

Ion Selective Transport of Alkali Ions through a Polyelectrolyte Membrane

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The ionic conductivity of a polyelectrolyte membrane consisting of 30 bilayers of poly(allylamine hydrochloride) and p-sulfonato-calix[8]arene, (PAH/calix8)₃₀, is investigated for two alkali ions, i.e., Li⁺ and Rb⁺. Two different transport pathways, a fast and a slow one, are identified for Li⁺ transport. By contrast, only the fast transport pathway is observed for Rb⁺ transport. This fast transport pathway is assigned to regular hopping through bulk material, whereas the slow transport pathway originates from retarding interaction with the calixarene rings, only operative for Li⁺ but not for Rb⁺. This observation constitutes a clear manifestation of ionic selectivity for transport in polyelectrolyte membranes.

1. Introduction

Polyelectrolyte multilayers (PEMs) produced by layer-by-layer (LBL) self-assembly methods^[1] have become popular materials in applications such as filtration,^[2] potential carrier vehicles for drug delivery,^[3,4] and sensors.^[5,6] PEMs can change the conductivity of different ions.^[7] In previous work of the authors'

groups, the ionic conductivity of planar PEM films consisting of sixteen bilayers of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene sulfonate) (PSS) with and without gold nanoparticles (NPs) trapped in-between the polyelectrolyte layers has been investigated.^[8] The potassium conductance was found to be both on the order of $G = 1 \times 10^{-9}$ S for PEMs with and without NPs, implying that the presence of gold NPs does not significantly affect the ion conductivity of the PEM.^[8] In a more recent study the dependence of the ionic conductance of ultrathin polyelectrolyte multilayer films on the temperature as

well as on the number of bilayers has been investigated.^[9] The conductance was found to depend nonmonotonically on the number of bilayers and was rationalized by a model accounting for the structural dependence of the conductivity.

A major part of the established polyelectrolyte membranes consists of cationic and anionic polyelectrolytes. However, another class of PEMs consists of cationic polyelectrolytes and anionic calixarenes.^[10] Macrocyclic compounds such as calix[n]arenes,^[11] polyazacrown ethers,^[12] and cyclodextrins^[13] are important building blocks in supramolecular chemistry, which exhibit specific and even selective interaction with certain molecules and ions by formation of host–guest complexes.^[14] As a prototypical example of such macrocycles we choose to discuss p-sulfonato-calix[8]arene (denoted as calix8) as cation receptor in this work. One goal is to demonstrate the selectivity of calix8 for alkali ion transport through suitable polyelectrolyte membranes. Due to the specific interactions of distinct metal ions with the eight unit rings of the calixarenes, we expect that the membranes exhibit a high selectivity in the rejection of specific ions. Such a selective behavior would be different from standard all-polyelectrolyte multilayer films reported previously in the literature.^[10,15] In order to study the ion transport of the alkali ions, we applied the recently developed charge attachment induced transport (CAIT) (originally termed bombardment induced ion transport, BIIT) technique.^[16] The principle of the CAIT technique has been described in a series of previous papers,^[9,17–20] and demonstrated to be widely applicable.

2. Theory

The experimental investigation has been supported employing numerical simulations based on the coupled set of

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Nernst–Planck and Poisson equations.^[17] The description of the ion transport is restricted to 1D perpendicular to the sample surface plane, assuming a homogeneous ion beam and radial symmetry. We refer to this axis as *I*-axis.

The Nernst–Planck equation describes the ion flux density as a function of the concentration and the electric potential gradient. It is given by

$$J_v = -D_v \left(\frac{\partial n_v}{\partial z} + n_v \frac{\partial \phi}{\partial z} \frac{Z_v e}{k_B T} \right) \quad (1)$$

where J_v is the ion flux density, n_v is the ion density, and $\frac{\partial n_v}{\partial z}$ its gradient perpendicular to the sample surface. ϕ is the electric potential and $\frac{\partial \phi}{\partial z}$ its gradient in the same direction. The ion charge is given by $Z_v e$ and $k_B T$ is Boltzmann's constant times temperature. We assume that D_v is an universal and effective constant, i.e., we do not include concentration dependencies and distinguish between concentration and potential driven coefficients that may in general differ from each other.^[21]

The electric potential is calculated self-consistently with the actual charge carrier distribution employing Poisson's equation

$$\epsilon_0 \epsilon_r \frac{\partial^2 \phi}{\partial z^2} = - \sum_v Z_v e n_v \quad (2)$$

with $\epsilon_0 \epsilon_r$ being the dielectric function in the material, Equation (2) represents a mean field approximation where the ions interact with the background structure and other ions mainly via the locally available excess charge.

The back side of the sample is in contact with a grounded electrode. Hence, the electric potential is fixed to zero there. The electric potential at the PEM's surface is given by a dynamic equilibrium between impinging ions and ions transported through the sample toward the backside electrode. These two pieces of information provide the boundary conditions for the electric potential calculation.

The time dependence of the charge carrier motion as a function of time is described employing Fick's second law making use of particle conservation

$$\frac{\partial n_v}{\partial t} = - \frac{\partial J_v}{\partial z} \quad (3)$$

Equations (1)–(3) are discretized into space elements and to each of the space elements an average ion density and an electric potential is assigned. After every time step, charge carriers are shifted between the space elements according to Equation (3). Then Poisson's Equation (2) is iteratively solved until the electric potential converges and it reflects the actual charge carrier distribution. The charge carrier distribution and the corresponding electric potential enter Equation (1) such that the carrier flux can be calculated according to Equation (3).

Experimentally, two different transport pathways are conceivable. On the one hand, it is expected that the calixarene rings retard the transport. Thus, a corresponding ion path results in a slow ion transport. On the other hand, ions that circumvent the calixarene rings are transported faster. We assume that the transport through the material is fast enough such that a retardation of the ion by the rings defines ultimately the transport speed. Consequently, we may define two independent transport pathways. Retarded ions are transported with the coefficient D_{slow} while such ions that circumvent the ring structure move

with D_{fast} . The amount of ions that enter the two different pathways as well as the transport coefficients are the fit parameter in the theoretical description.

Ions that reach the back side electrode are neutralized there. Numerically, these ions are counted such that the amount of ions that arrive at the backside of the sample is known. However, they leave the explicitly calculated sample and are thus not contained in the profiles that enter the Nernst–Planck Poisson calculation. Experimentally, these ions give rise to an interface density of neutral alkali between sample and electrode. Since the samples are not perfectly smooth, the corresponding concentration depth profiles acquired by the time-of-flight secondary ion mass spectrometry (ToF-SIMS) technique yield a profile that is smeared out at the internal electrode sample interface. We take this situation into account by Lorentz distributing the amount of ion density that has reached the back side electrode. The Lorentz distribution is added to the ion concentration profiles inside the samples calculated by the Nernst–Planck–Poisson simulation. The sum of both is then eventually compared to the experimental profiles.

3. Results and Discussion

In the following we describe the results of CAIT experiments on 30 bilayers of poly(allylamine hydrochloride)/p-sulfonatocalix[8]arene (PAH/calix8)₃₀ films employing Li⁺, K⁺, and Rb⁺ cations respectively. After the CAIT experiments, the Li⁺, K⁺, and Rb⁺ concentration profiles inside the (PAH/calix8)₃₀ samples have been analyzed with the help of the ToF-SIMS technique. The data obtained from the ToF-SIMS measurements are given in the form of counts as a function of sputter time. In order to compare these data with numerical calculations it is essential to transform the counts into a real concentration and the sputter time axis into a real space axis.

The spectroscopic ellipsometry measurements described in the experimental section provided access to the average thickness of the investigated PEM films. From those data, one can derive a linear relation of the LBL thickness as a function of bilayer number. The thickness of one bilayer amounts to 0.86 nm and the fitted refractive index to 1.47 (Figure 6, Experimental Section). The y-intercept of the linear fit amounts to (1.18 ± 0.81) nm and may constitute the initial mercaptopropionic acid in ethanol (MPA) layer. This is consistent with data obtained for other polymer combinations as detected with other techniques.^[22] The PEM layer thickness must directly correspond to the respective signals in the ToF-SIMS data. The secondary ion mass spectra contain several signals which can be assigned to fragments of either the calix8 or the PAH. For further analysis we focus on the C⁺ signal as this is the strongest signal correlating with the PEM.

Assuming a homogenous and conformal PEM coating of the gold foil, we defined the point at which the carbon signal C⁺ decreased to 50% of the maximum intensity and at the same time the Au₃⁺ signal exhibits its onset as the end of the PEM layer. Consequently the sputter time was converted to a depth scale using the thickness measured for 30 bilayers by spectroscopic ellipsometry (Figure 5, Experimental Section). In general, the sputter rate between the polymer and the gold electrode is different. However, we concentrate on the region of the polymer in front of the electrode such that this error does

not affect the following analysis. We note that the C^+ signal in fact extends as deep as 100 nm below the surface. This may be a result of the roughness of the sample which may further increase due to the alkali ion transport. We also cannot rule out the possibility that some swelling of the PEM film takes place during transport.

The ion counts of Li^+ , K^+ and Rb^+ have been transformed into a real density taking into account the area below the concentration trace of the relevant ion species, and the total amount of flown charge which has been recorded at the back side electrode. The ion density, n_v , can thus be calculated by

$$n_v = \frac{I}{\int I dz} \frac{Q}{A e} \quad (4)$$

where I is the raw data intensity, Q stands for the charge accumulated in Coulomb (calculated from the current time characteristic curves), A is the bombarded area and e is the elemental charge of the electron. $\int I dz$ represents the integral of the raw data ion intensity over the depth range considered.

For ensuring the reliability of the ToF-SIMS data recorded and their analysis it is important to perform control experiments on fresh PEM samples. Here, ToF-SIMS analysis on fresh reference samples of $(PAH/calix8)_{30}$ confirmed the absence of both Li^+ and Rb^+ ions from the PEMs and the gold substrate. However, this was not the case for the K^+ signal. K^+ ions were found to be present as contaminant in the gold substrate. Consequently, within the K^+ CAIT experiments it was not possible to distinguish where the K^+ signal was originating from. Ultimately, we decided not to consider the K^+ data for further transport analysis because of the contamination issue. **Figure 1** shows typical ion densities for Li^+ and Rb^+ introduced into the PEM for two different durations of the constant voltage attachment (CVA) experiment, a) 5 and b) 100 s. In a linear representation of the data the electrodeposition of alkali elements becomes evident in between the original membrane and the gold substrate.

Comparing the profiles of the alkali species in **Figure 1A** and **Figure 1B** clearly shows that the ion densities inside the films is significantly higher for an attachment time of 100 s as compared to 5 s, which is to be expected. It is worth noting that only the Li^+ signal shows a diffusion profile with its intensity dropping exponentially from the very beginning of the membrane layer to the end of the PEM film, whereas the Rb^+ hardly shows any concentration variation as function of the depth. A prominent feature of the Li traces in both graphs is the peak at 70 nm, which indicates accumulation of neutralized lithium at the interface between film and gold substrate. Such an accumulation is less obvious, but also present, in the case of the Rb^+ profiles. An explanation for that is given in the following section where we show simulations of the depth profiles for Li^+ and Rb^+ and we provide a model which describes the ion transport in both cases.

3.1. Simulation of Depth Profile for Li^+ (5 s)

In this section a detailed analysis of the lithium concentration profile for 5 s bombardment is given. In **Figure 2**, a comparison between experimental data and theoretical model is presented. The depth axis has been normalized such that the C^+ signal is at half of its maximum value at 25 nm below the sample

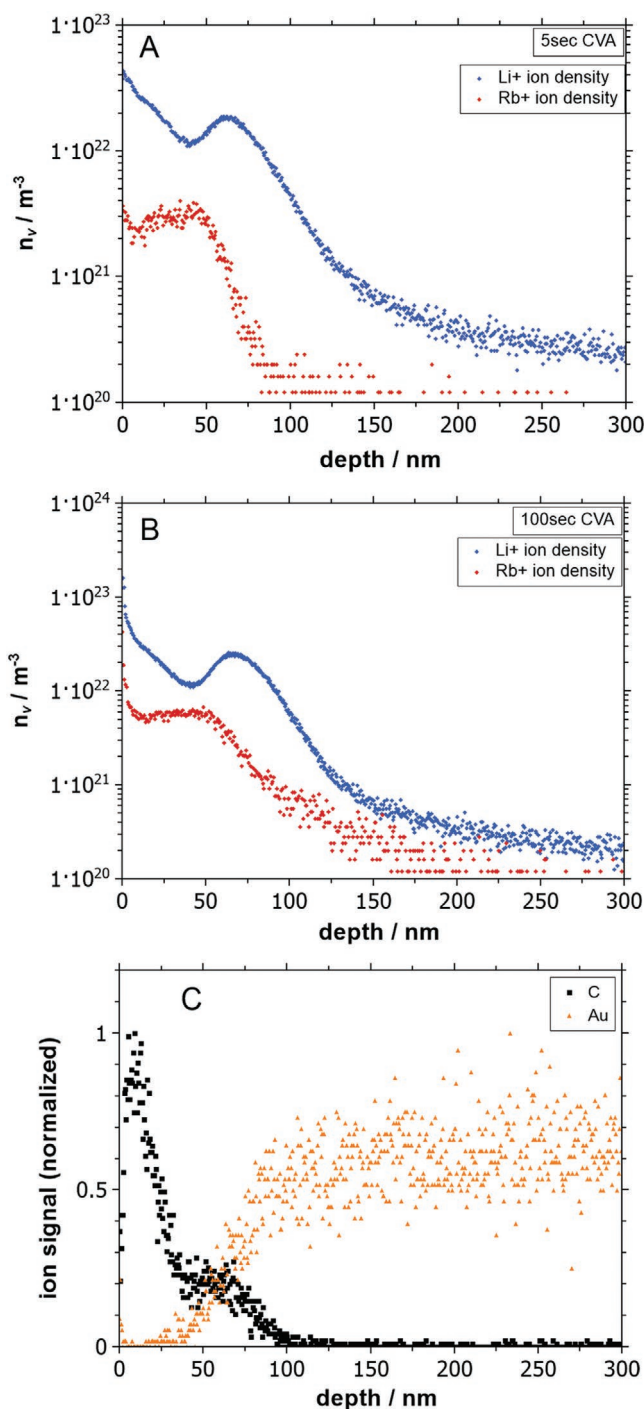


Figure 1. Graphs of ion densities versus depth for different alkali ions after attachment time of A) 5 s and B) 100 s. Note that the alkali ions traces belong to different CAIT experiments on different membranes, which are plotted in one graph for qualitative comparison. As an example, only one C^+ and one Au_3^+ trace is shown in graph (C). These data are taken from the Li^+ CAIT experiment. The C^+ and one Au_3^+ traces are indicative of the membrane (C^+) and the gold substrate (Au_3^+) and do not depend on the CAIT ion subjected to.

surface in line with the ellipsometry measurement. The Li profile however decays until 40 nm below the surface. The carbon signal decays to about 40 nm below the surface as well where

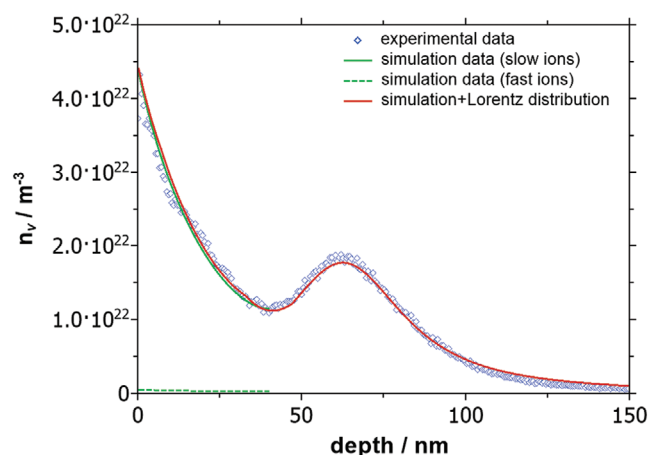


Figure 2. Ion density versus depth of experimental data (blue open diamonds), simulated slow pathway diffusion (green dashed), and fast pathway one (green dotted) together with total simulation + Lorentz distribution (red solid).

it levels off at a certain intensity level (compare Figure 1). We interpret that as the influence of the CAIT experiment which may cause the swelling of the film. As a consequence the transport is explicitly simulated to 40 nm below the surface. Ions that reach that position are neutralized and removed from the explicit calculation. The neutralized ions form an interphase between sample and electrode. Often the deposition of alkali ions occurs in the form of islands rather than in the form of a homogeneous layer. This feature leads to a broadening of the Li ToF-SIMS-signal at the interphase. As a consequence the neutralized Li is added in the form of a Lorentz distribution post calculation behind the explicitly calculated zone.

The simulations include a slow and a fast pathway for the ion transport. Best agreement between experiment and theory is observed for $D_{\text{slow}} = 0.9 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{fast}} = 9.6 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ and when 54% of the incoming Li^+ ions enter the slow pathway. In Figure 2, Li^+ ions that account for the slow pathway are indicated as green solid line, ions that account for the fast pathway are indicated as green dashed line. While the slow ions are basically responsible for the concentration profile inside the membrane, the fast ions basically account for the entire Li interphase. The red curve indicates the total Li^+ ion density, including the sum of the Li^+ ions from both pathways plus the ions that have been neutralized at the backside electrode. Experimental and numerical data agree very well.

The excellent agreement indicates that the two pathways for the Li^+ ion transport are operable. Numerical simulations with only one single diffusion pathway do not lead to an agreement between theory and experiment. Ion transport across PEMs containing calixarenes has been investigated earlier, e.g., by Toutianoush et al.,^[10] where p-sulfonato-calix[n]arene/poly(vinylamine) (PVA) multilayers were used as model system and the permeation rates of various electrolytes in aqueous solution were given. There the authors demonstrated that permeation of the metal ions across the calixarene/polyelectrolyte multilayer films is retarded compared with the all-PEM membranes, i.e., membranes without ring units from calixarenes. They claimed that in addition to the Donnan effect (which

refers to the rejection of permeating cations at the positively charged parts of the film),^[23] the presence of the calixarenes units may influence the type of transport. The cyclic arrangement induces indeed a highly negative charge density at the ring units, which can attract the cations depending on their size and charge density. Herein, we suggest a model which accounts for two pathways, one being slower than the other, leading to a diffusion profile of the ions as a combination of the two. Part of the lithium ions (according to the numerical calculation 54%) are retarded on their transport, due to the interaction with the negatively charged calixarene rings, while the rest of the ions pass through the membrane via hopping transport between discrete sites.^[24]

3.2. Simulation of Depth Profile for Rb^+ (5 s)

In order to shed further light on the mechanism of transport suggested from our model, a numerical simulation of rubidium diffusion profile has been conducted. In Figure 3 the simulated data as well as the experimental concentration profile is plotted as a function of the depth below the sample surface.

Comparing Li^+ and Rb^+ concentration profiles, the main difference between the two is the absence of a clear concentration variation of Rb^+ concentration. The concentration of Rb^+ is found to be almost constant across the film. Figure 3 shows the result of the simulations compared to the experimental data. The results of these simulations reveal that actually only the fast diffusion pathway is relevant for the transport of rubidium ions. From the results of the calculations, one can estimate that at most 0.02% of the rubidium ions enter the slow pathway while the rest uses the fast pathway, with a value for the diffusion coefficient of $D_{\text{fast}} = 1.1 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$. It is noticeable that the D_{fast} for the rubidium is eight times lower than the one found for the lithium but still 11 times larger than D_{slow} of Li^+ (see above), leading to the suggestion that the rubidium ions interact less with the calixarene rings in the film. The absence of Rb^+ ions retarded by the calixarene rings suggests that there is only negligible interaction of the Rb^+ ions with the negatively

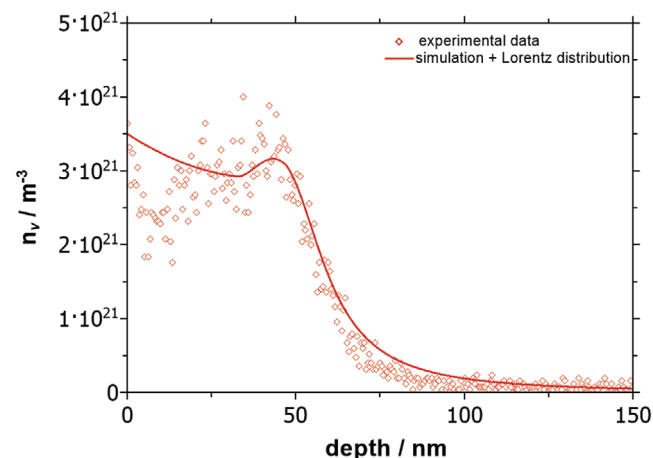


Figure 3. Ion density of rubidium versus depth of experimental data (red open diamonds), result of simulation (red solid).

charged rings. This remark appears to be consistent with the results of the study conducted by Toutianoush et al., where the permeation rate values of alkali-metal chlorides across calix8/PVA films increase in the series from LiCl to CsCl. According to their explanation the larger size of the rubidium cations (0.148 nm vs 0.068 nm) and its consequently lower charge density seems to play a crucial role on the electrostatic rejection of the ions from the equally charged parts of the membrane.

The apparent absence of the slow transport pathway for Rb⁺ leads to the fact that the membrane becomes quickly filled with Rb⁺ ions. This fact inherently makes discerning Rb electrodeposition difficult. By contrast, lithium ions are distributed with 54% to the slow pathway and 46% to the fast one, giving rise to a diffusion profile which reflects the combination of the two and not the predominance of only one. Relating the diffusion coefficients to the binding constants of the different alkali ions to the calix-based polyelectrolyte membranes is not possible, as binding constants for Li⁺, K⁺, Rb⁺ to the particular calix8 molecule used here are not available, and already slight variations in molecular structure may cause big changes in binding constants.

The films of (PAH/calix8)₃₀ investigated in this work exhibit high thermal and mechanical stability. These films can be prepared and stored under ambient conditions without changing form or color. This fact once more demonstrates the suitability of the cationic PAH polyelectrolyte for forming stable multilayers.^[25,26] Among the well-established calixarenes, calix4, calix 6 and calix 8, the calix8 is particularly suited for designed interaction with alkali ions. The larger number of ionic binding sites (eight sulfonates group for the calix8) favors adsorption of alkali ions to the calix8. Moreover, the ring conformation of the three mentioned calixarenes is different and calix8 attains mainly the flat-plane conformation, being well suited for adsorption.^[27]

4. Conclusion

The transport of alkali ions across calix-based polyelectrolyte membranes has been investigated in a charge attachment induced transport experiment. Pronounced specificity for selective alkali ion transport has been observed comparing Rb⁺ to Li⁺ ions. In general, two different transport pathways are accessible for alkali ion transport, a fast one due to ion hopping through the bulk of the PEM and a slow one dominated by attractive interaction of the alkali ion to the negatively charged calixarene anions. Both transport pathways appear to be operative for Li⁺ ion transport, only the fast transport channel has been observed for Rb⁺. The experimental ToF-SIMS data presented have been rationalized by a theoretical model providing quantitative representation of both, the absolute values for diffusion coefficients as well as for the percentage of ions entering the respective diffusion pathway. It is found that the ions that use the slow pathway lead to the formation of a concentration profile inside the PEM which is present for the Li⁺ but not for Rb⁺. The ions that move through the film via the fast pathway mainly lead to the deposition of a neutral alkali layer between sample and electrode. At the end of the experiment, only few ions from the fast pathway are found inside the film.

5. Experimental Section

Sample Preparation: 3 mg mL⁻¹ solution of PAH (Sigma-Aldrich, ref 283223) was used as cationic polyelectrolyte and 1.5 mg mL⁻¹ solution of p-sulfonato-calix[8] (TCI America, CAS Number: 137407-62-6, Product Number: S0471 [1489.48 g mol⁻¹]) as anionic counterpart (**Figure 4**). A 50 μm thick gold foil (HMW Hauner) was cut into pieces of 8 mm × 8 mm each and used as modified substrate via functionalization with 1 × 10⁻³ M 3-MPA (Sigma-Aldrich, ref M5801, M[106.14 g mol⁻¹], δ[1.218 g mL⁻¹]). Water used in all experiments was prepared in a three-stage "Milli-Q" purification system to a conductivity of less than 1 μS cm⁻¹.

In a first preparation step, an MPA-modified gold electrode was used as substrate for supporting the polyelectrolyte membranes. In detail, thin pieces of pure gold foil were first treated with a 20 s long plasma discharge (Sputter Coater ACE 600 from Leica) to improve the cleaning status of the surface. The substrates were then anionically functionalized by immersion for 24 h in MPA, then rinsed with milliQ water, and finally dried with a soft and continuous stream of nitrogen. Second step in the preparation of the membranes was the adsorption of the polyelectrolyte layers. For this purpose, the dipping method first reported by Decher et al.^[28–30] was used. In **Figure 5** this is schematically represented: First, the functionalized gold supports were dipped into a solution of PAH for 20 min, rinsed with milli-Q water to remove the excess of PAH and dried. Second, the protocol was repeated by immersing the covered substrate into a calix8 solution for 20 min, washing again with Milli-Q water, and finally drying. With these two steps the first bilayer of PEM was formed. The entire two-step protocol of dipping, rinsing, and drying was repeated 30 times, leading to samples with (PAH/calix8)₃₀ throughout the entire manuscript.

Characterization of LBL Films: The thickness of the LBL films in dependence of the number of layers was experimentally determined by spectroscopic ellipsometry. As the 1 μm thick gold foil used for the conductance measurements was not suited as support for spectroscopic ellipsometry measurements due to its overall surface roughness, the LBL films were deposited on a planar gold-covered Si substrate. In detail, the 1 cm² Si-wafer was sputter coated with 20 nm Cr (which act as adhesion layer for the subsequent deposited Au film) and two times (in order to avoid excessive heating) with 150 nm Au. No additional cleaning step had to be performed, as the substrate after sputtering had a highly reflective surface without visible defects/contamination. The substrate was then immersed for 24 h in a 1 × 10⁻³ M MPA-ethanol solution. After incubation the substrate was rinsed by dipping into Milli-Q water. No drying step was performed. For the coating with the first polymer layer, the substrate was immersed in 2 mL of 3 mg mL⁻¹ PAH solution for 20 min, followed by a dip rinse in Milli-Q water. To complete the first bilayer, the PAH coated substrate was then immersed in 2 mL of 1 × 10⁻³ M (1.5 mg mL⁻¹) p-sulfonato-calix[8]arene solution for 20 min, followed by a dip rinse in Milli-Q water. The procedure was repeated until the desired

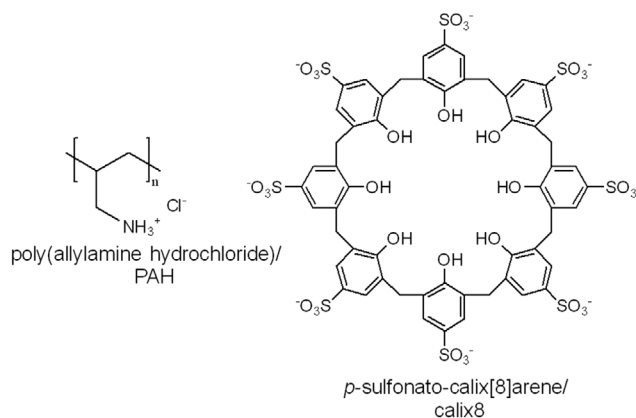


Figure 4. Representation of cationic polyelectrolyte (PAH) and anionic calixarene (calix8).

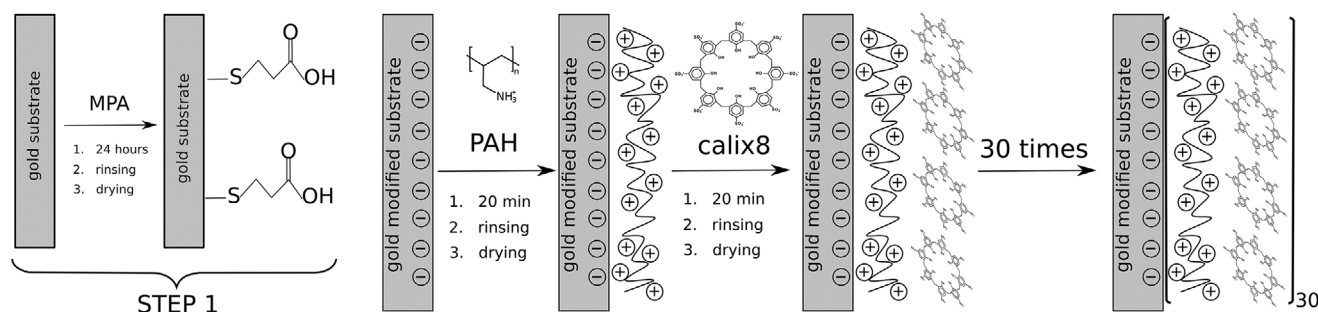


Figure 5. Schematic representation of the LBL technique to form alternating absorption of (PAH/calix8)₃₀.

number of bilayers had been added. Subsequently, the LBL-Au-silicon substrates were transferred to the spectroscopic ellipsometer SENTECH SENPro. The 300 nm thick gold layer had been set as fully reflecting substrate. Measurements were performed in a spectral region between 380 and 850 nm. For fit analysis, the LBL film had been modeled by a Cauchy model, and the fitted wavelength range was set to 400–800 nm. As starting point, since the exact refractive index of the LBL films was unknown, the Cauchy model of poly(methyl methacrylate) (PMMA, refractive index $n = 1.49$ @632.8 nm) was tested, leading to reliable measurement results. In subsequent measurements two samples of each batch were measured in two different configurations (at an incident angle of 70° and 55°). At that point the thickness as well as the refractive index were also fitted. For analysis, the four measured values per batch were averaged. The result of the ellipsometry measurements for samples with different number of bilayers is shown in **Figure 6**. The thickness of the PEM layer was later used to calibrate the depth axis of the concentration depth profiles.

CAIT Setup: The experimental setup for CAIT measurements consisted of three main parts: the ion source, the ion optic, and the sample holder (**Figure 7**). A continuous positively charged ion beam ($M^+ = Li^+, K^+, Rb^+$) was generated by thermionic emission from the heated ion emitter material.^[31,32] The ions were guided and focused toward the sample via an ion optics system consisting of electrostatic lenses. In particular, the ions leaving the emitter were repelled by a positive voltage applied to the repeller lense: U_{rp} ; this voltage ultimately defines the initial kinetic energy of the ions in the laboratory frame. In all the experiments conducted within this work the repeller voltage was chosen to be 5 V. An appropriate guiding through the electrostatic lenses L1 to L6 guaranteed

a spatially homogeneous ion beam of constant intensity. After passing a grounded aperture, the ions reached the sample surface. A 4 mm diameter mask was used to define the bombarded area of the sample. The ions impinged on the front surface of the sample, leading to the formation of a surface potential and a surface particle density. Since the backside of the sample was in contact with a backside electrode which was grounded, a potential and particle density gradient toward the backside of the electrode arose. The ions were transported according to these gradients and moved toward the grounded electrode, where they were neutralized and a corresponding neutralization current could be detected. The current at the electrode was measured by an electrometer amplifier (QME 311, Balzers). The current was then digitized and processed in a personal computer. The temperature of the sample could be controlled via a PID-controller (Eurotherm 3216) coupled with a PT-100 and a home-made heating device. Eventually, the setup was placed in a high vacuum chamber at a base pressure of $10^{-6}/10^{-7}$ mbar.

For the emission of the ion, a home-made thermionic emitter of potassium and rubidium aluminosilicates of composition $M[AlSi_2O_6]$ ($M = K, Rb$) was used as an ion source in the CAIT experiments,^[31] while synthetic spodumene ($LiAlSi_2O_6$) was chosen as the material for the Li^+ ion emission together with a filament type emitter.^[33] In all cases the ion current reaching the sample surface was set to a value lower than 1 nA, between 0.3 and 0.7 nA depending on the specific emitter. For each ion beam (Li^+, K^+, Rb^+) two kinds of experiments were performed, varying the time for the bombardment: 5 s in one case and 100 s in the other, leading consequently to a different amount of charge transported through the membrane. The reason for having chosen such a small irradiation time was connected to the small thickness, which does not allow for high ion current density to flow inside the membrane without compromising the ion transport properties of the material. All the experiments were conducted at a temperature of 193 K and each measurement was performed onto always fresh PEMs of the type (PAH/calix8)₃₀.

Since the experiment was conducted under vacuum conditions, one might expect that this would reflect properties under water-free conditions. On the other hand, the PEMs were prepared from aqueous solutions and previous experiments with analogous PEMs suggested that water maintains inside the PEM for thickness larger than about 10 bilayers even under high vacuum conditions.^[9] It is therefore concluded that the properties observed for the sample with 30 bilayers studied in this work reflects those under wet conditions in good approximation.

ToF-SIMS Conditions: Concentration profiles arising from diffusion of the different ions through the sample were analyzed by ToF-SIMS (IONTOF GmbH, Münster, Germany). For analysis of positive ions a Bi⁺-LMIG (liquid metal ion gun) was used in the high current bunched mode (25 keV Bi⁺-ions, pulsed target current 0.50 pA), while a Cs⁺ ion gun (30 nA; 3 kV) was used for the sputtering process. The analyzed area was 100 $\mu m \times 100 \mu m$ with a resolution of (128 $\times$ 128) pixels in the interlaced mode. The sputtered area was 300 $\mu m \times 300 \mu m$. Mass spectra were collected within the mass range up to the mass to charge ratio of $m/z = 800$, with a mass resolution of $m/\Delta m = 6000$ –8000. The integrated area of the investigated ion peaks was obtained as a function of sputter time. The calibration of the depth axis into a real space depth is described in section 3.

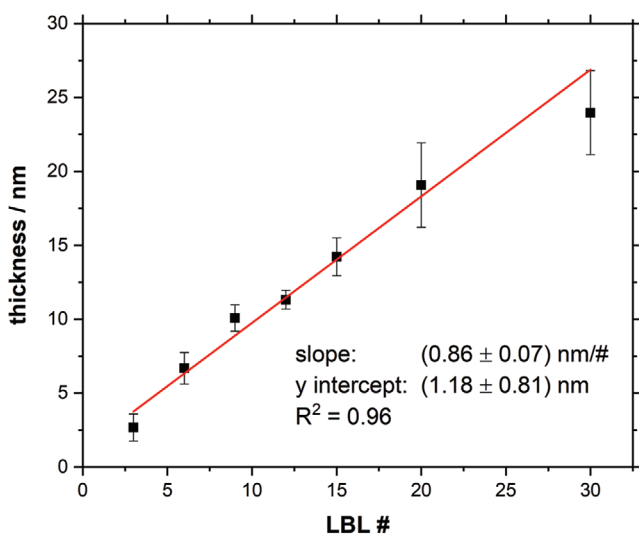


Figure 6. Thickness of the PEM layers on Au substrate as function of the number of bilayers.

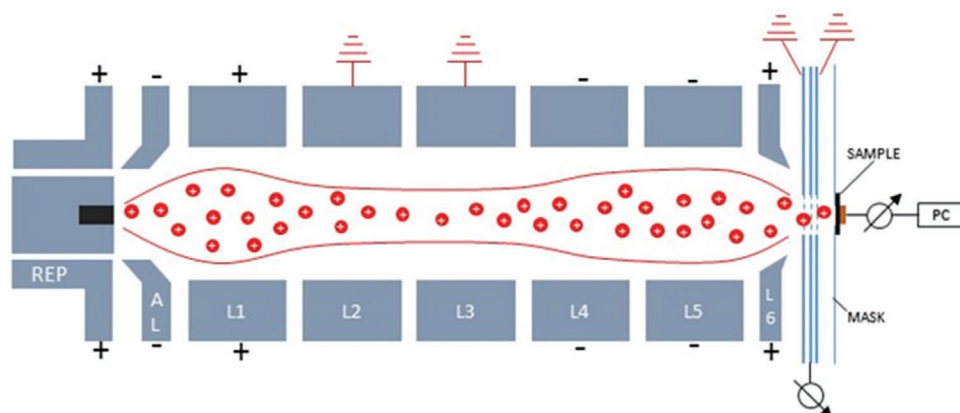


Figure 7. Experimental setup with the repeller lens U_{rp} , the abstraction lens AL, the ion optics L1 to L6 and the sample.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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