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ARTICLE

Humidity-Dependent DC Conductivity of Polyelectrolyte Multilayers: Protons or Other Small Ions as Charge Carriers?

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ABSTRACT: A range of different combinations of polyelectrolytes is employed to form multilayers by layer-by-layer assembly, which are investigated by impedance spectroscopy. In particular, the alkali counterion employed in the layer formation is varied. Impedance spectra of different multilayer systems are qualitatively similar, and they are changing in a similar way with relative humidity (RH). From the spectra, the dc conductivity σ_{dc} and its dependence on humidity are extracted. The humidity dependence of σ_{dc} follows a general law of $\log(\sigma_{\mathrm{dc}}) = a\mathrm{RH} + b$, which is valid for all systems. Absolute values of σ_{dc} and slopes a depend on the type of polyelectrolytes employed but are independent of the type of alkali counterion involved. On the basis of these data, we discuss the contribution of different small ionic species, i.e., anions, alkali cations, or protons, to the conductivity and conclude that the differences between different polymer systems as well as the humidity dependence are consistent with the conduction of protons or hydronium ions, while the contribution of other cations or anions to σ_{dc} is negligible.

Introduction

In the search for suitable materials as ion conductors in separation membranes in Li ion batteries or fuel cells, there is a strong demand for solid polymer membranes, which exhibit large ionic conductivities but are nevertheless mechanically stable. For example, for Li conduction an up-to-date approach is to apply salt-in-polymer electrolytes made from comb-shaped copolymers. These exhibit short oligoether side chains that can solubilize and transport the ions,[1−3] while the backbone can be cross-linked to provide mechanical stability. As opposed to this, for proton conduction in fuel cells, a widely investigated benchmark material is Nafion, a fluorinated polyelectrolyte. Nafion is mechanically stable due to a phase separation into hydrophobic regions and aqueous channels, where the interface, carrying free sulfate groups, provides the proton conduction properties.[4−6]

In this context polyelectrolyte multilayers (PEM) prepared by layer-by-layer-assembly (LbL) have attracted interest, since two of the three main requirements are already fulfilled by the generic material properties: First, PEM are prepared from a defined number of monolayers, each with a thickness in the nm range, such that ultrathin films can be obtained with a defined thickness in the nm to μm range. A low film thickness is of advantage to yield low overall resistance and fast loading. Second, in spite of the low thickness, PEM are a tremendously stable material, which is an effect of the multiple electrostatic interactions between subsequent layers. Their mechanical properties have been extensively investigated in free-standing geometries, and Young's moduli of the order of GPa have been found.[7,8]

A challenge remains however to fulfill the third requirement, which is to achieve large ionic conductivities in these films. In several publications dc conductivities of PEM of the order of $(10^{-12}-10^{-5})$ S cm^{-1} have been reported.[9−12] A major problem in the interpretation of conductivity data is the lack of knowledge about the composition of the films: Since PEM are formed by self-assembly, the compensation of surface charges upon chain adsorption is controlling the stoichiometry in the films. The excess charges of an outermost polyelectrolyte layer might become fully compensated by the oppositely charged segments of the subsequent layer ("intrinsic charge compensation"), or if this is sterically not favorable, small counterions might incorporate into the film in order to compensate the polyion charges ("extrinsic charge compensation"). Thus, PEM are a material of unknown stoichiometry. Though in first approximation the translational entropy of the small counterions would always lead to intrinsic charge compensation being favored, in a number of polyion combinations a deviation from a 1:1 stoichiometry of the polyions has been found. In such films, a substantial degree of extrinsic charge compensation by small counterions could be concluded.[13−15] Nevertheless, systematic knowledge about the composition of self-assembled multilayers is lacking, which is so far hindering the interpretation of conductivity data.

As a reference system with a controlled and variable stoichiometry, polyelectrolyte complexes (PEC) have been employed. Here, the content of small cations and anions is known, as it depends on the mixing ratio of the polyions. Furthermore, systems with only one type of counterion can be prepared, when excess salt is removed by dialysis. In this way conductivity data in dependence of the composition can be related to the conductivity contribution of a single type of charge carrier.[16,17] In dry PEC the conductivities are much larger for the small cation $\mathrm{Na^+}$-rich composition than for the small anion $\mathrm{Cl^-}$-rich ones. The conductivity increases monotonously with the composition, i.e., with decreasing $\mathrm{Cl^-}$ and increasing $\mathrm{Na^+}$ content. This implies a negligible contribution of chloride to the conductivity, while the current is dominated by the contribution of the small cations, $\mathrm{Na^+}$.[16]

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In hydrated multilayers, however, the contribution of different charged species is more difficult to judge. Several authors employ Nafion in multilayer formation and discuss the transport of protons as the mechanism dominating the dc conductivity.[18−21] Following the first report on dielectric properties of multilayers by Durstock and Rubner,[9] a number of different constituents of multilayers have been employed with the aim to enhance conductivity, such as weak polyelectrolytes,[10] poly(ethylene oxide),[11] or poly(phosphazenes).[12] It is known that the hydration state of the layer assembly has a strong influence on the conductivity, since in a number of studies films were compared in the dry and the hydrated state. A review of the activities up to 2007 is given by Lutkenhaus and Hammond.[21] There, and in references therein, it is generally argued that protons carry the current, but a detailed discussion of potential contributions of other small counterions is so far missing.

Here, we study different combinations of polyelectrolytes in multilayers made of different pairs. We particularly study small cations involved by varying the size of the counterion to the polyanion. All the films are investigated systematically in dependence on the relative humidity, where we identify an exponential dependence as a general feature of the conductivity. Analyzing the data, we discuss the relevance of the contributions of different ionic species, such as the alkali cations, anions, or protons, to the conductivity and yield the conclusion that in hydrated PEM the conductivity is dominated by proton conduction.

Materials and Methods

Materials. Poly(sodium 4-styrenesulfonate) (NaPSS; M_w = 70 000 g/mol) and poly(lithium 4-styrenesulfonate) (LiPSS, M_w = 75 000 g/mol, 35 wt % aqueous solution) are purchased from Acros and Sigma-Aldrich, respectively. They are dialyzed (cutoff: M_w = 10 000 g/mol) against ultrapure water and lyophilized. Poly(rubidium 4-styrenesulfonate) (RbPSS) and poly(cesium 4-styrenesulfonate) (CsPSS) are obtained from ion exchange of freeze-dried NaPSS: Strongly acidic cation exchange resin (Amberlite, IR120 hydrogen form) from Fluka is used for the ion exchange. Ion exchange salts rubidium chloride (RbCl) and cesium chloride (CsCl) are delivered from ABCR GmbH and Fluka, respectively. Poly(ethyleneimine) (PEI, M_w = (50 000 to 60 000) g/mol, 50 wt % aqueous solution), poly(allylamine hydrochloride) (PAH, M_w = 70 000 g/mol), and poly(diallydimethylammonium chloride) (PDADMAC, M_w = (100 000 to 200 000) g/mol; 20 wt % aqueous solution) are obtained from Sigma-Aldrich and used without further purification. Ionically modified polyphosphazenes, i.e., cationic (poly(bis(3-amino-*N*,*N*,*N*-trimethyl-1-propanaminium iodide)phosphazene) (PAZ^+) and anionic poly(bis(lithium carboxylatophenoxy)phosphazene) (PAZ^-) are synthesized and characterized as described previously.[12]

Several salts are employed for humidity control, i.e., sodium chloride (NaCl, Merck), potassium acetate (KAc, Fluka), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, Fluka), potassium chloride (KCl, VWR ProLABO), potassium carbonate (nonaqueous) (K_2CO_3, Fluka), ammonium nitrate (NH_4NO_3, Merck), potassium sulfate (K_2SO_4, Fluka), and lithium chloride (LiCl, Acros). All these chemicals are at analytical grade. LiCl is dried in an oven at 110 °C for at least 90 min in order to remove water prior to preparing solutions from it. Throughout all preparation procedures, ultrapure water (H_2O, three-stage purification system (Millipore), resistivity > 18 MΩ·cm) is used.

Indium−tin oxide (ITO)-coated glass substrates (ITO thickness 180 nm; size 40 mm × 15 mm, glass thickness 1.1 mm, area resistivity ≥ 10 Ω/square) are provided by PGO, Präzisionsglas and Optik GmbH, Iserlohn. Oxidized Si wafers are received from SilChem GmbH, Freiberg, with a nominal thickness of the SiO_2 layer of either (500 or 300) nm.

Solutions. Polymer solutions with a concentration of the monomer repeat unit of 0.01 mol/L are prepared with additional low molecular weight salts, except for PEI, which is prepared without low molecular weight salt. The combinations of polyelectrolyte and salt are NaPSS in 0.1 M NaCl, LiPSS in 0.1 M LiCl, RbPSS in 0.1 M RbCl, CsPSS in 0.1 M CsCl, PAH in 0.1 M NaCl, PDADMAC in 0.1 M NaCl, PAZ^+ in 0.1 M LiCl, and PAZ^- in 0.1 M LiCl. The PAZ^+ solution is adjusted to a pH value of 5.1 by a buffer consisting of 0.064 M potassium hydrogen phthalate and 0.037 M sodium hydroide.

Table 1. Ellipsometric Thickness Data at Ambient Atmosphere for Different Layer Compositions with *n* Layers

PEM system	*n*	*d*/nm
PAH/LiPSS	100	115
PAH/NaPSS	100	105
PAH/RbPSS	100	110
PAH/CsPSS	100	115
PDADMAC/NaPSS	100	264
PDADMAC/LiPSS	100	250
PAZ^+/PAZ^-	80	118
PAZ^+/PAZ^-	100	155
PAZ^+/PAZ^-	120	197
PAZ^+/PAZ^-	200	323

Multilayer Preparation. A series of layers in the order PEI/polyanion/(polycation/polyanion)$_{49}$ are deposited. Before starting the deposition, ITO-coated glass substrates or oxidized silicon wafers are cleaned in RCA solution (H_2O_2/ammonia/water, 1:1:5 vol/vol), which is heated to 70 °C for 15 min. Extensive rinsing of the substrates with ultrapure water follows. Cleaned hydrophilic substrates are stored in ultrapure water and used within hours.

Polyelectrolyte adsorption and intermediate washing steps are performed automatically using a dipping robot (DR 3, Riegler and Kirstein, Berlin) immersing the substrates into polymer solutions and into ultrapure water for washing. The first layer is always built up from PEI, followed by an alternating sequence of the respective polyanion and polycation. The adsorption time is always 20 min. After each adsorption step, the substrate is immersed four times (2 min each time) into a beaker with ultrapure water. The depth of immersion into the solutions is programmed such that the number of monolayers, *n*, on one substrate can be locally varied.

The following polyelectrolyte combinations are investigated: PAH/LiPSS, PAH/NaPSS, PAH/RbPSS, PAH/CsPSS, PDADMAC/NaPSS, and PAZ^+/PAZ^-. The number of monolayers *n* is always 100. In the case of PAZ^+/PAZ^-, *n* is 80, 100, 120, and 200, respectively.

Thickness Determination. To determine the film thickness, *d*, ellipsometric measurements are performed on PEM prepared on oxidized silicon wafers. The measurements are carried out using a Null-Ellipsometer (Multiskop, Optrel GbR, Kleinmachnow) equipped with a HeNe laser (λ = 632.8 nm; P = 4 mW). The ellipsometric measurements are performed at ambient conditions. Resulting thickness data are given in Table 1.

Conductivity Measurements. Conductivity spectra are determined at (22 ± 2) °C at various constant relative humidities (RH) employing an impedance analyzer (HP 4172, Hewlett-Packard) covering a frequency range from 5 Hz to 13 MHz. The PEM are placed in a sandwich geometry between the ITO electrode on the one and sputtered gold electrodes on the other side. All measurements are performed in a sealed glovebox, where saturated salt solutions are applied for RH adjustment. The complex conductivity is obtained from the measured complex admittance $\hat{Y}(\nu)$ via $\hat{\sigma}(\nu) = \hat{Y}(\nu) \cdot d/A$, where ν is the experimental frequency and A denotes the area of the gold electrodes. The sample thickness d was determined from ellipsometric measurements of a silica wafer with an identical PEM coating (see results in Table 1). More experimental details are given in ref 12.

Results

Conductivity Spectra. Complex conductivity spectra from the above-mentioned PEM systems are determined at ambient

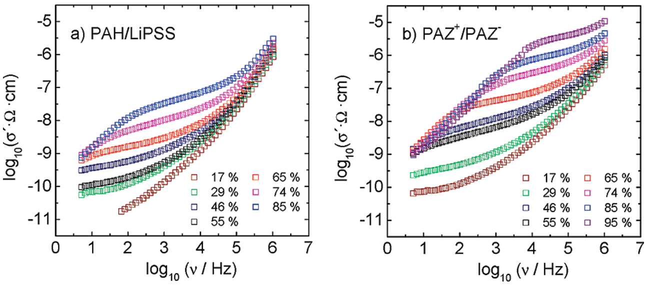

Figure 1. Conductivity spectra of (a) PAH/LiPSS multilayers and (b) PAZ^+/PAZ^- multilayers taken at different RH.

temperature and at relative humidities (RH) varying from 17% to 85% or 95% (mostly in steps of roughly 10%). Representative sets of conductivity spectra of two PEM materials, viz. PAH/LiPSS and PAZ^+/PAZ^-, are shown as examples in Figure 1.

The real part of the conductivity, σ', is shown against the experimental frequency ν in a log−log plot. The frequency regime extends from 5 Hz to 1 MHz. Conductivities at frequencies higher than 1 MHz are cut off because the data are influenced by inductive contributions of the cables. Figure 1 shows that at constant frequency the conductivity increases significantly with RH. At low frequencies and at a relative humidity of 17%, the sample conductivity of PAH/LiPSS is too low to be measurable by the HP 4192A impedance analyzer (see Figure 1a). A so-called dc conductivity plateau, σ_{dc}, where the conductivity is independent of frequency is therefore not detectable for this humidity. The dc regime is, however, seen in the conductivity spectra taken at higher RH (29% and 46%) in the low-frequency part. At even higher relative humidities, the low-frequency part of the conductivity spectra is more and more influenced by electrode polarization effects superimposing the dc regime. As both the ITO and the gold electrodes are blocking electrodes for the moving ions, some ions accumulate at the electrode surface. This leads to a decrease in the conductivity with decreasing frequency, which becomes more important the thinner the sample and the higher the conductivity is.

At each relative humidity we observe that for frequencies higher than those of the dc regime $\sigma'(\nu)$ increases monotonously with frequency (dispersive regime). With increasing relative humidity, the onset of dispersion shifts to higher frequencies.

The same features as described above are seen in the conductivity spectra of PAZ^+/PAZ^- (see Figure 1b) as well and also in the spectra of all other investigated polyelectrolyte multilayers (data not shown). In fact, the spectral shape does not depend much on the kind of PEM system. Investigation of the spectral shape for all PEM shows some similarities, and also distinct differences between their conductivity spectra and those of other ion conducting materials, which have been investigated and analyzed before.[12,22] A detailed quantitative analysis of the spectral shapes in dependence on humidity will be the subject of a forthcoming paper.

DC Conductivity. From the conductivity spectra we determine the values of dc conductivity by extrapolating the conductivity to low frequencies while neglecting the polarization effects according to a fitting procedure using a reference curve, which was described earlier.[12,22] In addition, we determine the dc values from Nyquist plots of the complex impedance by fitting an equivalent circuit consisting of an Ohmic resistance and a parallel constant phase element to the data. Both methods yield dc values which are in very good agreement within experimental error (see Figure 2). The only remarkable deviation is seen at RH = 17% in the PAH/LiPSS PEM (Figure 2a), where σ_{dc} was not detectable within the measured frequency window and had therefore to be extrapolated. All other data obtained by the two different methods are in very good agreement.

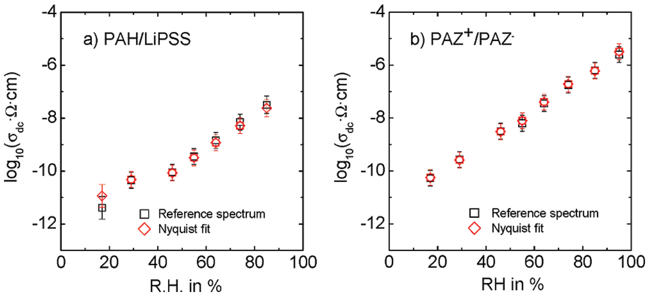

Figure 2. Dc conductivity of (a) PAH/LiPSS PEM and (b) PAZ^+/PAZ^- PEM at varying RH determined by different kinds of analysis methods.

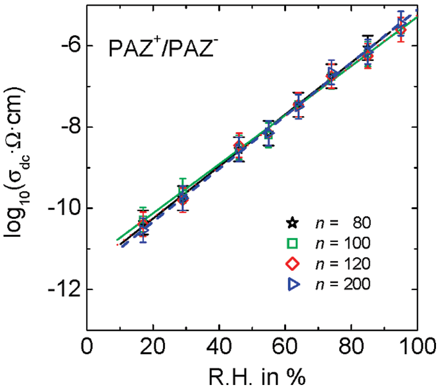

Figure 3. Dc conductivity of PAZ^+/PAZ^- PEM with varying film thickness.

Note that layer thickness values d employed for the calculation of σ_{dc} from the complex admittance are determined at ambient conditions. Since the layers swell with increasing relative humidity and at full hydration thickness values of 130% of the dry thickness are typically observed,[23,24] the humidity dependence of the thickness would have to be taken into account. However, throughout this paper we discuss conductivity data on a logarithmic scale. The error of layer thickness values determined at an intermediate humidity causes errors up to about 6% in $\log(\sigma_{dc})$, which is smaller than other error contributions.

In order to verify that the measured conductivities are really due to the ionic conductivity of the PEM material and not affected by interface effects, conductivity spectra of different layer numbers are determined for the PAZ^+/PAZ^- system. These measurements are also done in view of a potential incorporation of sputtered gold atoms penetrating a part of the layer and thus reducing the effective electrode distance with respect to the thickness determined by ellipsometry. Another potential artifact could be the interface resistance of the ITO/film interface, which is not compensated in the two-probe method employed for the impedance measurement. Such interfacial resistance would add to the film resistance. However, between n = 80 and 200 layers we find a very good agreement between the different data sets. Figure 3 shows the dc conductivities of the PAZ^+/PAZ^- PEM determined for four samples of different thickness which are, within experimental error, in perfect agreement. This demonstrates that the experiment detects the true

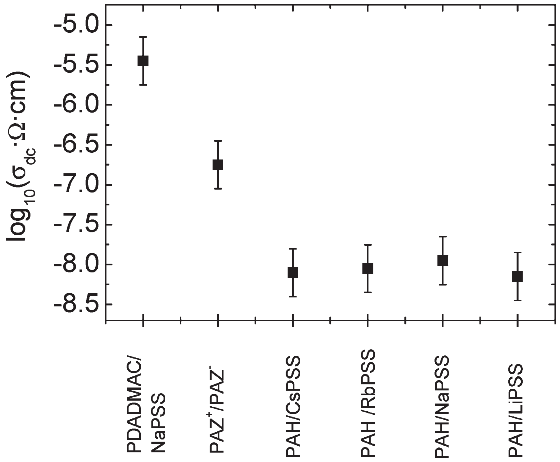

Figure 4. Logarithm of the dc conductivity of different polyelectrolyte multilayers at RH = 74%.

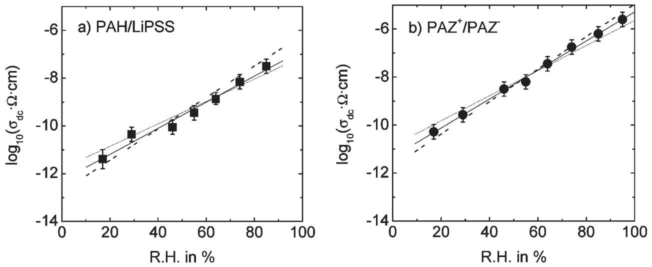

Figure 5. Logarithm of the dc conductivity of (a) PAH/LiPSS multilayers and (b) PAZ^+/PAZ^- multilayers as a function of relative humidity. The solid lines result from linear regression. The dashed and dotted lines show those straight lines acceptable within the error bars, which have maximal and minimal slope, respectively.

film material impedance, while the resistance of the setup is negligible compared to that of the film and electrode penetration can be neglected.

Figure 4 gives the σ_{dc} values determined at one particular relative humidity as a comparison between all systems investigated. The largest dc conductivity is found in the PEM containing PDADMAC. The lowest conductivity is found for films prepared from PAH and PSS. There is no systematic change on variation of the counterion of PSS in layers composed of PSS and PAH. The σ_{dc} value of the PAZ^+/PAZ^- PEM is between that of the PDADMAC/NaPSS PEM and those of the multilayers containing PAH.

Influence of Humidity. In Figure 5 the σ_{dc} values of PAH/LiPSS and PAZ^+/PAZ^- PEM are plotted against the relative humidity (RH). The error bars include the experimental errors, the uncertainties in determining the dc conductivity from the spectra, and the change of the layer thickness d with increasing RH due to film swelling.[23]

A strong dependence of the dc conductivity on the relative humidity is seen: Figure 5a shows that the change of conductivity with RH is of about 4 orders of magnitude for PAH/LiPSS. The logarithm of σ_{dc} increases linearly with RH. The slope of 0.055 of the straight line in Figure 5a is obtained from linear regression. In order to estimate the error of this slope, we also determine the minimal (0.047) and the maximal (0.066) slope of straight lines which would be acceptable within the given error bars. A similar evaluation of the system PAZ^+/PAZ^- also yields a linear dependence (see Figure 5b). Here, the conductivity changes by almost 5 orders of magnitude in the RH regime under consideration.

The linear dependence $\log(\sigma_{dc}) = a\mathrm{RH} + \mathrm{const}$, as seen in these two examples of Figure 5, is consistent with our previous finding for PAH/NaPSS multilayers.[12] The linearity of $\log \sigma_{dc}$ with RH is also found to be valid in all other PEM systems investigated here (data not shown). The values of the slope a vary between 0.04 and 0.08 and are summarized in Figure 6.

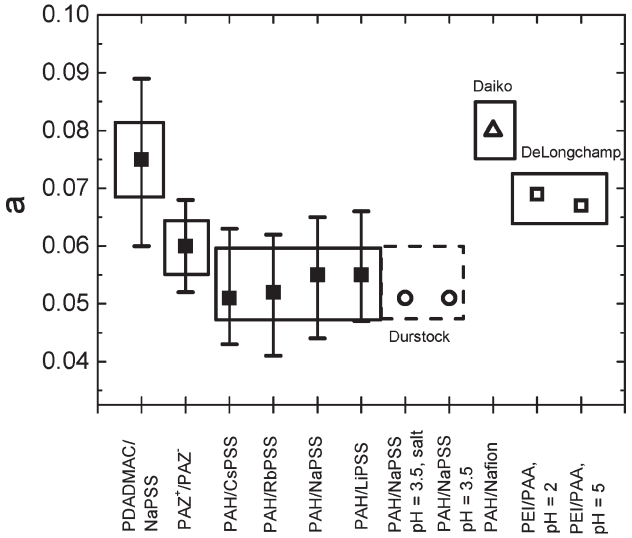

Figure 6. Slopes of log(σ_{dc}) vs RH including error bars (as determined from maximal and minimal slopes) for different polyelectrolyte multilayer systems (full symbols). Open symbols: slopes derived from interpolation of conductivities published by other authors;[9,10,18] the open circles present lower limits of the slope (see text).

From Figure 6 it is obvious that slopes of the same type of polyelectrolytes have nearly the same value. The largest dependence of the dc conductivity on the relative humidity is seen for the polyelectrolyte system containing PDADMAC and NaPSS, which has the largest slope. The smallest slopes are seen in the PEM with PAH and AlkaliPSS. The polyphosphazene PAZ^+/PAZ^- PEM shows an intermediate slope. It is also remarkable that the values of the slopes seem to correlate with the absolute values of σ_{dc} (see comparison to Figure 4). At a given relative humidity, the dc conductivity always follows the order $\sigma_{dc}(\mathrm{PAH/AlkaliPSS}) < \sigma_{dc}(\mathrm{PAZ^+/PAZ^-}) < \sigma_{dc}(\mathrm{PDADMAC/NaPSS})$.

In Figure 6, we have also included slopes which are determined from published values of the dc conductivity of different types of PEM, where data are available at different humidities.[9,10,18] It should be noted that, in contrast to the present study, these literature data are not determined in a series of relative humidities, but only at some values. An interpolation of the conductivity, for example between two[10] or four[18] humidity values, yields the slope data which are included in Figure 6, under the assumption of a similar exponential law for all of these systems. The open circles present lower estimates of the slopes, since Durstock and Rubner could only give upper estimates of the conductivity in the dry state.[9] Though the precision of these estimated data is not very high, we see that they are consistent with the interpretation of our slope values: Different PEM systems yield different slope values a, whereas the data by Durstock et al. obtained on the same kind of PAH/NaPSS−PEM as in our study show very similar slopes, although the PEM are treated differently (different pH values, swelling in salt solutions). These results stress that solely the choice of the polyanion/polycation combination determines how the resulting PEM reacts to a changing relative humidity in its environment.

Discussion

From our systematic study of impedance spectra for various combinations of polyelectrolytes, determined at different relative humidity, we have obtained absolute values of the dc conductivity as well as slopes characterizing the dependence of the dc conductivity on relative humidity. These data now form the basis of the discussion of the contribution of different charge carriers to the conductivity. In principle, there can be different small ionic species contributing to σ_{dc}: (1) small cations in the layer which result from incorporated counterions of the polyanion; (2) small anions in the layer, resulting from incorporated counterions of the polycation; and (3) protons, which could transport charge either as proton or in form of hydronium ions, following the Grotthuss mechanism. Generally, the dc conductivity contribution arising from a charged species *i* is given as the product of the mobility μ_i, the charge z_i, and the number density N_i of the mobile ion of type *i*, i.e.

$$\sigma_{\mathrm{dc},i} = z_i N_i \mu_i \tag{1}$$

As shown in Figure 4, within experimental error, the absolute conductivity values do not vary for different PAH/AlkaliPSS systems. How can we explain this finding? It has been generally discussed that in PEM systems the counterion content is rather low due to the intrinsic complexation of the layered polyelectrolytes.[13,25-29] On the other hand, in several systems a significant amount of small counterions was found and is apparently necessary to compensate polyion charges.[14,15] Thus, we have to assume that also in our PEM there might be some sites which are compensated extrinsically by small counterions, i.e., Alkali^+ or Cl^-.

Cation Contribution to Conductivity. We will first discuss the role of the alkali cation, which is present during layer formation as the counterion to PSS. In general, the counterion binding strength depends on the counterion species. For sulfonate groups the counterion binding strength increases in the order $\mathrm{Li}^+ < \mathrm{Na}^+ < \mathrm{K}^+$.[30-33] On the other hand, in the case of polycarboxylate and polymers containing carboxylate groups the binding strength of alkali ions is inverted, viz. $\mathrm{K}^+ < \mathrm{Na}^+ < \mathrm{Li}^+$.[30,32] For the investigated PAH/AlkaliPSS systems this implies that alkali ions of higher mass should bind stronger to polysulfonate groups than alkali ions of lower mass. Small ions incorporated into the LbL film might generally be condensed at the site of a polyion charge and localized to this site; we will term such ions as "bound" ions. On the other hand, small ions might be mobile to migrate through the layer; we will term those "free" ions.

First, one can discuss the dependence of conductivity on the type of counterion under the assumption of the same total incorporated amount of alkali ions for each layer system: Then, extrapolating the reported trends in the binding strength of the alkali ions to Rb^+ and Cs^+, we would expect that Cs^+ ions will be more tightly bound to sulfonate groups than Rb^+ or Na^+ or Li^+ ions. In other words, the lighter the alkali ions are, the higher would be the fraction of mobile ions within the PEM. According to eq 1, their contribution to the dc conductivity would thus increase with decreasing alkali ion size. In addition with the fact that, without influence of the hydration shell, the mobility of the cations will increase with decreasing alkali ion size, the conductivity of PEM with heavier alkali ions should be lower, which is not experimentally seen.

Second, assuming that the *total* number density of small cations depends on the type of alkali counterion employed, an explanation for identical dc conductivities of different PAH/AlkaliPSS films is the following: The higher binding strength of large alkali ions to the sulfonate groups could yield a larger charge carrier density in the film for Rb^+ and Cs^+ as opposed to Na^+ or Li^+. Assuming again an ion transport without influence of the hydration shell, one would expect a larger mobility for smaller alkali ions. In principle, a larger mobility of the smaller ions might exactly compensate the lower density of the same ions, such that according to eq 1 the same conductivity might result. However, an exact compensation for the whole series of alkali ions investigated is rather unlikely, and therefore it is unlikely that the overall conductivity is dominated by the contribution of alkali cations.

There is another argument against cation conduction: If the ion mobility differed strongly for different alkali ions, one would also expect that the dependence of the conductivity on RH would be different in the PEM systems with different alkali ions. Therefore, the slopes of the PAH/AlkaliPSS systems obtained from the plots of log σ_{dc} vs RH should be different. But as shown in Figure 6, the slopes are nearly the same. So we might also conclude at this stage that although the small cations present in PEM might contribute to the ionic conductivity, they will not dominate the total conductivity.

Anion Contribution to Conductivity. We might therefore ask whether the ion transport is instead governed by the small anions, viz. Cl^-. As the Cl^- ion content in PEM materials is unknown and controlled by the self-organization process during film preparation, we will consider polyelectrolyte complex (PEC) materials which are similar to PEM but which have the advantage that the number density of small counterions can be tuned. In recent work on polyelectrolyte complexes prepared with defined stoichiometric ratios the mobility of the anion (Cl^-) was shown to be negligible in comparison to the mobility of the cation (Na^+), since even in complexes with anion excess it was the residual amount of cations carrying the current.[16] In fact, with increasing content of chloride ions in the PEC, the experimentally determined dc conductivity is observed to *decrease*. And even if we assume that the measured conductivity in those PEC with an excess of Cl^- ions was due to Cl^- and not to residual alkali cations, we cannot explain the absolute values of σ_{dc} measured in PEM in this work: The dc conductivity in PEC materials with excess of Cl^- is for example only 10^{-10} S/cm for dry PEC with 20 mol % Cl^- excess at $T = 563$ K and about 8 orders of magnitude less at room temperature.[16] $\sigma_{\mathrm{dc,Cl^-}}$ is thus many orders of magnitude lower than the dc conductivity measured in the current study for the PEM material consisting of the same polycations and polyanions. This holds even for an extrapolation of σ_{dc} of PEM to zero humidity, where the conductivity is about 10^{-12} S/cm. It can thus be concluded that anions are not dominating the ionic conductivity in our PEM either. There is now only one reason remaining which explains the same conductivities and slopes for different PAH/AlkaliPSS, which is proton conduction.

Humidity Dependence of Proton Transport. For proton conducting hydrated polymers described in the literature, a linear relation between RH and the logarithm of the dc conductivity has, indeed, been reported in various bulk and thin film materials.[34-41] The slopes calculated from literature data are in the range of 0.07 ± 0.02. The slopes are slightly varying in dependence on the material properties. This implies that proton conductivity is slightly matrix-dependent. This behavior is also seen in the case of LbL films studied in this work. The slopes are in the range of 0.06 ± 0.02, and differences occur only if the type of polyelectrolyte is changed (see Figure 6). This can be taken for another indication that the conductivity of our PEM is governed by protons.

Similar conclusions are drawn based on earlier conductivity measurements on PEM in dependence of RH (see refs 9−11). The paper by Daiko et al.[18] concerns the *lateral* proton conductivity in PEM, built up by alternating layers of PAH and the proton conductor Nafion. The calculated slope from the log σ_{dc} vs RH dependence is 0.08, which is of the same order of magnitude as our slopes. Daiko et al. conclude that proton conduction occurs via conductive lateral pathways of the Nafion. On the basis of our results and the above arguments against alkali cation or anion conduction, it therefore is evident that proton conduction also occurs in PEM in the direction of the surface normal which implies that protons do not only move within the layers but also perpendicular to it. In addition, we conclude that proton conduction is the dominant contribution to the overall conductivity even in PEM which do not contain Nafion.

Conclusions

The investigation of humidity-dependent conductivity spectra of polyelectrolyte multilayers from different constituents shows a general exponential dependence of the dc conductivity on humidity. This behavior resembles that of proton-conducting materials. Variation of the alkali cation employed as the counterion in PEM formation shows that the alkali cation is not the ionic species dominating the ionic conductivity. Neither the anions are carrying the major part of the current, such that indeed protons are identified as the charged species dominating ionic conductivity. As a proton conductor, PEM—not only those prepared with Nafion or other known proton conductors—will have applications in fuel cells.

Nevertheless, the question of alkali ion—especially Li^+—transport remains interesting, since in dry PEC it is clearly the transport of residual alkali cations dominating the ionic conductivity. Therefore, in the future it will be interesting to study the crossover and relative contributions of cations and protons in dependence on complex stoichiometry and humidity and to tailor materials with defined contributions of protons or other small ions to the conductivity.

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