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Use of Polyelectrolyte Multilayer Systems for Membrane Modification

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Summary: Membranes with designed surface and filtration properties were prepared by the adsorption of polyelectrolyte multilayer systems on membrane surfaces using the layer-by-layer electrostatic self assembly (ESA) technique. Microfiltration membranes with a first polyelectrolyte layer grafted onto the surface showed excellent stability during filtration process. Although a twofold higher permeate flux was observed for a three-layer polyelectrolyte complex membrane compared to a just grafted one the protein retention did not change remarkably. Additionally, a reduced protein adsorption was detected for repulsive electrostatic forces between the substrate and the protein under applied conditions. Pervaporation membranes with an anionically functionalized polyamide-6 support or Nafion®-117 support and a dense separating layer consisting of poly(acrylic acid) and poly(ethylenimine) were prepared. Those membranes were used to separate aqueous organic mixtures. Six double layers were sufficient to obtain membranes with high water permselectivity. Membranes with similar properties but a lower number of deposited layers were obtained, when the adsorption process was carried out at 80°C.

Introduction

Hydrophobic polymers are commonly used for the preparation of microfiltration or ultrafiltration membranes due to their high mechanical strength and their long lifetime. On the other hand, hydrophobic surfaces are sensitive to adsorption of biological matter e.g. proteins, natural organic matter (NOM) caused by hydrophobic interactions between feed components and the membrane surface (fouling). This fouling is one of major factors limiting the use of membranes[1 - 5]. To meet the specific requirements in biosensors, pervaporation or gas separation applications membranes with functionalized or hydrophilized surfaces are needed[6]. Beside the bulk modification of membrane polymers, surface modification has become a versatile tool to design membranes with tailor-made filtration properties[7, 8]. Interactions between feed components and membrane surface are altered by permanent hydrophilization and/or the introduction of charges to the membrane surface. Therefore fouling caused by hydrophobic or electrostatic interactions is reduced substantially. Furthermore, porous membranes have been converted into other types of membranes such as pervaporation or gas separation membranes by surface modification techniques[9 - 11].

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A smart method to obtain hydrophilic and charged surfaces is given by the layer-by-layer adsorption of oppositely charged polyelectrolytes and the build-up of polyelectrolyte multilayer complexes on polymeric substrates which has been initiated by Decher et al.[12, 13]. The simple adsorption procedure involves dipping of charged surfaces into aqueous solutions of oppositely charges polyelectrolytes. This electrostatic layer-by-layer self-assembly process (ESA) opens up the opportunity to control the surface and filtration properties by the number of adsorbed polyelectrolyte layers and the choice of polyelectrolytes used. Up to now several groups reported on the modification and preparation of gas separation membranes[14], pervaporation membranes[11, 15] or microfiltration membranes with polyelectrolyte multilayer systems[16 - 18].

In this work the potential of the polyelectrolyte multilayer assemblies for membrane modification is demonstrated. On one hand, microfiltration membranes were modified with polyelectrolyte complexes to create low-fouling surfaces. A second example describes the preparation and the properties of dense membranes for separation of aqueous organic mixtures by pervaporation.

Experimental

Two different types of membranes were employed for the experiments described in this work. For the microfiltration experiments a commercially available polypropylene flat sheet membrane (Celgard 2400) was used. A home-made asymmetric membrane from a carboxyl functionalized polyamide-6 and a Nafion® 117 membrane were employed as support for the pervaporation membranes based on polyelectrolyte multilayer assemblies. The material properties and the key experimental conditions are given in Table 1.

Surface modification of polypropylene membranes

The first polyelectrolyte was grafted onto the membrane surface i) to obtain a multilayer assembly that is stable under filtration conditions and ii) to provide a large number of charges for the multilayer build-up.

Polypropylene membranes were treated first with a CO_2 plasma which creates peroxide species on the membrane surfaces (experimental conditions: 70W, 3 min, 10 sccm CO_2, 10 Pa). Those peroxides were used as initiators for the subsequent grafting of acrylic acid. Nitrogen was bubbled through the aqueous monomer solution, containing 3 wt.-% acrylic acid to remove oxygen before starting the grafting reaction. The grafting reaction was carried out at

70°C for 30 – 120 min. The grafted samples were treated with hot water to remove residual monomer and non-grafted homopolymer. The graft yields, which were calculated using equation (1), varied between 0.1 and 5 wt.-%, depending on the reaction time.

$$\text{graft yield} = \frac{\text{weight}_{\text{grafted}} - \text{weight}_{\text{ungrafted}}}{\text{weight}_{\text{ungrafted}}} \times 100\% \qquad (1)$$

Table 1. Materials used throughout this work and key experimental conditions

	Microfiltration	**Pervaporation**
Membranes	Polypropylene (PP) Celgard 2400	mod. Polyamide-6 Nafion® 117
Polycation	Poly(dimethyldiallylammonium chloride); (PDADMAC) FhG Teltow; M_W 99000 branched Poly(ethylenimine) (PEI); Aldrich; M_W 750000	branched Poly(ethylenimine) (PEI); Aldrich; M_W 750000
Polyanion	Poly(acrylic acid) (PAAc) Polysciences; M_W 90000	Poly(acrylic acid) (PAAc) Polysciences; M_W 90000
PEL concentration (ref. monomer units)	20 mM	20 mM
temperature	25°C	25°C; 50°; 80°C
Filtration apparatus and test conditions	stirred dead-end filtration cell Millipore Type 8050 25°C; 300 kPa	Laboratory test cell P28 CM-Celfa 50°C or 80°C; 20 mbar
Test solutions	Human-Serum-Albumin (HSA) 0.1 wt.-%	Water/2-Propanol Water/Ethanol Water/Methanol

Preparation of modified polyamide-6

The modified polyamide-6 (CMI-3) was obtained by reacting polyamide-6 (Miramid SH3) with poly(α-methylstyrene-*alt*-ε-caproic acid maleimid) in the melt phase according to the procedure reported earlier[19]. The CMI-3 had a comb-like structure with carboxyl terminated polyamide-6 side chains. The carboxyl end group concentration was approx. 203 μmol/g.

Preparation of the polyamide support

Asymmetric membranes were prepared from CMI-3 by the well-known phase inversion process[20]. A polymer film with a thickness of approx. 200 μm was casted from a solution containing 15 wt.-% CMI-3 in formic acid/water (85/15 wt./wt.) onto a glass plate. After an appropriate time (10 min), the film was immersed into cold water (4°C) for precipitation. The resulting asymmetric membrane (Fig. 1) was stored in water for several days to leach out residual formic acid, and was dried finally at room temperature.

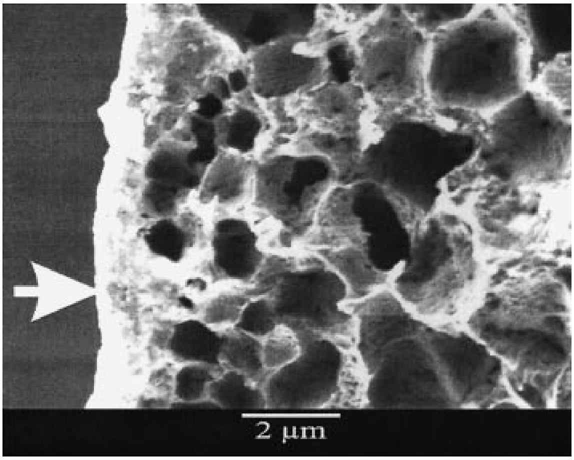


Figure 1. Scanning electron micrograph from a cross section of an asymmetric CMI-3 support; the dense top layer is indicated by the arrow, the total thickness of the dry membrane is approx. 45 μm.

Build-up of polyelectrolyte multilayer assemblies

The formation of the polyelectrolyte multilayer assemblies was carried out by alternative dipping of the initially anionically functionalized membranes into aqueous solutions of oppositely charged polyelectrolytes as listed in Table 1. The deposition of polyions was done at room temperature and the time was 30 min. For some pervaporation membranes the adsorption temperature was set to 50°C and 80°C in order to check the influence of preparation conditions on the membrane properties. After each adsorption step the membranes were rinsed extensively with pure water to remove weakly bound polyions.

Characterization of the modified membranes

The successful adsorption of polyelectrolytes was proven by streaming-potential measurements at different pH values (EKA, A. Paar KG, Austria).

The human serum albumin (HSA) concentration was determined by UV/VIS spectroscopy (CADAS 100, Dr. Lange, Germany) using the typical protein absorption at 287 nm.

The feed and permeate compositions of the pervaporation experiments were determined by density measurements using a DMA 58 density meter (A. Paar KG, Austria). The separation factor α was calculated using equation (2) where c is the concentration of water and alcohol in the feed and the permeate, respectively as symbolized by the subscripts W, A, F, P.

$$\alpha = \frac{c_{W,P} \cdot c_{A,F}}{c_{W,F} \cdot c_{A,P}} \tag{2}$$

The permeate flux was measured gravimetrically in pervaporation experiments and volumetrically in microfiltration experiments.

Results and Discussion

Characterization of surface modified membranes by ζ-potential measurements

The unmodified and modified membranes were characterized by streaming-potential measurements at different pH values. Typical streaming-potential vs. pH plots for polypropylene-based microfiltration membranes and polyamide-based pervaporation membranes are shown in Figures 2A and 2B, respectively. The streaming-potential pH plots of both, the unmodified CMI-3 support and the PAAc graft-modified PP-membrane (PP-g-PAAc) show the characteristic course for acidic surfaces. The isoelectric point (IEP) is at an acidic pH (CMI-3: pH 5.4; PP-g-PAAc: pH 3.3) and a negative ζ-potential is observed over a wide pH-range. The occurrence of the definite plateau above pH 6 is attributed to the large number of carboxyl at the membrane surfaces. The complexation of polycations led to a reverse of the surface charge. This is displayed by a definite shift of the IEP from the acidic to the basic pH range and by a sign reversal of the ζ-potentials over a wide pH range investigated. This is due to the presence of cationic ammonium groups of the adsorbed layer. However, a distinct difference between the two polycations used, namely PEI and PDADMAC is observed. The PEI-modified surface has a positive over the whole pH-range

(IEP 9.4) under investigation while the PDADMAC shows a negative surface charge at pH above 7.9. Upon further reverse of the surface charge achieved by adsorption of poly(acrylic acid), the IEPs shift again to the acidic pH range but the IEPs of CMI-3 and the grafted PP-membrane were not reached again This observation is explained by the fact that a large number of carboxyl groups of the adsorbed poly(acrylic acid) is fixed by the complexation with the basic groups of the preceding layer. These results demonstrate the possibility to control the surface charge of membranes by adsorption of oppositely charged polyelectrolytes using the layer-by-layer technique.

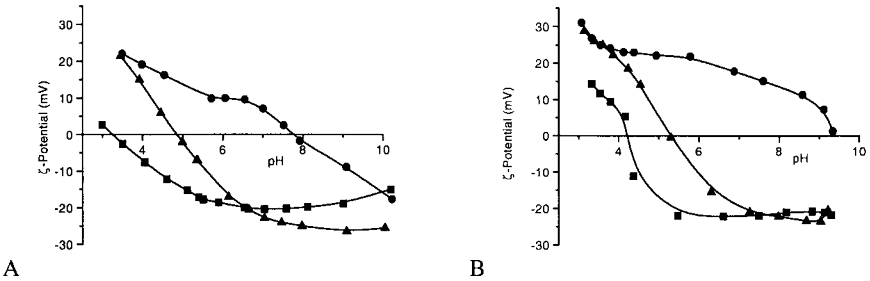


Figure 2. Plot of ζ-potential vs. pH of A) Polypropylene microfiltration membrane after grafting with 3.3 wt.-% PAAc (■), after grafting and complexation with PDADMAC (●), after grafting and complexation with PDADMAC/PAAc (▲); B) CMI-3 support (■); CMI-3 after complexation with PEI (●), and after CMI-3 complexation with PEI/PAAc (▲).

Filtration experiments with surface modified polypropylene microfiltration membranes

The water flux of PP-membranes is susceptible to modification reactions carried out at the surface due to changes in pore diameter and hydrophilic/hydrophobic properties (Fig. 3). Plasma treatment leads to a flux enhancement, because the membrane structure is partially destroyed (polymer degradation) and the introduction of hydrophilic groups. Grafting of a first polyelectrolyte layer results in a dramatic decrease of permeate flux. The original flux is recovered by deposition of one or two additional polyelectrolyte layers. On the other hand adsorption of more than two layers lowers permeate flux again. The results can be explained by a conformational change the grafted poly(acrylic acid) chains induced by the adsorbed second polyelectrolyte layer. The PAAc chains are thought to be in a stretched conformation in the uncomplexed state. This conformation helps minimizing the repulsive electrostatic forces between equally charged carboxyl groups. As the charge of the grafted PAAc-layer is partially compensated by the complexation of the polycation, the repulsive forces are weakened and the conformation becomes more compact and the pore diameter is enlarged, resulting in the observed flux enhancement. Further increase of the polyelectrolyte layer number led to a flux decline due to decreasing pore diameter, which can lead to total pore plugging.

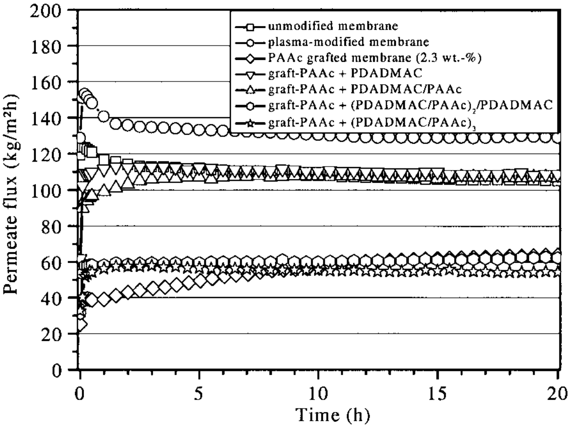


Figure 3. Effect of graft modification and polyelectrolyte complex layer on the water flux of modified polypropylene membranes.

The fouling behavior of modified polypropylene membranes was tested with 0.1 wt-% aqueous HSA solution of pH 6.4. The HSA has a negative net charge at pH 6.4, which is well above the IEP (pH 4.8). As observed for the pure water flux, the protein filtrate flux through a three-layer polyelectrolyte membrane (PP-3-PEL) with same graft yield is the approx. double that of a just grafted membrane (Fig 4A). For graft yields below 1 wt.-% the protein flux through the PP-3-PEL membrane is even higher than through the unmodified membrane. Although the filtrate flux of the PP-3-PEL membrane is higher than that of the just grafted membrane the protein retention of the latter membrane was only slightly higher than that of the PP-3-PEL membrane (Fig 4B). Beside the influence on the filtration properties the polyelectrolyte modification has also a pronounced impact on the adsorption of proteins on the membrane surface. In the case of repulsive electrostatic forces between the membrane surface and the dissolved protein the amount of irreversible adsorbed protein was reduced by 90% (graft yield ≥ 1 wt.-%) compared to the amount of protein adsorbed on the unmodified membrane.

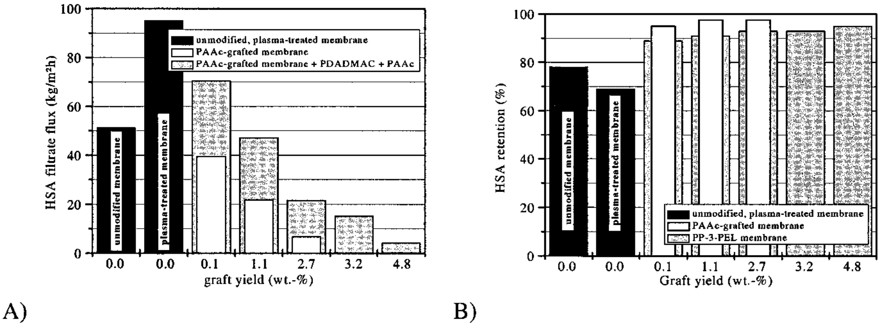


Figure 4. Influence of graft yield and polyelectrolyte complex layers on A) protein filtrate flux and B) protein retention.

The results of the filtration experiments were confirmed by in-situ ATR-FTIR spectroscopic investigations on model PP-surfaces prepared on ATR-crystals. This technique enables the examination of adsorption processes on for example membrane surfaces without the influence of hydrodynamic forces[21].

The lowest and highest relative amount of adsorbed protein were found in the case of repulsive and attractive electrostatic forces between the surface and the protein, whereas the adsorbed amount of protein on the unmodified membrane was between these two extremes (Fig. 5). The obtained data were used to calculate the absolute amount of HSA adsorbed on the differently modified surfaces. The results are summarized in Table 2. The amount of adsorbed protein on the negatively charged surface is very low and in the range of the detection limit of this method. For attractive electrostatic forces (positively charged surface) a monomolecular protein layer can be estimated for an adsorbed amount of 0.20 $\mu g/cm^2$, when taking into account the size of a HSA molecule (3.8 x 15 nm^2 [22]) and assuming a *side-on* adsorption of the molecules on the surface. The results are in good agreement with data reported earlier by Gölander et al.[23].

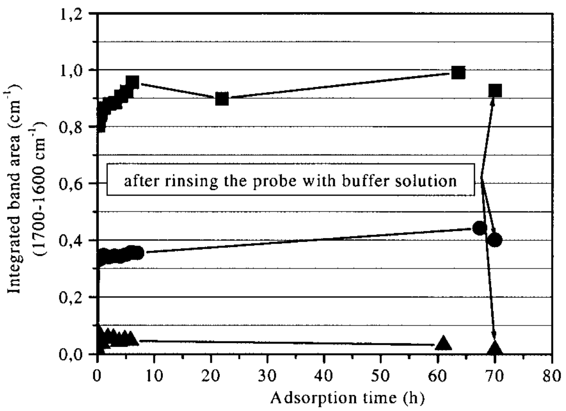


Figure 5. HSA adsorption on PP-PEL model surfaces investigated by in-situ ATR-FTIR spectroscopy; untreated PP film (attractive hydrophobic forces) (●); CO_2-treated PP-film + 5 PEL layers, (PEI/PAAc/PEI/PAAc/ outermost layer PEI; attractive electrostatic forces) (■); CO_2-treated PP-film + 4 PEL layers, (PEI/PAAc/PEI/ outermost layer PAAc; repulsive electrostatic forces) (▲).

Table 2. Calculated amount of HSA adsorbed on modified and unmodified model surfaces

model surface	film thickness[a] (nm)	integrated IR band (1700 - 1600 cm^{-1})	adsorbed amount of HSA ($\mu g/cm^2$)
unmodified PP	32	0.379	0.12
PP[b]/PEI/PAAc/PEI/PAAc/PEI	35	0.651	0.21
PP[b]/PEI/PAAc/PEI/PAAc	100	0.015	<0.01[c]
PP[b]/PDADMAC/PAAc/ PDADMAC/PAAc	51	0.073	0.03

[a] determined by X-ray reflectometry

[b] polyelectrolytes were deposited on a CO_2-plasma-treated PP-film

[c] in the range the detection limit of this method

Modification of pervaporation membranes from carboxylterminated polyamide-6

The dependence of pervaporation separation properties of CMI-3 polyelectrolyte complex membranes on the number of deposited is shown in Fig. 6.

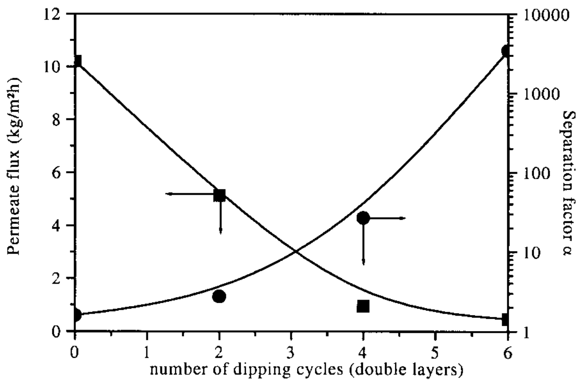
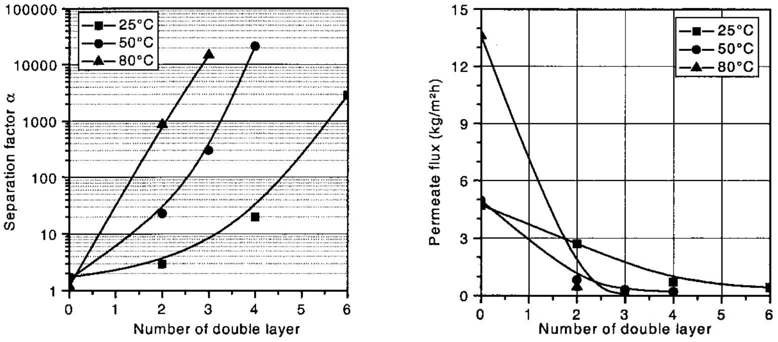


Figure 6. Effect of the layer number on the permeate flux (■) and the selectivity (●) of PEL modified CMI-3 for a water/2-propanol mixture (30/70 wt/wt); T = 50°C.

Pervaporation experiments were done with a test mixture of 30 wt.-% water and 70 wt.-% 2-propanol at 50°C. The support material had low selectivity and high permeate flux. With increasing number of deposited polyelectrolyte layers an increasing selectivity but a decreasing permeate flux is observed. Only six double layers consisting of poly(ethylenimine) and poly(acrylic acid) were sufficient to obtain a membrane with high water selectivity. These results can be explained i) by coverage of very small pores in the substrate by the polyelectrolyte complex layer, and ii) by higher hydrophilicity of the polyelectrolyte layer system compared to the substrate, which favours the uptake of water. Furthermore, the influence of preparation conditions on the membrane performance was investigated. As a result, the preparation temperature had the highest impact on the membrane performance. Raise of the adsorption temperature from 25°C to 80°C, led to membranes with a selectivity, which is approx. 500 times higher than that of a membrane prepared at 25°C (Fig. 7). As observed before, the permeate flux decreases with increasing selectivity. However, the overall performance of the membrane prepared at 80°C (PSI = 390), as expressed in terms of the pervaporation separation index (PSI)[24], is approx. 70 times higher than that of a membrane prepared at 25°C (PSI = 6). Results from FTIR- and ^{13}C nmr spectroscopic investigations (not shown here) may led to the conclusion, that amide bonds between poly(acrylic acid) and poly(ethylenimin)have been formed during the preparation of polyelectrolyte multilayer assemblies at elevated temperatures.

Those chemical linkages act as crosslinks between polyelectrolyte layers, which will reduce the swellability. Now, the diffusion of the comparatively smaller water molecules through the PEL-layer is favored.



A) B)

Figure 7. Effect of preparation temperature on pervaporation properties A) selectivity, and B) permeate flux of PEL modified CMI-3 membranes; test mixture water/2-propanol 30/70 wt/wt; pervaporation temperature 50°C.

The layer-by-layer technique was also used to modify Nafion®-117 membranes, which are widely used in fuel cell applications. One disadvantage of the Nafion membranes is the high methanol crossover when used in direct methanol fuel cells (DMFC), which leads to undesired side reaction at the cathode. The modification of Nafion® membranes with polyelectrolytes, especially at higher temperatures, resulted in a dramatic enhancement of water selectivity (Table 3). Such membranes showed high stability and high methanol retention when tested in direct methanol fuel cells. However, the electrical properties were poorer than that of unmodified Nafion® membranes. Nonetheless, polyelectrolyte multilayer assemblies seemed to be promising materials for proton conductive membranes in fuel cell applications.

Table 3. Results of pervaporation experiments with unmodified and PEL modified Nafion® membranes

Preparation temp. (°C)	MeOH in the feed (wt.-%)	MeOH in the permeate (wt.-%)	Permeate flux (kg/m²h)	Operating temp. (°C)
pure	10	13	5,8	50
pure	29	31	4,7	50
25	9	2	5,9	80
25	26	13	5,5	80
80	11	0,02	1,0	80
80	24	0,12	0,9	80

Conclusions

The consecutive alternating polyelectrolyte adsorption was found to be a versatile tool for the preparation of membranes with controlled surface charge properties and hydrophilicity as demonstrated by streaming-potential measurements.

The adsorption of only two additional polyelectrolyte layers onto a PAAc-grafted microfiltration membrane surface resulted in a reduced protein adsorption in the case of repulsive electrostatic interactions between the membrane surface and the feed components (e.g. proteins). Higher protein retention was simultaneously observed. From these results a reduced fouling of PEL complex layer membranes was deduced when the membrane surface and the feed components are equally charged. Results from filtration experiments were confirmed by in-situ FTIR-ATR investigation on model films.

Dense pervaporation membranes showed an improved water selectivity after the formation of a PEL complex layer system consisting of PEI and PAAc. The permeate flux decreased with increasing selectivity and increasing layer number. It is possible to control the properties of pervaporation membranes by the number of adsorbed polyelectrolyte layers, the chemical structure of the polyelectrolytes used and the preparation conditions. Membranes with only one additional polyelectrolyte complex layer having high water selectivity were obtained when the adsorption was carried out at elevated temperatures (80°C). Polyelectrolyte multilayer membranes based on Nafion® showed promising results in direct methanol fuel cell applications.

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