus neutrality of Cl^- in both cell were maintained. Salt ion (K^+ or Li^+ or the mixture of both) neutrality was balanced by the H^+ . Therefore we achieve the cation concentration difference in feed and receiving compartment.

Due to the ion concentration difference in both feed and receive compartment, ion transport occurred through the membrane according to the Equation 2 (1st term of the Nernst Plank flux equation i.e. Ficks law). In every 15 min, 0.3ml sample was taken from both feed and receiving compartment by micropipette. The duration of one experiment was considered for 90 minute. Several experiments were conducted with different salt concentration, PEM modified sample and FKB base membrane.

The sample withdrawn during an experiment was further diluted 10 times by demiwater. The concentration was measured by the BWB flame photometer. Prior to analyse the sample, the photometer was calibrated for precise concentration (The calibration method and the scheme of basic BWB Flame photometer are given in Appendix A. 1.).

Each sample concentration was measured in mmol/l and plotted as concentration vs. time. Mostly a linear increase ion concentration in the receiving side as well as concentration decrease in feed side was found. Using the slope of the receiving side linear fit, flux was calculated according to equation 5. Reproducibility of the each experiment was confirmed by repeating the same experiment with fresh membrane. Volume change in both compartments due to the sample withdrawal was considered negligible.

The flux is the amount of moles transported through the effective membrane area per unit time, thus flux can be calculated by the equation 5.

$$J = \frac{V}{A} \frac{dC}{dt} \quad (5)$$

V is the total volume of the compartment [cm^3], C is the concentration of the compartment at time t [mmolm^{-3}], t is the time [s], A is the Effective membrane area [cm^2]

3.3 Data analysis. and calculation

Origin Pro 9.1 was used for all the data calculation and graph. For electrical resistance current supply and corresponding voltage drop was calculated and measured by. Nova Autolab 1.10. Spectra Suite software allowed to record the UV-Vis profile and contact angle snapshot was measure by the OCA 20 in sessile drop mode

4. Result and discussion

4.1 Membrane Characterization

4.1.1 Characterization by UV-Vis spectroscopy

The UV-Vis spectroscopy technique was used to observe the polyelectrolyte multilayer and their deposition trend. The UV-Vis spectra of PDADMAC-PSS multilayers on FKB membrane and PDADMAC-PSBMA-PSS modified FKB membranes are shown in this section.

4.1.1.1 UV-Vis spectra for PDADMAC-PSS modified FKB

The UV-Vis spectra of PDADMAC/PSS bilayers on quartz glass are shown in figure 21(a) and the spectra of PDADMAC/PSS bilayers on FKB membrane are shown in figure 21(b).

Zapotoczny et al (2005) [65] has reported the UV-Vis absorbance of PSSS-block-VN at 228 nm though the absorption peak can be found in the range of 280-320nm. PDADMAC absorption was reported as negligible in the spectroscopic region. Based on this study we have assigned the absorption band at 280nm for PSS and found more/less clear peak of bilayers on quartz substrate. The steady increase of the absorbance was observed with the increase of number of bilayers.

The spectra of bilayers on FKB membrane did not give any distinct peak but shows the spectra in an approximate range of 270-350nm. FKB is a polyether ether ketone (PEEK) reinforced membrane and PEEK gives the absorbance peak at around 335nm, though contradicts with some other literature [109]. In fact there might be an effect of absorbance by PEEK in the FKB membrane. Considering the effect of PEEK on UV-absorbance, the spectra is shown in figure 22(b), we can say that the peak range 270-350nm may be a result of two peaks in the spectrum. Since we were interested to observe the PEM layer deposition trend therefore 280nm was also assigned for figure 22(b). Though the assumption is not very straight forward however a steady increase of absorbance with number of bilayers is also observed.

It is also often reported that PEM (for strong polyelectrolyte pair) growth depends on the nature of substrate and also termed sometime as substrate dominated PEM growth [33-38,41] which contradicts according to AFM results reported by Zapotoczny et al [65]. Nevertheless

our UV experiment shows different absorbance value for bilayers when substrate is different for example absorbance values of bilayers on FKB are higher than the absorbance in quartz glass.

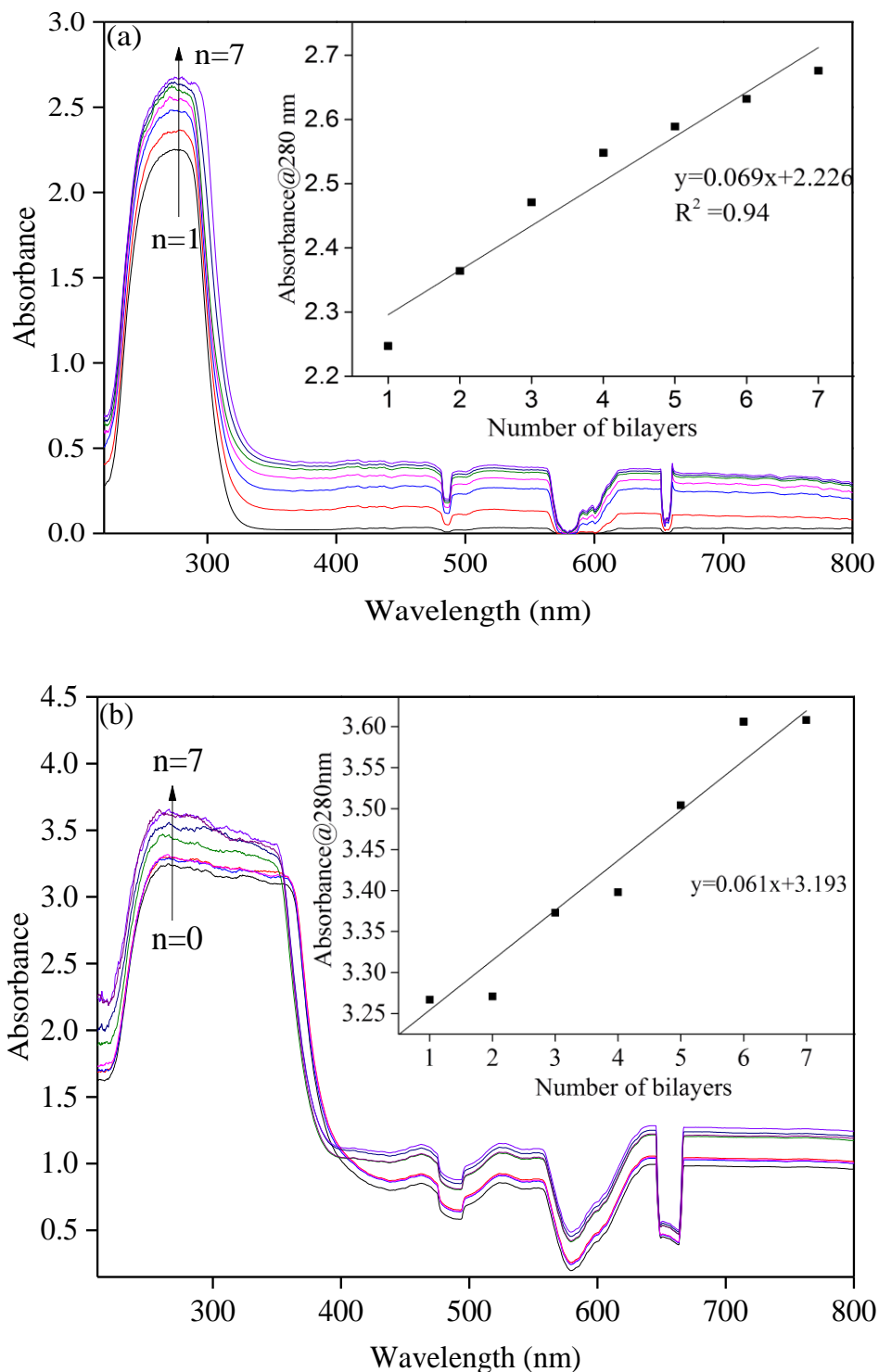


Figure 21: UV-Vis spectra for PDADMAC/PSS bilayers on (a) Quartz glass (b) FKB cation exchange membranes; n= number of bilayers from zero to seven

The UV-Vis absorbance (at 280nm) vs. number of bilayers shows a linear trend which gives the information of layer growth. Thus we have successfully deposited PDADMAC-PSS multilayer on both quartz glass and FKB substrate (spectra) and the linear trend (insert) shows that in each dipping cycle same amount of the polyelectrolyte was deposited. Thus multilayers were formed in a regular manner.

Nestler et al (2013) [110] showed that when molecular weight of PSS is >25kDa and PDADMAC is >80 kDa the PEM growth is observed linear. In our experiment, we used PDADMAC, $M_w = 150$ kDa and PSS, $M_w = 100$ kDa, thus a linear fit for the figure 21 is logical. Also the asymmetric model (section 2.3.2) suggests the linear growth of the PDADMAC/PSS multilayer on Si substrate when layer number is < 10-12. [41].

Though the nature of the linearity is kind of scattered distribution for both cases however can be hypothetically co-relate with the roughness and/or thickness variance in different points. It can be assumed from the data point's distribution (insert of figure 21) that PEM on FKB exhibits rougher structure then PEM on quartz glass.

4.1.1.2 UV-Vis spectra for PDADMAC-PSBMA-PSS modified FKB

The UV-Vis spectra for PDADMAC-PSBMA-PSS trilayers are shown in Figure 22.

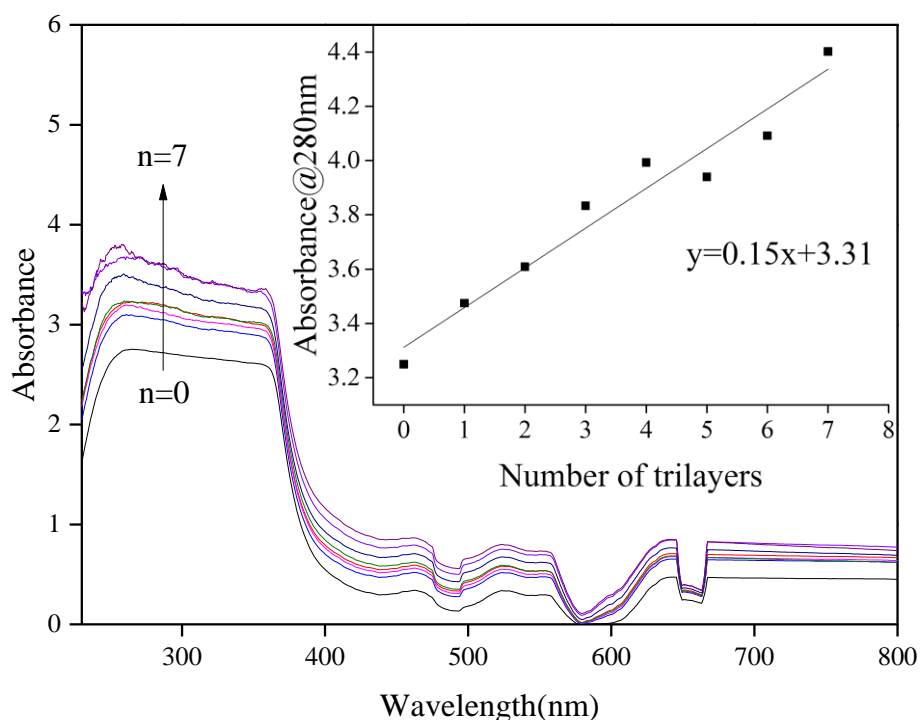


Figure 22: UV-Vis absorbance spectra for PDADMAC-PSBMA-PSS multilayer and absorbance vs. number of trilayer at 280nm (inset).

The absorbance spectra are quite similar to the figure 21(b). The absorbance peak was assigned at 280 nm and the range of the absorbance peak (figure 22) could be a result of absorption of PSS (peak range 280-320 nm) and PEEK.(around 335nm) as explained before (section 4.1.1.1) [65,109]. A steady increase of the absorbance peak was found with the increase of number of trilayers which means that the trilayer growth on FKB membrane by PDADMAC-PSBMA-PSS was successful. The absorbance vs. number of trilayer at 280 nm gives a linear trend. Thus we can say that the multilayer deposition was stoichiometric.

Comparing with figure 21(b) and figure 22, the absorbance for base membrane (n=0) and linear trend were found same but the slope of inset figures are different. Hypothetically we can say that PSBMA layer influences the deposition trend and thickness. PSBMA is zwitterionic and growth of PEM may not solely rely on charge-charge interaction [104].

Nevertheless, for PDADMAC/PSS layer thickness linearity depends on molecular weight along with other variables [110] but for PDADMAC-PSBMA-PSS, more literature investigation and experiments are required to have the idea about the layer thickness and other characteristics.

4.1.2 Characterization by contact angle

The contact angle measurement was used to characterize the polyelectrolyte modified membrane by its hydrophilic/hydrophobic behaviour. The water contact angle of PDADMAC-PSS multilayers on FKB membrane and PDADMAC-PSBMA-PSS modified FKB membranes are shown in this section.

4.1.2.1 Contact angle measurement for PDADMAC-PSS modified FKB

The contact angle (CA) vs. number of bilayer is shown in figure 23 in which bilayer 0 is for the FKB membrane without any modification. Other than bilayer 0 each (+) marked data shows the CA of PDADMAC terminated layers and (-) marked ones are for PSS terminated layers. (Appendix B for contact angle values)

An oscillating change of the contact angles upon alternating deposition of PDADMAC and PSS can be observed from figure 23. In general, all membrane samples show hydrophilic behaviour except the 0.5 bilayer which is slightly hydrophobic. An odd/even and hydrophilicity/hydrophobicity trend is observed from figure 23.

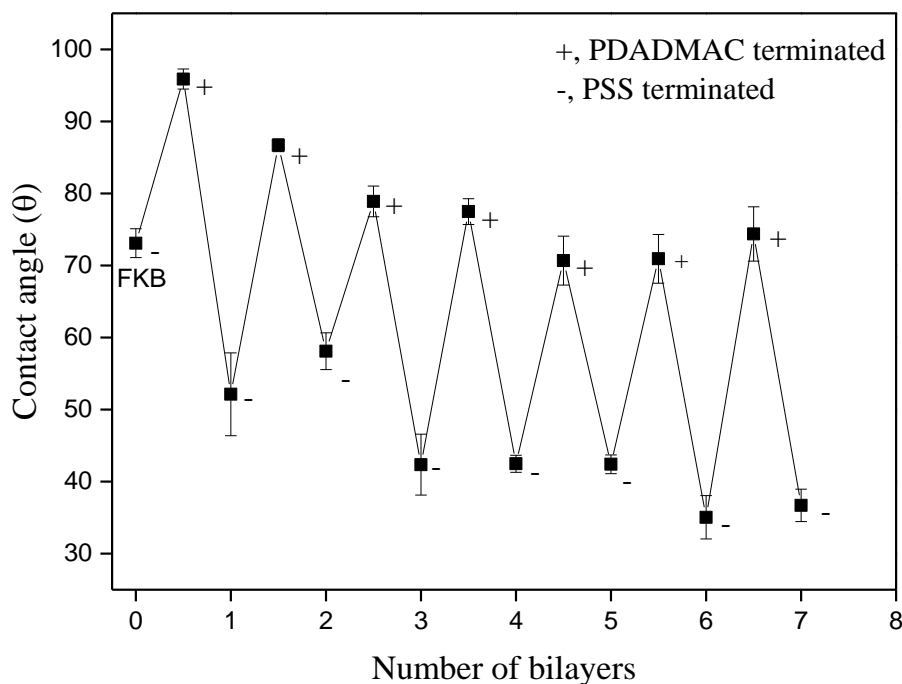


Figure 23: PDADMAC/PSS Contact angle vs. number of bilayers.

This odd-even trend is explained by the polar surface properties of PEM multilayers [103]. The polarity reverts with each monolayer deposition. Also we can draw attention to the charge reversal phenomenon of polyelectrolyte multilayer (described in section 2.3.2). Thus in each PDADMAC deposition step the surface become positive and shows higher CA value and in each consecutive PSS deposition step the surface become negative which gives lower CA value. In other words each PDADMAC terminated layer shows more hydrophobic nature than PSS terminated layers and contact angle values are dependent on outermost layer [59].

We also can observe that layer to layer oscillation is in between 20 -40°. Köstler et al (2005) [103] reported about CA odd-even trend when PDADMAC-PSS multilayer was deposited on PTFE and PET substrate but CA oscillation differs from substrate to substrate, for example PDADMAC-PSS multilayer on Si gives a CA oscillation about 10° whereas on PTFE gives around 20° for same electrolyte pair. The reason of such behaviour can be explained by the low surface energy character. It has been reported that PTFE has a low surface energy character and gives high layer to layer oscillation; in contrast Si has comparably high surface energy and gives low CA oscillation [65,103]. From this study we can say that our FKB might have a low surface energy character and thus gives a high contact angle oscillation.

We can draw a contradiction here; if the outermost layer and underlying substrate are solely responsible for contact angle oscillation then CA for all PDADMAC terminated layers and

CA for all PSS terminated layers are expected to be same but the experimental results shows that for each PDADMAC and PSS terminated layers, contact angle values decreases with increasing the layer number. We can say that there might be an effect of underlying polyelectrolyte layer. Hsieh et al (1997) [111] has reported that water contact angles for same polyelectrolyte pairs exhibits different values depending on the underlying polyelectrolyte layers which suggests a high degree of layer interpenetration. Another study of Faibish et al (2002) [112] suggests that the contact angle value is related with the coating density. For first few layers the coating can be assumed as incomplete. As the layer number increase, coating density also increases which may can contribute to lowering the contact angle values.

Nevertheless a high degree of interpenetration of polyelectrolyte gives a very thin layer and PEM in contact of water swells immediately and polymer become hydrated which increases the thickness. It means the reduction of degree of interpenetration at swollen state [113]. Hence water contact angle can be assumed to be affected only by the outermost layer. Meanwhile hydrophbization effect is relevant since the contact angle exhibits different value with different drying protocol [59,65,103].

We can summarise that the odd-even and hydrophilic/hydrophobic effect occurs because of the polarity change with each layer deposition. The FKB substrate contributes to significant effects on the oscillation together with the outermost layer. As the number of bilayer increases higher degree of layer interpenetration becomes gradually effective with an increasing coating density therefore the contact angle value decreases with increasing the layer number (considering the CA trend separately for all PDADMAC terminated and PSS terminated layers) i.e. increases the hydrophilicity with increasing the layer numbers while exhibiting the same odd-even trend.

In general we can say that-as the number of bilayer increase (PDADMAC-PSS modified FKB membrane), no matter whether the membrane is PDADMAC terminated or PSS terminated, the hydrophilicity of the membrane increases with the number of bilayers. Extrapolating the hydrophilic behaviour it also can be assumed that at higher bilayer number PDADMAC terminated layer can be sufficiently hydrophilic and may be able to influence ion transport behaviour.

4.1.2.2 Contact angle measurement for PDADMAC-PSBMA-PSS modified FKB

The contact angle (CA) of the PDADMAC-PSBMA-PSS vs. number of trilayer is shown in the figure 24

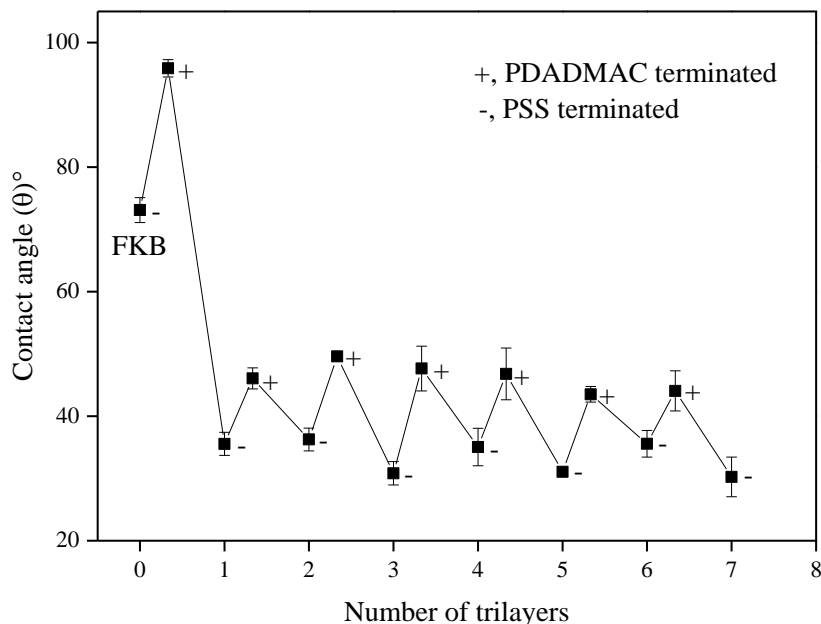


Figure 24: Contact angle vs. number of trilayers

Contact angle for FKB base membrane and first monolayer gives the higher values than other trilayers. A significant decrease of CA can be observed at first trilayer and then an alternating trend of CA is observed. It can be noted that first PDADMAC terminated layer refers to a single monolayer on the surface and trilayer 1 forms with a PSBMA layer in between PDADMAC and PSS layers. At this point the effect of PSBMA can be noticed by comparing with Figure 23 which suggests that PSBMA make the membrane more hydrophilic and also reduces the layer to layer oscillation to 10° to 15°, similar to the PDADMAC-PSS multilayer on a Si [65,103]. Also we can say that PSBMA can change the hydrophilicity/hydrophobicity of the PDADMAC/PSS multilayer system and the surface charge characteristics.

PSBMA grafting on hydrophobic surface can reduces contact angle about 15° reported by Chang et al (2011) [118]. Taking into account the effect of PSBMA we can say that the first PDADMAC terminated layer was found slightly hydrophobic. Later contact angle decreases significantly because of PSBMA and PSS layer (CA of trilayer 1). Comparing with Figure 22, it seems like the contact angle reduces due to the contribution made by PSBMA because the substrate, other polyelectrolytes and deposition condition was same. From trilayer 1 to 7,

the similar oscillating behaviour can be observed. We can assume that; at PSS terminated trilayer 1, surface charge density is already influenced by the PSBMA which affects the next PDADMAC deposition step and so on.

Nevertheless substrate effect on PEM is reported as significant for PDADMAC/PSS system [111] whereas PDADMAC/PSBMA is substrate independent [104] however PSBMA affects the charge reversal process [119]; also can be understood by the UV-Vis linear trend comparison between figure 21(b) and figure 22. Thus hydrophilicity/hydrophobicity controlling by PSBMA could be an interesting aspect to investigate in future.

4.2 Membrane performance

4.2.1 Membrane electrical resistance

The electrical resistance (R) of the membrane was measured by a direct current method in 0.5M NaCl salt solution. A current-voltage relation was measured in ohmic region which gives the membrane electrical resistance. Polyelectrolyte multilayer on cation exchange membrane and determining their electrical resistance behaviour were the primary focus. The membrane electrical resistance is significant because it can give information about the membrane characterization and performance. The electrical resistance of PDADMAC-PSS multilayers on FKB membrane and PDADMAC-PSBMA-PSS modified FKB membranes are shown in this section.

4.2.1.1 Electrical resistance for PDADMAC-PSS modified FKB

The membrane electrical resistance (R) vs. number of bilayer is shown in figure 25

Bilayer 0 represents the FKB membrane without any polyelectrolyte layer. Other than bilayer 0 each (+) marked points are the resistance of PDADMAC terminated layers and (-) marked points are the resistance for PSS terminated layers. As the number of bilayer increases an alternating trend of resistances are observed.

Considering all PDADMAC and PSS terminated layers separately, the membrane resistance increases with the increase of bilayer which is opposite to the contact angle values. Comparing figure 23 with figure 25 we can see that membrane electrical resistance increases as the number of bilayer increases whereas contact angle decreases i.e. hydrophilicity of the membrane increases.

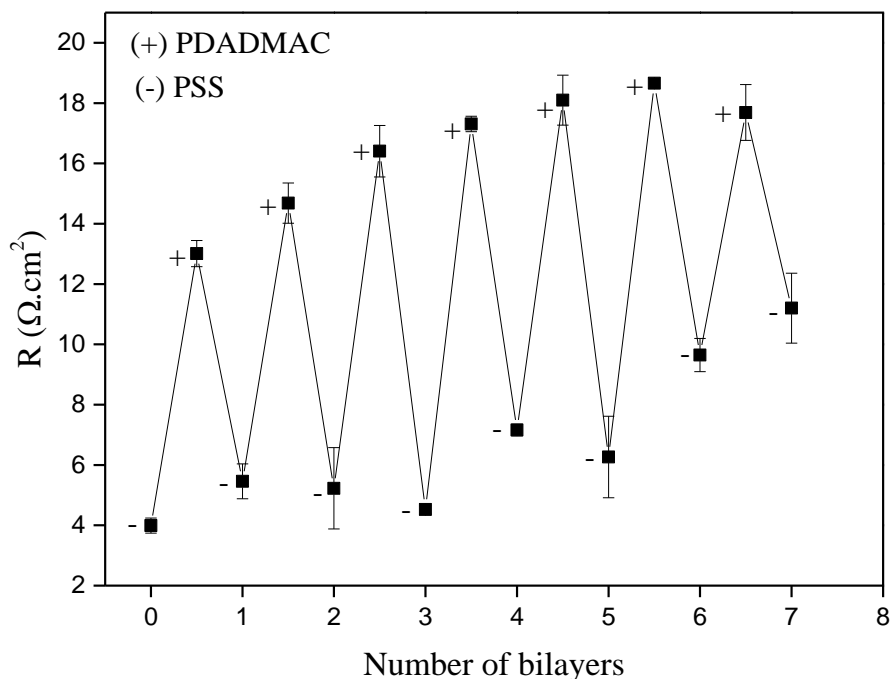


Figure 25: Electrical Resistance vs. number of bilayers.

FKB cation exchange membrane, by nature it has a negative surface (See appendix C1 for the properties of the FKB cation exchange membrane). According to charge reversal process (described in section 2.3.2) each PDADMAC deposition step convert the surface from negative to positive which gives a high R value; in contrast each PSS deposition step make the surface as negative which gives lower R value. [27,28]

The alternating deposition of PDADMAC-PSS thus gives a zig-zag trend of electrical resistances. This behaviour exhibits more likely an odd-even trend (similar to the contact angle result shown in figure 22). The reason can be the surface potential of the outer layer. The odd-even effect is defined as the reversible variations with the sign of charges of the terminating layer [106]. As evidence, ζ -potential of PDADMAC/PSS has been reported as reversibly alternating [105]. Thus one hypothesis can be the surface potential changes with every layer deposition results the odd-even electrical resistance trend [107]. When surface become positive due to the PDADMAC terminated layer, it contributes to repeal the cation to pass though i.e. Donnan exclusion may become dominant which can also contribute to increase the resistance.

For the base membrane the electrical resistance was found as $3.98 \pm 0.24 \text{ ohm.cm}^2$ which is an agreement with the supplier information, $<4 \text{ } \Omega.\text{cm}^2$ (at 0.5M NaCl). At this point we can

comment that the membrane was correctly preconditioned and was in H^+ level for the deposition of the polyelectrolyte. With a PDADMAC monolayer the resistance was found as $13.01 \pm 0.34 \text{ ohm.cm}^2$. In successive PSS deposition steps the R value come back as 5.45 ± 0.74 . (Appendix C.2 for resistance data). In general monolayer thickness is reported as 0.5 nm to 5 nm (Table 3) and the FKB membrane thickness was 80-100 μm (appendix C.1).

The thickness of monolayer on FKB membrane is very small compare to the original membrane thickness. We can say that the thickness of PEM layer solely should not contribute to high resistance rather a combination of surface potential, cation Donnan exclusion and thickness due to swelling behaviour can be assumed. Taking into account the asymmetric model for PSS/PDADMAC system which suggests a PEM with PDADMAC terminated layer has many positive sites and thickness increment is linear (<10-12 bilayers) [40].

Taking into account all information above; we can mention about several possibilities of the resistance zig-zag behaviour. First of all alternating surface potential occurs due to each monolayer deposition which gives the zig-zag resistance trend. Though each monolayer thickness is considerably small but the complexity of the structure obtained from each monolayer cannot be avoided at higher number of layers. Hence it can contribute to increase the resistances. Higher resistance values for PDADMAC terminated layer originates because of the swollen thickness and surface potential along with the Donnan exclusion as PDADMAC terminated layer has many positive sites according to the asymmetric model.

Again taking into account the contact angle results shown in figure 23 it was assumed that as the number of bilayer increases the layer interpenetration and coating density increases which reduces overall contact angle however; the coating density and layer interpenetration also can give surface complexity which may can increases the overall resistance (Figure 23).

Nevertheless the resistance measurement in a direct current method gives not only the membrane resistance but also include resistance of membrane-solution interface i.e. diffusion boundary layer and electrical double layer [101]. Therefore it could be an assumption that resistance of polyelectrolyte multilayer can be influenced by the electrical double layer and diffusion boundary layer, when exposed in the solution.

4.2.1.2 Electrical resistance for PDADMAC-PSBMA-PSS modified FKB

The electrical resistance (R) vs. number of trilayers of PDADMAC-PSBMA-PSS modified FKB membranes are shown in the Figure 26.

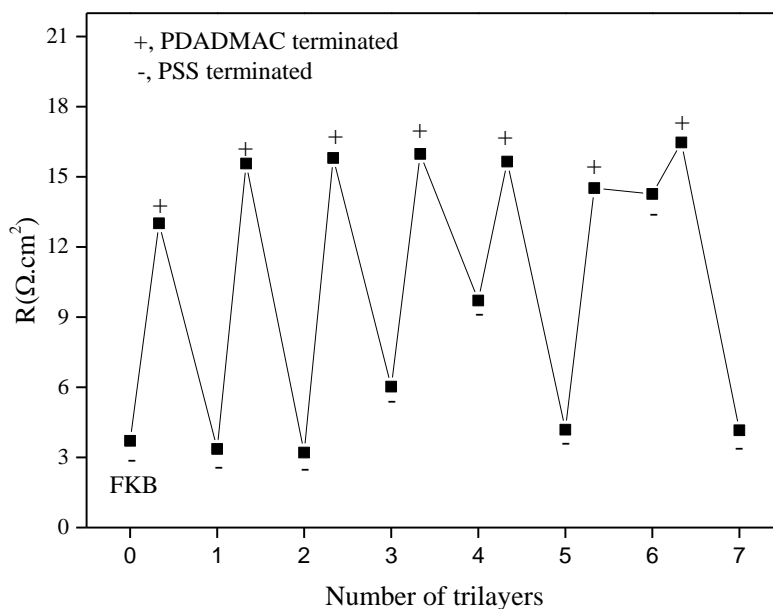


Figure 26: Electrical resistance vs. trilayers.

The layers which are PDADMAC terminated show higher resistances than PSS terminated layers and resistance changes alternatively with each monolayer deposition. The reason can be explained by the surface charge reversal. Though in every trilayer there is a PSBMA zwitterion layer in between, even so resistances zig-zag trend is comparable with the figure 23 which primarily gives the assumption of charge inversion due to cationic and anionic terminated layer depositions. [27,28]. From this comparison it seems that PSBMA layer does not effect on the electrical resistance.

It should be noted that for first few PSS terminated layer R was found smaller than the FKB base membrane which ideally should not happen. Considering the increase of layer thickness with the increase of the number of trilayers (as shown in figure 22); it was expected to see the resistance increasing trend (considering R separately for all PDADMAC or PSS terminated layers) with the increase of the number of trilayers (similar results as shown in figure 25). However, the reason could be the experimental error during the measurement and partial decomposition of the PSBMA layer in the 0.5M NaCl solution. PSBMA is reported as an

ionic strength responsive polymer and at 0.5M NaCl solution it suffers melting off from the surface [104]

4.2.2 Limiting current density

The limiting current density (i_{lim}) of different membrane samples has been measured. First of all a typical current-voltage curve is shown in figure 27

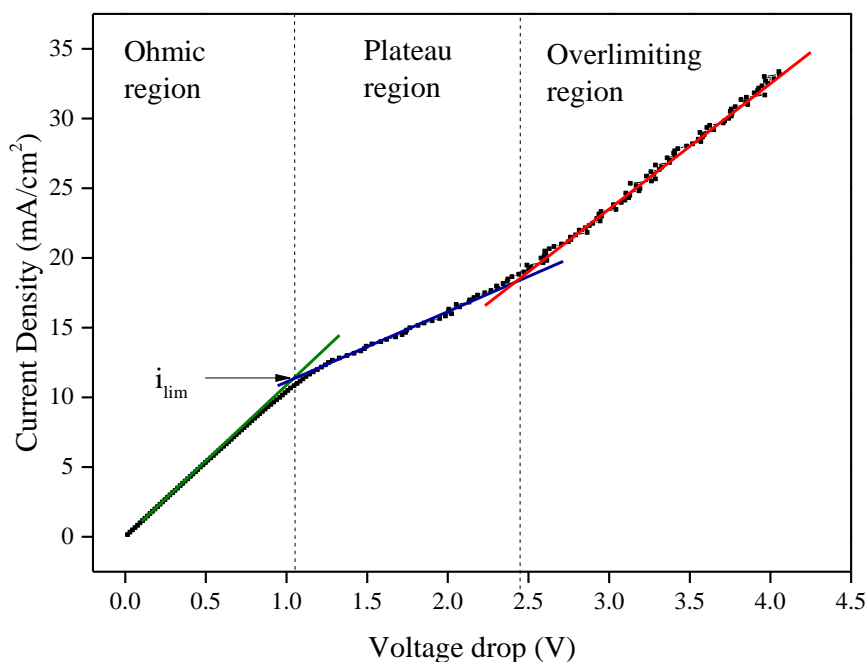


Figure 27: Current-voltage curve for the relation between current through a membrane and corresponding voltage drop over the membrane and its boundary layer. (Measured at 50mM KCl and LiCl)

We can distinguish three regions from the current-voltage relationship, a sharp linear increase of current density with voltage drop which is namely ohmic region. After the sharp increase a plateau region is observed where slow increase of current density occurs due to the concentration polarization. In plateau region, concentration in the dilute boundary layer decreases and therefore the resistance increases; which results a deviation in the linear behaviour. Finally again a sharp increase can be observed (over limiting region). In this region electro-convection occurs [1,2,8,101,102]

The current-voltage relation gives important information about resistances against ion transport and boundary layer. [101]. Also i_{lim} value indicates the operating current level for electro dialysis (ED) because in ED, it is unexpected to have the concentration polarization

(CP).since concentration polarization is directly related to the ED operating efficiency with power consumption. Thus i_{lim} value gives the idea about the maximum operating current level at certain salt concentration.

We have considered FKB base membrane, bilayer 6 and 6.5.membranes for i_{lim} measurement. These samples were selected based on the previous characterization and resistance results. Previously measured UV-Vis, contact angle and electrical resistance shows that lower number of bilayers may have lower surface coverage, lower thickness and lower polyelectrolyte density. Therefore higher number of the layers was preferentially selected and considered for i_{lim} measurement. For each individual sample current density (mA/cm^2) vs. voltage drop was plotted from which the i_{lim} value was calculated.

The i_{lim} of base membrane, PSS terminated (-) bilayer 6 and PDADMAC terminated (+) bilayer 6.5 were measured at salt concentration of 50mM KCl, 50 mM LiCl and mixture of 50 mM KCl and LiCl. These salt concentrations were selected because ion transport experiments were conducted with the same salt and same concentration.

The changes of limiting current density with number of bilayers are shown in figure 25

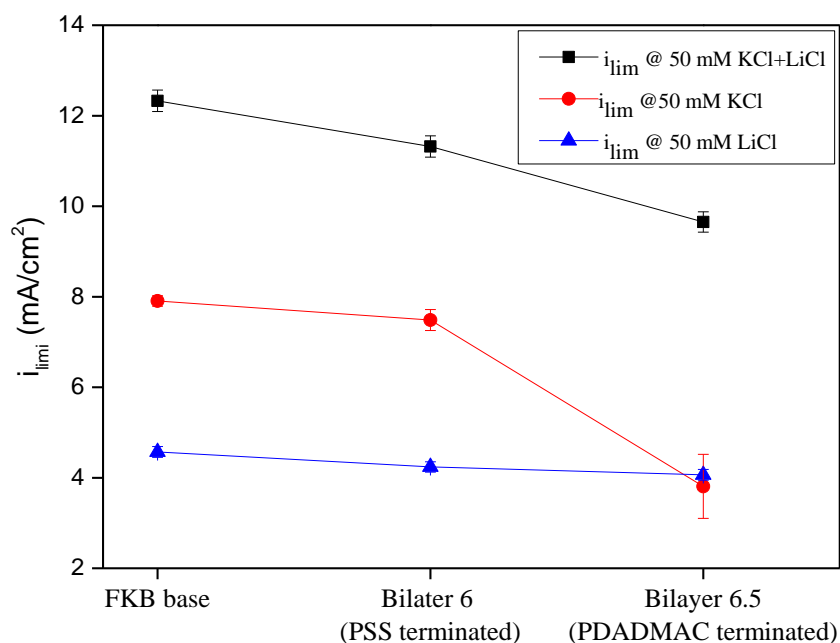


Figure 28: Limiting current density behaviour with different bilayer.

In general, i_{lim} values decrease with the increase of number of bilayers. Different monovalent salt gives different i_{lim} value (at certain concentration) which signifies valuable information to

select an approximate operating current in case of involving these polyelectrolyte membranes in ED. (i_{lim} data is given in appendix D.1).

FKB base membrane shows higher i_{lim} when measured in the mixed salt solution compare to the i_{lim} values in single salt. In both single and mixture of salts, the concentration was used as same however for the same volume; number of ions in the mixed salt solution was double then the number of ions in the single salt. Therefore high i_{lim} is logical when measured in the mixed salt. Also i_{lim} is proportional to the concentration of the salt solution [114].

The limiting current density (i_{lim}) of base membrane in .KCl shows higher value then LiCl; which could be related to ion transport number and salt diffusion co-efficient. It was reported for CMX membrane that the counterion transport number and salt diffusion co-efficient are higher for K^+ then Li^+ . Also the i_{lim} value of CMX was found higher in KCl than LiCl when measured in the same salt concentration [1]. Therefore the i_{lim} values of the base FKB membrane differs due to the salt type and the concentration of the solution, ion transport number and salt diffusion co-efficient.

Bilayer 6 membranes are PSS terminated and have (-) surface (from the contact angle and the resistance data shown in figure 23 and 25). Thus the Bilayer 6 gives more/less similar i_{lim} value though a slight decrease can be noticed which could be the effect of PEM on the FKB membrane. .

At the bilayer 6.5, the important observation is the steep decrease of the i_{lim} for KCl in single salt whereas i_{lim} for LiCl and i_{lim} for mixed salt shows the same trend. It worth to mention that the bilayer 6.5 is PDADMAC terminated, have a positive surface and also exhibits higher electrical resistance (R) and higher contact angle (CA) (Figure 23 and 25). If we account high R and comparably hydrophobic nature as primary reasons, a steep decrease of i_{lim} could be expected for all the three cases which do not agree with the results that we obtained (bilayer 6.5 at figure 25). However, i_{lim} is proportional to the salt diffusion co-efficient and inversely proportional to the boundary layer thickness [1,101]. In lower concentration boundary layer thickness could be considered as less effective [101,102]. Thus we can assume that i_{lim} at bilayer 6.5 in KCl (single salt) decreases significantly than i_{lim} at bilayer 6 because polyelectrolyte multilayer on FKB reduces the KCl salt diffusion co-efficient in the membrane phase due the modification.

We can summarise that i_{lim} value decreases at bilayer 6 due to the polyelectrolyte multilayer on FKB membrane and at bilayer 6.5, surface charge reverts to positive. Therefore KCl receives high Donnan exclusion and also salt diffusion co-efficient may be reduces significantly. As a result i_{lim} of bilayer 6.5 at KCl decreases significantly.

Nevertheless the surface positive charge of bilayer 6.5 and thus the Donnan repulsion may be able to affect the boundary layer even at lower concentration and also influence the salt diffusion coefficient at membrane phase. Ionic and hydration radii (for ionic radii $K^+ > Li^+$, hydration radii $Li^+ > K^+$) also can play a vital role on i_{lim} .

4.2.3 Membrane performance for PDADMAC-PSS modified FKB

The diffusion experiment for K^+ , Li^+ and a mixture of K^+ and Li^+ is shown in the section 4.2.3.1, 4.2.3.2. and 4.2.3.3. The salt concentration was considered as 50 mM for each experiment. The Cl^- ion and the cation electroneutrality was balanced by involving the equivalent amount of HCl. Hence we obtained ion transport behaviour of K^+ and Li^+ in FKB membrane and also in polyelectrolyte modified FKB membranes. Figure 29-31 shows the ion diffusion experiment results for the base FKB membrane, bilayer 6 and 6.5. In each diffusion experiment we can see that; as the feed concentration decreases, the receiving concentration increases which is logical according to the Fick's law (1st term of equation 2). Feed and receive concentration changes with time are shown in all left side figures of section 4.2.3.1 to 4.2.3.3.

The flux of each ion was calculated from concentration changes vs. time in the receiving side and using the equation 5. Thus ion concentration changes vs. time in receiving side for each experiment is separately shown (right side graphs of figure 29-31).

In every experiment a linear increment of concentration with time is observed, hence we can say that the diffusion experiment time (90 min) is not sufficient enough to reach Donnan equilibrium at the considered initial ion concentration difference (50mM) between feed and receiving compartment. However the effect of different bilayers, ion types (both single and mixed), and effect of ion concentration differences can be primarily understood from the ion diffusion experiment i.e. concentration vs. time plot shown in figure 29-31.

The concentration vs. time plot was further used to calculate the flux and selectivity is shown in section 4.2.4

4.2.3.1 Diffusion experiments for K^+

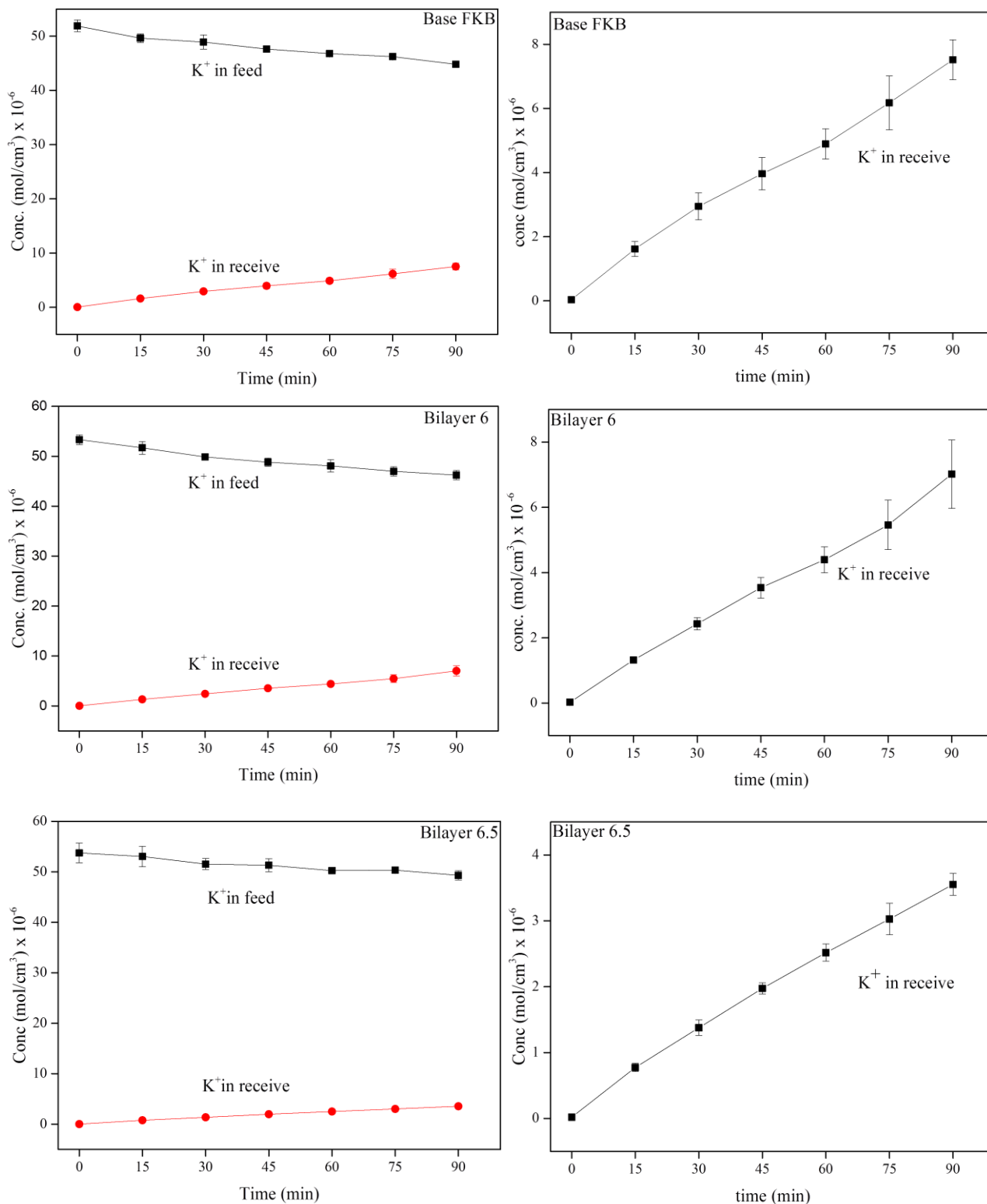


Figure 29: Diffusion of K^+ in Base, (top), bilayer 6 (middle) and bilayer 6.5 (bottom).left side figures are the overall profile and right side ones for receiving compartment profile.

4.2.3.2 Diffusion experiments for Li⁺

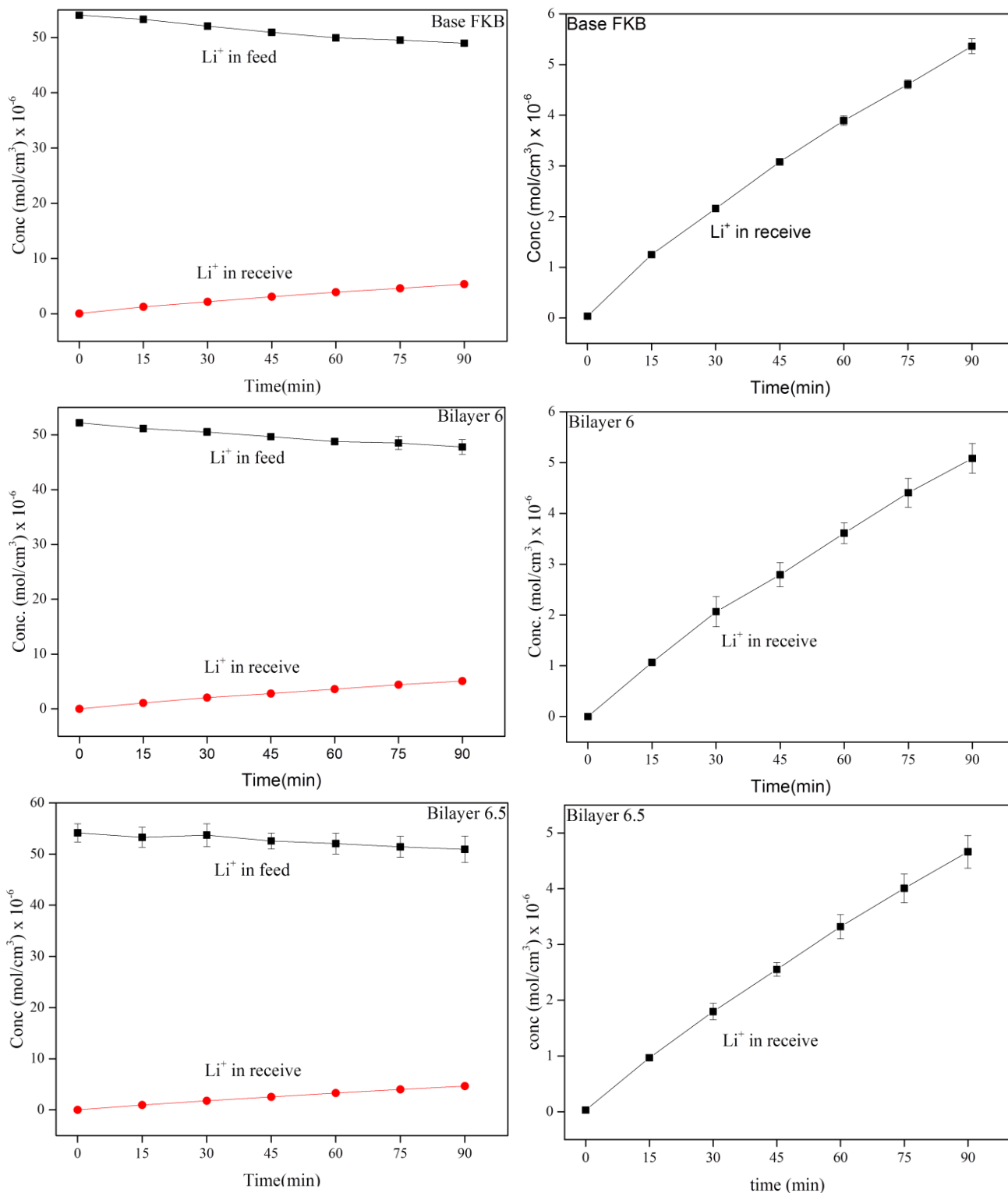


Figure 30: Diffusion of Li⁺ in Base, (top), bilayer 6 (middle) and bilayer 6.5 (bottom). Left side figures are the overall profile and right side ones for receiving compartment profile.

4.2.3.3 Diffusion experiments for mixture of K^+ and Li^+

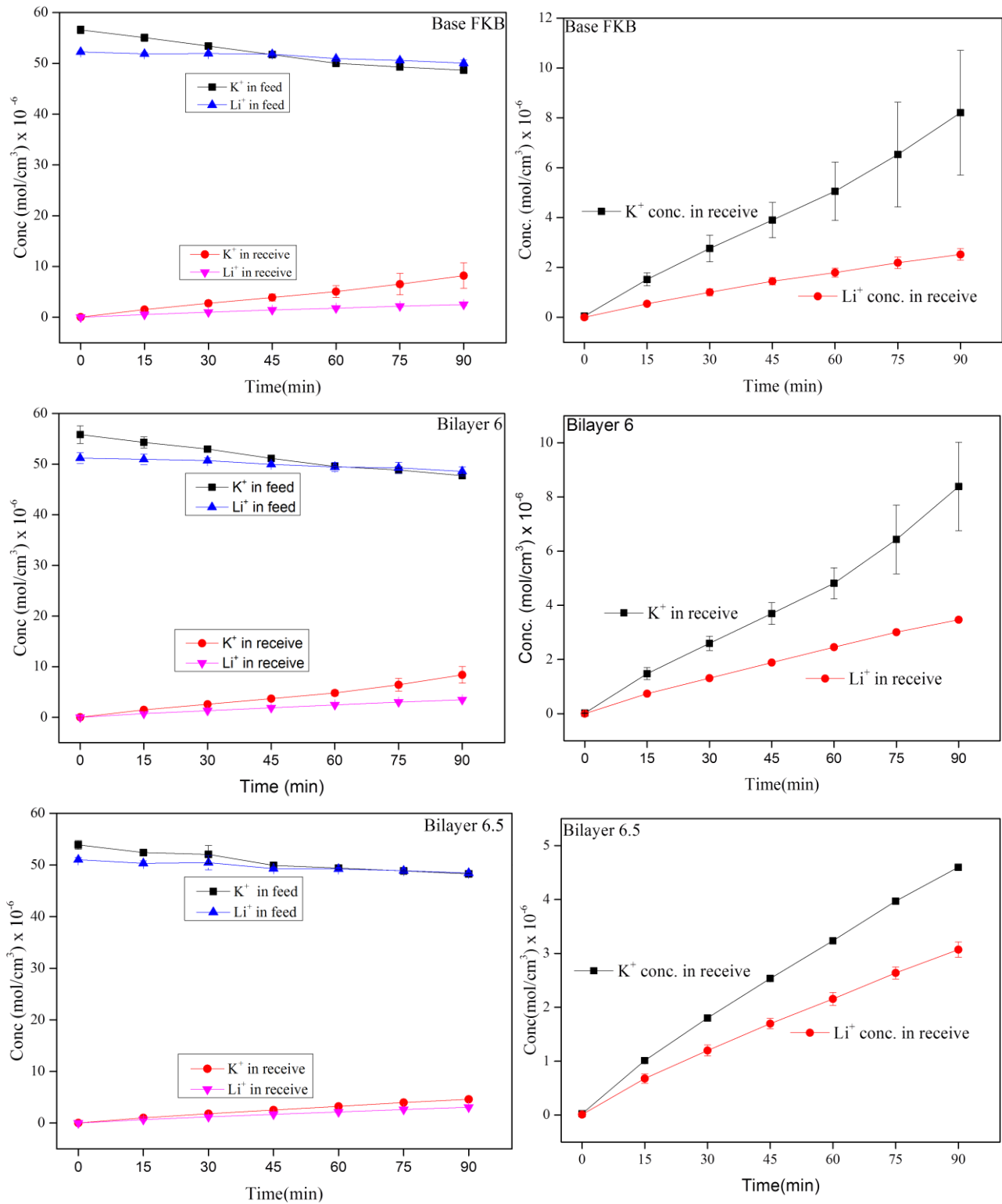


Figure 31: Diffusion of mixed salt experiment (50mM KCl and 50mM LiCl) i.e. K^+ and Li^+ in Base, (top), bilayer 6 (middle) and bilayer 6.5 (bottom). Left side plots are overall profile and right side ones for receiving compartment profile.

4.2.4 Flux and selectivity

Individual ion flux in different membranes were calculated from figure 29-31 and using the equation 5. The ion flux vs. number of bilayers is shown in figure 30. and the selectivity K^+/Li^+ vs. number of bilayers is shown in figure 31.

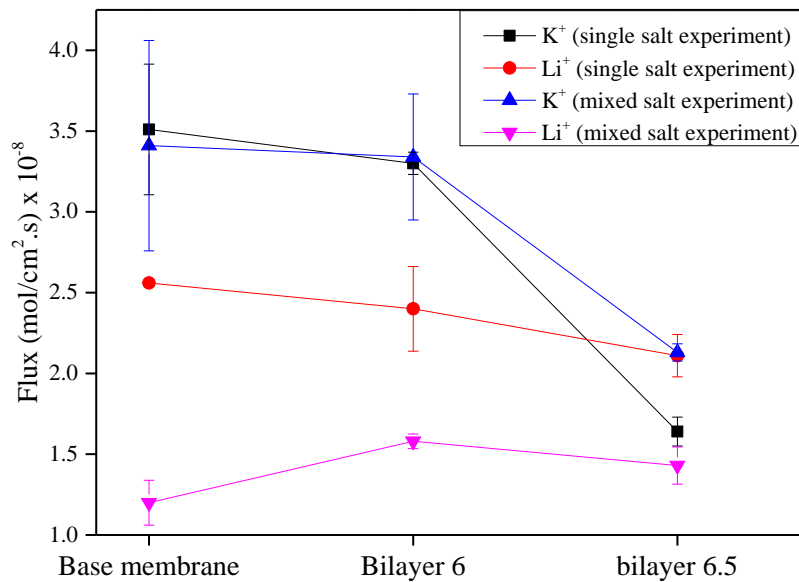


Figure 32: Different ion flux vs. bilayers.

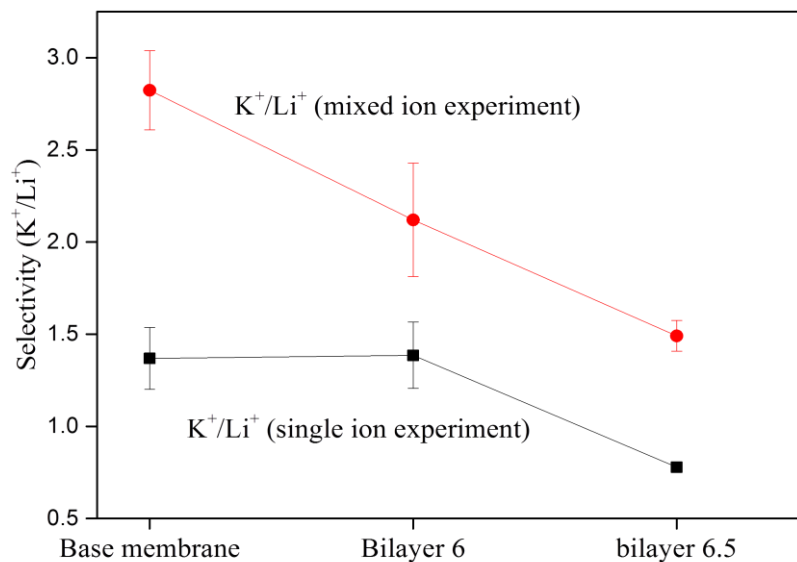


Figure 33: selectivity (K^+/Li^+) vs. bilayers.

The ion transport behaviour and the effect of bilayers shows that as the number of bilayer increases the ion flux decreases but in a different rate.

The flux of K^+ decreases more than the flux of Li^+ which affects the selectivity of K^+/Li^+ (Figure 33)

The flux of K^+ and Li^+ (both single ion and mixed ion experiment) in base and bilayer 6 shows more/less same behaviour. However comparing fluxes of base and bilayer 6, the K^+ flux decreases with the increase of bilayers but Li^+ flux stays almost similar, though a small increase for mixed ion experiment can be observed. At bilayer 6.5, flux values for both single ion and mixed ion decreases. For K^+ , flux decreases significantly then Li^+ (Figure 32). Thus the selectivity of the K^+/Li^+ also decreases with increasing the layer number (Figure 33). In Table 5 and Table 6 flux and selectivity results are given.

Table 5: K^+ and Li^+ flux in FKB and PEM by LbL.

Type of Membranes	J_{K^+} (single ion experiment) [mol/cm ² .s]x10 ⁻⁸	J_{Li^+} (single ion experiment) [mol/cm ² .s]x10 ⁻⁸	J_{K^+} (mixed ion experiment) [mol/cm ² .s]x10 ⁻⁸	J_{Li^+} (mixed ion experiment) [mol/cm ² .s] x 10 ⁻⁸
FKB Base	3.51±0.41	2.56±0.02	3.41±0.65	1.20±0.14
Bilayer 6	3.30±0.07	2.40±0.26	3.34±0.39	1.58±0.05
Bilayer 6.5	1.64±0.09	2.11±0.13	2.13±0.05	1.43±0.12

Table 6: Selectivity of K^+/Li^+ for single ion and mixed ion experiments.

Type of Membranes	K^+/Li^+ (single ion experiment)	K^+/Li^+ (mixed ion experiment)
FKB Base	1.37±0.17	2.82±0.21
Bilayer 6	1.39±0.18	2.12±0.31
bilayer 6.5	0.78±0.01	1.49±0.08

The Li^+ has lower ionic radius but higher hydration shell then the K^+ [117] and the bilayer 6 membrane is more hydrophilic (water contact angle 35.05±3°) then base membrane (Section 4.1.2.1). Bilayer 6.5 membranes is PDADMAC terminated and has a positive surface, exhibits the water contact angle 74.4±3.7° and electrical resistance as 17.68±0.92 ohm.cm² (Figure 23 and 25). From these characterization values we can say that bilayer 6.5 bears the opposite surface characteristics then bilayer 6 in terms of the surface charge and conductivity. Therefore both K^+ and Li^+ receive stronger Donnan exclusion in bilayer 6.5 and as a result lower flux values was obtained [115]

If Donnan exclusion is solely responsible for lower flux of K^+ and Li^+ at higher bilayer numbers; then the flux changes is expected to show the same trend at bilayer 6.5 for either ion but we obtained the flux of K^+ decreases significantly then Li^+ . Therefore the Donnan exclusion is not solely responsible but partially influencing the flux behaviour. As a second consideration thickness at swollen state and hydrated cation radius become important.

PEM theory describes that the thickness increment occurs with every monolayer deposition which is approximately 3-5 nm when linear increment is observed [110]. Also we have found a linear increment trend for our sample, showed in figure 21(b). The thickness increment contributes significantly in swelling of the membrane in the salt environment [55]. Apart from it the FKD fumasep membrane (similar to FKB) exhibits approximately 30% degree of swelling. [100]. Therefore we can consider that thickness of our membrane is much higher at swollen state than in the dry state. Due to the higher membrane thickness in swollen state and approximate barrier properties from the PEM complexity, flux values of the K^+ could be smaller than base membrane. The charge complexation is a related phenomenon with PEM growth where intrinsic and extrinsic charges make the membrane to have a highly complex structure [41] (also explained in section 2.3.2). Taking into account this complex structure we can comment that K^+ is partially hindered in the membrane phase so that the flux of K^+ is significantly low at bilayer 6.5 but not the Li^+ . It also affects notably in the K^+/Li^+ selectivity. Therefore one hypothesis could be the change of diffusion coefficient in the membrane phase due to the complex PEM structure, surface charge and significant thickness increment in swollen state. show the low K^+ flux then Li^+ at the bilayer 6.5.

Jingyi et al [3] has demonstrated competitive diffusion based on ion size (smaller size exhibits higher mobility). Since Li^+ has smaller ionic radii then K^+ , thus the permeation behaviour of Li^+ and K^+ could be affected differently due to the PEM layer. Regarding to the transport behaviour by diffusion, Stachera et al [116] demonstrated about a three phase model that describes the transport through hydrophobic polymer phase, active phase including ion exchange fixed sites and membrane interstitial phase where hydrated cation moves preferentially following a hopping and dragging mechanism. Bilayer 6.5 has a positive surface and comparably hydrophobic then the base FKB and bilayer 6. Thus K^+ flux decreases more at bilayer 6.5 then Li^+ due to the different hydrated radius ($Li^+ > K^+$) and Donnan repulsion. Also the hydrophobic polymer phase transport in the three phase model might become effective to facilitate Li^+ more than then the K^+ .

Hence we can compare the result obtained in i_{lim} behaviour (figure 28). At bilayer 6.5, i_{lim} at KCl and K^+ ion flux both decreases significantly and almost synergic result can be observed. Taking into account the effect of Donnan exclusion, the hydrated radius of K^+ and the surface charge of bilayer 6.5; it seems that due to the Donnan exclusion overall K^+ flux reduces at the bilayer 6.5 but because of the bigger cation size of K^+ than Li^+ , K^+ is partially hindered and therefore it retains more than Li^+ at bilayer 6.5.

For monovalent cation selectivity Balster et al [117] has reported about the effect of water uptake and low charge density behaviour which describes that at a low charge density favours to increase monovalent selectivity. In our contact angle results we observed an oscillation of 20-40 ° which partially gives the information of low surface energy character [65,103] therefore could be a possibility for different flux values at bilayer 6 and 6.5.

It worth to mention that in the diffusion dialysis experiment salt electroneutrality was maintained by the equal amount of HCl and H^+ exhibits higher mobility (from receiving to feed side) then K^+ and Li^+ (from feed to receiving side). Thus the actual mobility of K^+ and Li^+ is partially influenced by H^+ to maintain electroneutrality. At lower concentration diffusion boundary layer is less pronounced [100], however need to be considered. Counterion transport number of $K^+(0.49) > Li^+(0.32)$ and salt diffusion coefficient for KCl is higher than LiCl in CMX membrane[1] which also could be comparable for FKB and signifies to conduct more related experiments for clearer explanation of ion transport in the PDADMAC-PSS modified FKB membrane .

5. Conclusion

The layer by layer technique was applied to modify cation exchange membrane (FKB) to improve the monovalent ion selectivity of the membrane. Cationic polyelectrolyte PDADMAC, anionic polyelectrolyte PSS and zwitterionic polymer PSBMA were used to modify FKB cation exchange membrane. Two approaches such as PDADMAC-PSS modified and PDADMAC-PSBMA-PSS modified FKB membranes were considered for the sample preparation. For two polyelectrolytes modified membrane both the characterization and performance were conducted while three polyelectrolytes modified membranes were considered for characterization. Several techniques were used for this purpose namely measurement of the electrical resistances, UV-Vis spectroscopy, water contact angle and limiting current density. Membrane performance was investigated by diffusion dialysis.

UV-Vis measurement gives the information of the layer formation trend with the multilayer propagation on the FKB. We obtained a linear absorbance increment with the increase of bilayers for the both two polyelectrolyte modified and the three polyelectrolyte membrane which suggests a stoichiometric layer growth on substrate. Thus we deposited PEM multilayer successfully on FKB substrate.

The membrane electrical resistances and the water contact angle (CA) values showed a zig-zag alternating trend (PDADMAC-PSS modified FKB) because of the surface potential change of outermost layer with each monolayer deposition. Oscillating water contact angle was found for our samples which gives the hydrophobicity/hydrophilicity behaviour due to the surface charge reversal process in each monolayer deposition. Also one important observation was the hydrophilicity increases for higher bilayer number which ultimately tunes the PEM membrane surface properties. An alternating surface charge with the effect of hydrophilicity/hydrophobicity was observed. The resistance trend and the contact angle trend suggest a higher degree of layer interpenetration and higher coating density when bilayer number is high. At the same time when bilayer number is high it gives a high resistance and more hydrophilic behaviour than the base membrane. A good barrier property with a hydrophilic nature thus can be expected which can improve the ion selectivity when bilayer number is high.

For three polyelectrolyte system several effects of PSBMA was observed comparing with the characterization results with two polyelectrolyte system. The three polyelectrolyte system

was considered keeping the PSBMA deposition step in between PDADMAC-PSS deposition. The membrane UV-Vis spectra and the linear trend suggest a stoichiometric increment of the layer thickness but slope of the linear fit was found different than that of two PE systems. This means PSBMA affect the layer thickness. The contact angle oscillation for three PE systems was observed low as 10° which was 20° - 40° for two polyelectrolyte system. Thus PSBMA influence the nature of the outermost layer and increases the hydrophilicity. The first PSBMA deposition step (after a PDADMAC monolayer) on FKB made the membrane significantly hydrophilic and it suggest that we can use PSBMA to tune the hydrophilicity of the membrane. Also contact angle trend suggest a stable oscillation behaviour which was different then the two polyelectrolyte system. We can say that the layer interpenetration also decreases when PSBMA is used in between PDADMAC-PSS.

The resistance for the three PE systems gives the alternating trend with the trilayer propagation but for some PE trilayer the R was smaller than the base membrane. It was suggested that at 0.M NaCl, PSBMA suffers internal melting thus more experiment with PSBMA need to consider.

The limiting current density (i_{lim}) values are indicative for future research to explore in migration transport. We have found that i_{lim} of bilayer 6.5 decreases significantly when measured at 50 mM KCl salt environment. The strong possibility is the Donnan exclusion because of the positive surface. Also bilayer 6.5 may be able to give the barrier properties due to the high layer interpenetration as shown in contact angle and resistance data trend.

Ion transport experiment of single ion and mixed ion (K^+ and Li^+) by diffusion dialysis was conducted and found that at bilayer 6.5, flux of the K^+ decreases significantly then Li^+ which ultimately lowers the K^+/Li^+ selectivity. In other word we can say that the Li^+ selectivity is improved at bilayer 6.5. Donnan exclusion and strong barrier property due to the highly interpenetrated layer formation seems logical for such behaviour. We can say from the R and CA values of bilayer 6.5 that membrane resistance and hydrophilic nature increases with the bilayer number thus gives a strong barrier to K^+ but not to the Li^+ Thus a cation and it's hydrated radius becomes more effective to improve the monovalent selectivity for PEM membrane.

The results obtained from diffusion experiments have been used to calculate flux and selectivity of the ions and their effect on polyelectrolyte multilayer. Finally flux of different ions and PEM have optimized with in the experimental boundary. The important finding from

diffusion experiment is cationic multilayer (Bilayer 6.5) influence the flux value as such K^+ flux decreases more than the Li^+ , apparently selectivity of either compound can be changed by PEM multilayer on a cation exchange membrane. The important result we have found that at bilayer 6.5 K^+ decrease significantly than Li^+ which occurs due to the combination of Donnan exclusion, hydrated ionic radius of K^+ and Li^+ along with the membrane surface charge.

From this work several insights have been obtained which are briefly given the following discussion section.

6. Recommendation

1. Rinsing volume for LbL by dip coating

The layer by layer (LbL) by dip coating is a simple modification technique to obtain numerous surface properties and remarkably potential method to influence characteristics of the object; from nanoscale to the bulk [45]. However this simple technique becomes critical when specific properties are targeted. While preparing the FKB-PEM sample by LbL, polyelectrolyte and rinsing water volume was used as 1:1. Electrical resistance trend of those samples were found as alternating but shows remarkably big error margin (not shown in this report). Thus data reproducibility became a question to consider. A root cause analysis suggests that deposition time, PE and salt concentration was maintained carefully and for achieving stable layer, therefore rinsing water could be the possibility.

With this instance, rinsing water volume was increased couple of times for new sample preparation and resistances were found as reproducible standard. It was also reported by Decher et al (2011) [45] that amount of rinsing volume is often ignored in LbL modification and one of the guiding principles of the LbL. The term dilution factor thus addressed which can be defined by dividing the volume of the first rinsing bath by the estimated volume of the adhering liquid. The number and volume of the rinsing baths should be chosen such that the overall dilution factor is at least $1:10^6$. We can recommend that -To obtain reproducible results from LbL modified FKB (PDADMAC/PSS) sample; it has found quite important to choose right rinsing volume and it also leaves behind a scope of determining the dilution factor by a model with some approximation like PE concentration change with each adsorption step, surface charge density, adhering PE volume, membrane surface coverage to effective PE volume in deposition bath etc.

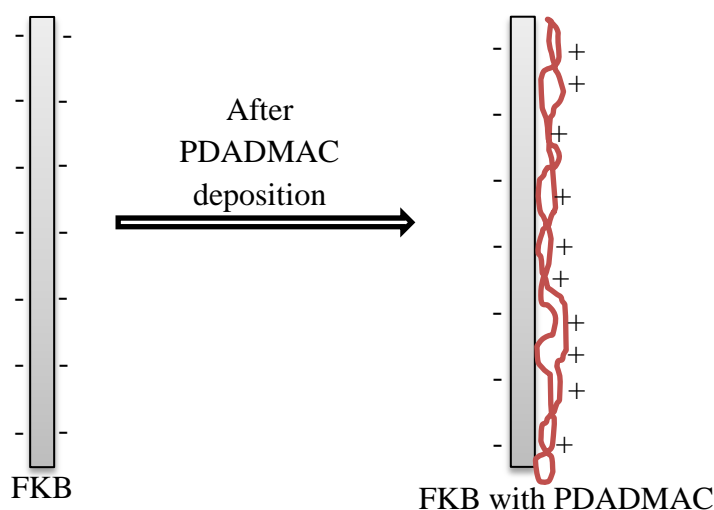
2. Tuning the surface properties of PEM

We used 0.2 M NaCl to prepare our PEM sample. It was explained that PEM surface properties can be tuned by varying its vast deposition condition. (Table 4), however salt concentration, pH, type of ion, polyelectrolyte pairs, type of substrate can be considered as most important which influences the layer growth as well as the surface properties. By varying either of the parameter we can have different properties of PEM which suggest a very big research scope in with PDADMAC-PSS polyelectrolyte system with a particular focus on

improving Li⁺ selectivity. We can assume from our results that PDADMAC-PSS multilayer of higher order may be able to give highly hydrophilic behaviour with a high barrier properties, however also can be tuned with varying the above mentioned deposition condition and thus can be recommended for further research on PDADMAC-PSS multilayer by varying deposition condition and substrate specially for Li⁺ selectivity.

3. Membrane surface and charges

Our LbL dip coating fabrication was designed in such a way that one side of the membrane was exposed to the PE solution and other side is hindered by the glass support. It can be assumed that after depositing the cationic layer on to it, a possibility is to obtain a bipolar like membrane which can be named as for instance a quasi-bipolar membrane as shown in the following figure



Scheme for the FKB membrane after PDADMAC coating

Here we can argue that after each PDADMAC deposition steps on FKB, the membrane become positively charged on the one side but the other side of the membrane which was hindered from the PE solution is still bears the negative charge. If this phenomenon is considered as logical then each PDADMAC terminated layer should make the membrane as quasi bi-polar like membrane and the properties investigated could resemble the property of bipolar membrane.

Though the FKB membrane thickness is 80-100 μm and each monolayer gives a 3-5 nm thickness increment however for higher number of bilayers and the swollen state thickness of the membrane cannot be overlooked.

May be if we coat both side of the FKB membrane in a single deposition step by PDADMAC, probably it will make the whole surface positive. One comparative study could be done by preparing different samples by coating on single side and double side of the membrane and comparing the evaluated properties with bipolar membrane.

4. Combined PEM of PDADMAC/PSS and PDADMAC/PSBMA

Grooth et al (2014) [104] demonstrated the ionic strength responsive PEM which was prepared by the PDADMAC/PSBMA polyelectrolyte. At 0.5 M NaCl such PEM suffers internal melting. One of our PEM systems were considered with PSBMA and electrical resistance (R) was measured at 0.5M NaCl. Thus it can be assumed that while measuring the R we partially lost some layer in the salt medium which might have affected our consecutive characterization as well as the resistances itself. Therefore measurement of R for PSBMA contained PEM should be done at <0.5M NaCl. We can measure R at three or four concentration <0.5M and extrapolating the R vs C (concentration) relation to obtain standard resistance value.at 0.5M NaCl.

Also PSBMA was found to adsorb on PDADMAC layer but not onto PSS layer because of its selective interaction behaviour [120] which means preparing PDADMAC/PSBMA/PSS sample leaves behind a doubt to be a coherent approach because there is a possibility of not having PSS layer at all on the PSBMA. Rather PEM by combining PDADMAC/PSS and PDADMAC/PSBMA could be logical and interesting since it exhibits ionic strength responsive behaviour [104].

5. Electrical Impedance Spectroscopy (EIS)

Electrical resistance (R) was measured in direct current method which gives not only the resistance of membrane but also includes electrical double layer resistance and diffusion boundary layer resistance.[101] And the boundary layer thickness in a two compartment system was found as 350 μ m [121] therefore cannot be avoided. To obtain the actual membrane resistance Electrical Impedance Spectroscopy (EIS) can be considered. EIS is regarded as a powerful technique for evaluating functional and structural characteristics along with membrane resistance [100]. Therefore EIS spectroscopy measurement for PEM could be highly effective to know the PEM modified IEM membrane in detail.

6. UV-Vis, reflectometry and ellipsometry

UV-Vis measurement gives the co-relation of layer thickness in terms of absorbance in UV-Vis region, however the intensity absorbed by the material at the exposure point can be regarded to understand and evaluate the thickness however, to determine the thickness we need extinction co-efficient which is not very straight forward for measuring the absorbed amount. Therefore to quantify the membrane thickness is rather difficult. Instead/along with of UV-VIS, reflectometry and ellipsometry measurement could be recommended predominantly to quantify the adsorbed amount and % swelling of PEM.

7. Contact angle, ξ potential and streaming potential

Contact angle measurement (CA) was considered to obtain the hydrophilicity/hydrophobicity of the membranes and nature of the surface. However CA values of same sample largely depends on the drying protocol. A small change in drying condition gives different CA values for PDADMAC/PSS [65,103]. Along with CA measurement ξ potential and streaming potential measurement could be recommended for comprehensive understanding of the surface.

8. Diffusion dialysis and electro dialysis:

Diffusion experiment was conducted for K^+ and Li^+ in which ionic neutrality was maintained by the HCl. to obtain ion flux. It was found that the PEM bilayer decreases the K^+ more than Li^+ , in other word we have achieved the higher selectivity of Li^+ which put two future work possibility.

From our experimental result we have obtained that K^+ reduced significantly whereas the Li^+ stays more/less same at bilayer 6.5. Extrapolating this behaviour we can say that there is a strong possibility that we may be able to achieve a good improvement in Li^+ selectivity when the layer number will be high enough. Thus PEM of higher bilayer number can be recommended to prepare and investigate under diffusion dialysis. According to the hydrated ion radius value ($K^+ > Na^+ > Li^+$) [1], thus Li^+ and Na^+ effective separation might be possible at higher layer PEM number. Though ξ potential of higher order membrane does not show alternating charge behaviour and also swelling/deswelling [14] effect makes the resistance alternation diminished. A contradiction might be possible about the properties that can be predicted from the lower bilayer results; even though new interesting behaviour might appear

at higher order PE. However we can have particular attention on it to separate Li^+ in this regard.

Since diffusion dialysis (DD) is comparably a slow process then electro dialysis (ED), however the same condition of the diffusion experiment can be easily translated to the ED with a current load and migration under current would be interesting to obtain considerable flux and Li^+ selectivity. As primary information for such experiment, resistances and i_{lim} values were measured. We also can co-relate i_{lim} to the transition time (time to reach to the plateau region in current-voltage relation) to obtain the transport number [101].

A combined method of diffusion and electro dialysis thus could be predominantly recommended to achieve effective Li^+ separation.

7. References

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Appendix

A. Flame photometer calibration and basic scheme of the BWB flame photometer.

A.1. Flame photometer calibration

For the calibration of the Flame photometer, five concentrations points were considered depending on the approximate concentration of the ion at the start of the diffusion experiment. For example let's say

Initial K^+ ion concentration (at the start of the experiment) = 50mM

Sample considered = 0.3 mL/ 15 min.

Dilution factor = x10

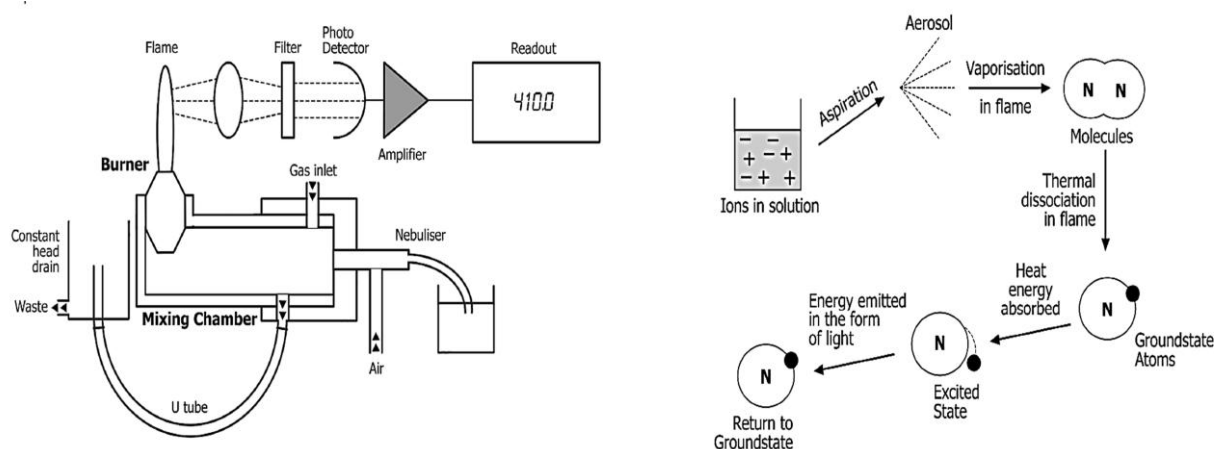
Thus after dilution the concentration of initial sample becomes= 5 mM.

Based on this above mentioned information 5 concentration points were considered for the calibration keeping the concentration ranges above and below then the initial sample concentration

Thus the calibration for the BWB flame photometer was conducted with 0.5, 1, 2.5, 5, 10 mM KCl solution.

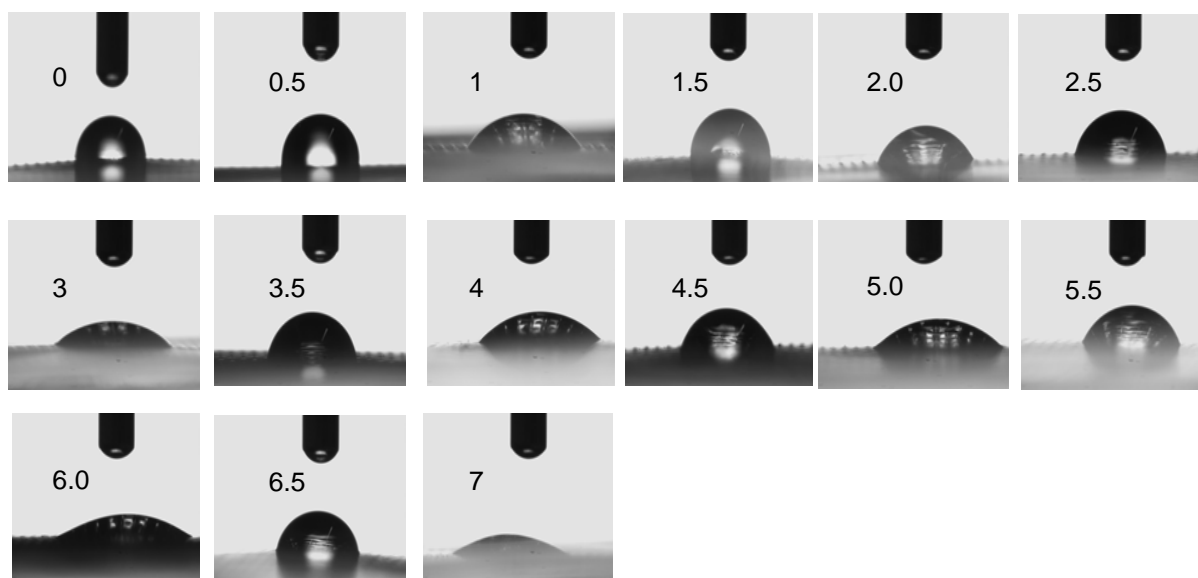
The same method was used for all the diffusion measurement.

A.2. Basic component of BWB Flame photometer:



Basic component of BWB flame photometer (left) and the process involved in flame photometry (right). [<http://www.bwbtech.com/>]

B. Contact angle changes with different bilayers on the FKB membrane.



Number of bilayer	Water contact angle(θ)°
0	73.1±2.01
0.5	95.88±1.3
1.0	52.13±5.7
1.5	86.7±0.8
2.0	58.1±2.5
2.5	78.9±2.1
3.0	42.35±4.2
3.5	77.48±1.7
4.0	42.48±1.1
4.5	70.68±3.3
5.0	42.41±1.2
5.5	70.93±3.3
6.0	35.05±3.0
6.5	74.38±3.7
7.0	34.46±2.2

Number of bilayers and the corresponding contact angle value

C. FKB membrane properties and polyelectrolyte membrane properties.

C.1 Physical and chemical data of FKB cation exchange membrane

Physical and chemical data

fumasep FKB, cation exchange membrane, PEEK-reinforced		
selectivity	%	>0,98**)
electric resistance *)	$\Omega \cdot \text{cm}^2$	<4*)
stability		acid and caustic stable
thickness ***)	mm	0,08 –0,10
specific conductivity	mS/cm	>2 *)
ion exchange capacity	meq/g	0,9-1,0

*) measured in Sodium form in 0,5 M NaCl @ RT 25°C

***) determined from membrane potential measurement in a concentration cell 0,1/0,5 M KCl @ 25°C

****) in dry form

Physical and chemical data of FKB cation exchange membrane.

[<http://www.fumatech.com/NR/rdonlyres/58CD330B-882C-426F-8399-C856BC481FC3/0/fumasepFKB.pdf>]

C.2 Membrane electrical resistance (Direct current method)

Number of layers	Average Resistance* ($\Omega \cdot \text{cm}^2$)
0	3.99±0.35
0.5	13.01±0.35
1	5.46±0.75
1.5	14.68±0.23
2	5.23±0.67
2.5	16.40±1.07
3	4.53±0.12
3.5	17.31±0.12
4	7.16±0.27
4.5	18.10±1.17
5	6.26±1.83
5.5	18.66±0.23
6	9.64±0.38
6.5	17.69±0.78
7	11.20±1.23

*each data is the average of three sample measurement.

D.1 i_{lim} values for different PDADMAC/PSS bilayers in different salt solution

Sample*	i_{lim} 50mM 1:1 KCL+LiCl	i_{lim} , 50mM(KCl)	(i_{lim} , 50mM(LiCl)
FKB base	12.33±0.237	7.907±0.116	4.57±0.12
Bilayer 6	11.32±0.236	7.485±0.233	4.239±0.114
Bilayer 6.5	9.651±0.225	3.81±0.707	4.065±0.12

*each sample data point refers to the 3-5 fresh sample measurement.