226 *Chem. Mater.* **2010,** *22,* 226–232
DOI:10.1021/cm902769m

CHEMISTRY OF MATERIALS
Article

Ion Conduction and Water Transport in Polyphosphazene-Based Multilayers

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Received September 4, 2009. Revised Manuscript Received October 30, 2009

Layer-by-layer (LbL) assembled films of poly[bis(methoxyethoxyethoxy) phosphazene] (MEEP) and poly (acrylic acid) (PAA) are demonstrated by utilizing the hydrogen bonding between these two polymers. These films show controlled thickness growth, high ionic conductivity, and excellent hydrolytic stability. The ionic conductivity of these films is studied by changing the assembly pH of initial polymer solutions and thereby controlling the hydrogen bonding characteristics. MEEP/PAA LbL films assembled at higher pH values have enhanced water uptake and transport properties, which play a key role in increasing ion transport within the films. At fully humidified conditions, the ionic conductivity of MEEP/PAA is 7×10^{-4} S cm^{-1}, more than 1 order of magnitude higher than previously studied hydrogen-bonded LbL systems. Finally, free-standing films are isolated from low-energy surface substrates, which allows for bulk characterization of these thin films.

Introduction

Many electrochemical energy conversion and storage devices such as fuel cells, batteries, and dye-sensitized solar cells rely on electrolytes for ionic transport. Conventional electrolytes consist of a polar liquid capable of solvating ions. The need for a safe and lightweight solid-state electrolyte has driven extensive research to replace caustic or flammable liquid electrolytes to circumvent problems associated with leakage. A known compromise in this area is the balance between high ion transport and mechanical integrity. Often, high ionic conductivity values are achieved by utilizing polymers with low glass-transition temperatures and low degrees of crystallization, at the expense of mechanical durability. Poly(ethylene oxide) (PEO) has been one of the most thoroughly investigated polymer electrolytes because it bears cation-solvating ether groups and a flexible backbone for facile ion mobility.[1−3] However, its crystallinity and limited chemical stability are major limitations for realistic applications. To minimize crystallization, researchers have used small molecule plasticizers with PEO in lithium-ion batteries; however, these plasticizers are typically highly flammable and result in a more liquidlike electrolyte system, both of which lead to serious hazards if a device were to be breached. For applications such as fuel cell or flow cell membranes in which the electrolyte is often hydrated, the chemical stability of PEO becomes a greater issue.

To address the above issues, Allcock and co-workers have designed a hybrid organic−inorganic polymer, poly[bis(methoxyethoxyethoxy) phosphazene] (MEEP),[4,5] by functionalizing a polyphosphazene backbone with ethylene oxide chains (Scheme 1). The phosphazene backbone has numerous advantages over that of PEO, such as higher chain flexibility and thermo-oxidative stability. The properties of the polymer can be tuned through substitution reactions on the highly versatile parent polymer, poly(dichloro phosphazene). Furthermore, the dry (0% RH) ionic conductivity of MEEP is more than 2 orders of magnitude higher than that of PEO in non-plasticized systems (1×10^{-3} vs 1×10^{-5} S cm^{-1}),[6] an essential property for solid polymer electrolytes to reduce electrical resistance. Because of the highly flexible nature of both its backbone and side chains, MEEP lacks mechanical integrity. Moreover, MEEP is water-soluble, which makes it impractical for use in highly hydrated environments such as fuel cells. A way to address this issue is by exposing the polymer to γ[7] or UV[8] radiation, which results in a cross-linked MEEP network.

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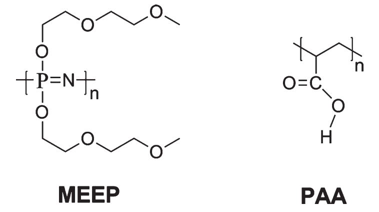
Scheme 1. Chemical Structures of Poly[bis-(methoxyethoxyethoxy) phosphazene] (MEEP) and Poly (acrylic acid) (PAA)



Due to the stability of the phosphazene backbone, the cross-link occurs only on the side chain and increases the mechanical stability of MEEP. However, γ radiation is not easily accessible and the UV radiation method involves sensitizers that need to be removed upon cross-linking process. A better strategy to stabilize MEEP films, as well as providing mechanical robustness, is much needed.

Layer-by-layer (LbL) assembly is a versatile thin-film fabrication method which consists of the repeated, sequential immersion of a substrate into aqueous solutions of complementary functionalized materials.[9,10] The LbL method provides stable polymer blends and allows for composition, morphology, and property control through the adjustment of assembly parameters such as pH. The tunability, environmentally benign aqueous processing, and nanoscale blending of materials which are otherwise impossible to construct make this system a significant competitor to create novel solid state electrolytes for various energy applications.[11,12] In addition to commonly used electrostatic interactions for LbL film growth, secondary interactions such as hydrogen bonding have proven effective in incorporating neutral, water-soluble polymers into LbL films.[13,14]

In this work, we introduce the LbL assembly method to create homogeneous blends of MEEP, a hydrogen-bonding acceptor, and poly(acrylic acid) (PAA), a hydrogen-bonding donor, with controlled film growth, high ionic conductivity, and excellent hydrolytic stability. To the best of our knowledge, this is the first incorporation of a phosphazene based polymer into a multilayer structured thin film. These films are promising candidates as truly solid-state polymer electrolytes in electrochemical devices such as fuel cells and batteries. We show the relative humidity dependence of conductivity as well as the water transport characteristics of these unique blends. The LbL assembly process allows fine-tuning of the desired properties by simple adjustments to the assembly conditions. We also show the isolation of MEEP/PAA LbL assembled films from the substrate, which allows bulk characterization of free-standing films.

Experimental Section

Chemicals. MEEP ($M_w \approx 264$K determined by aqueous GPC) was synthesized according to previously published procedures.[5] Poly(acrylic acid) (PAA) (250 000 M_w, Polysciences) was used as received. Both MEEP and PAA were weighed and diluted to the desired concentration using Millipore Milli-Q deionized water (18.2 MΩ cm filtered through a 0.22 μm membrane).

LbL Assembly Methods. Assembly of the LbL films was completed by using a programmable ZEISS DS50 slide stainer. To construct LbL films, we first immersed substrates (glass, patterned ITO, polystyrene, or ZnSe) in aqueous MEEP solution (10 mM calculated on the basis of the repeat unit) for 20 min, followed by three 2 min rinses in water, and then in PAA (10 mM) for 20 min followed by three 2 min rinses in water. The pH of both polymer solutions and rinse baths were identical and adjusted prior to assembly by adding 1 M HCl solution dropwise. The dipping process was repeated numerous times to produce a film of desired thickness. The free-standing films were peeled from polystyrene substrates.

Ionic Conductivity. For in-plane conductivity measurements, LbL films deposited on microscope slides (VWR) were placed in a conductivity cell with platinum wires as the electrodes and tested in a humidity- and temperature-controlled chamber (Electro-tech Systems, Inc.). Relative humidity was controlled down to 10% RH, and dry (0%RH) measurements were performed in a nitrogen-filled glovebox with < 1 ppm water content. Through-plane conductivity measurements were performed by depositing LbL films on patterned ITO substrates (Delta Technologies), and gold electrodes were thermally evaporated (~100 nm) on the multilayers. The active area was 6 mm^2. Ionic conductivity values were determined by electrochemical impedance spectroscopy with a Solartron 1260 impedance analyzer by sweeping the frequency from 1 MHz down to 1 Hz.

Bulk Characterization. Thickness measurements were made by scoring the films with a razor blade and measuring the step change in height between the film and substrate with a Tencor P16 profilometer (1 mg applied force). FTIR spectra were obtained from thin films deposited on CVD grown, IR transparent ZnSe substrates. Free standing films were analyzed with a TA Instruments Q1000 differential scanning calorimeter. Films were cut to yield samples of ~2−3 mg, and all temperature ramp rates were 10 °C/min. Samples were equilibrated at −90 °C, heated to 150 °C, and cooled back to −90 °C. At least two thermal cycles were repeated for each film. The glass transition temperature was calculated from the inflection point of the sigmoidal portion of the heating curve.

Water Uptake Behavior. A Masscal G1 (quartz crystal microbalance/heat conduction calorimeter) was used for analysis of water uptake and transport properties of LbL films. LbL films were deposited onto 1 in. diameter quartz crystals (5 MHz frequency) with gold electrodes from Masscal Scientific Corp. For all experiments, the temperature of the G1 sample chamber was maintained at 30 °C. Two mass flow controllers supplied nitrogen streams to the G1 sample chamber. One nitrogen stream was kept dry, whereas the other was humidified to 100% relative humidity (RH). Varying the ratio of these to streams through the G1 software allowed fine control of the sample chamber RH. The total gas flow rate was 50 cm^3(STP)/min for all experiments. The RH of the G1 samples chamber was monitored using a Sable Systems R300 water vapor analyzer. Films were exposed to a dry nitrogen purge to determine the amount of film formed on the crystal by comparison with the

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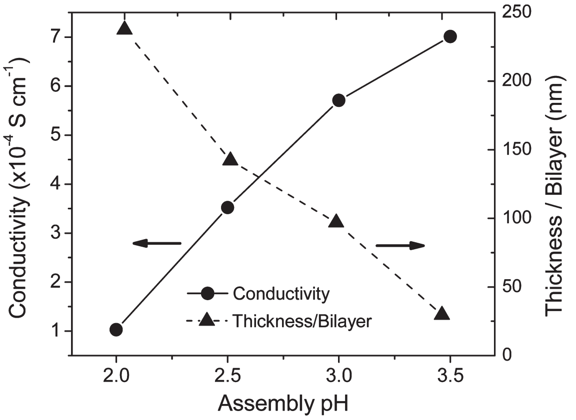

Figure 1. Assembly pH dependence of ionic conductivity at 100% RH (circles) and bilayer thickness (triangles).

frequency of the blank crystal before coating. After the films were fully dried, a step change in RH of the sample chamber from 0 to 100% was introduced. The frequency change of the coated crystal caused by water uptake into the films was monitored in real-time. Mass uptake is directly proportional to the frequency change, as given by the Sauerbrey equation.[15] Dried films were also exposed to incremental step changes in relative humidity (~15% per step) up to 100% RH to yield a sorption isotherm. To ensure that condensation in the sample chamber did not occur, we verified the frequency change of a blank QCM crystal to be negligible when exposed to a full range of relative humidity conditions.

Results and Discussion

Multilayer Assembly and Ionic Conductivity. The LbL assembly of the polymers MEEP and PAA is performed by utilizing the hydrogen bonding interaction between the COOH groups of PAA and ethylene oxide side chains of MEEP (Scheme 1). The ionization degree of PAA is controlled during thin-film assembly by systematically varying the assembly pH from 3.50 down to 2.00 for all polymer and rinse solutions. In all cases, the MEEP/PAA films grow linearly up to as many as 75 bilayers across the entire assembly pH range (not shown here, see Figure S1 in the Supporting Information). This linearity has also been observed with PEO/PAA multilayers[16] and with other hydrogen-bonded systems.[14] Figure 1 shows the bilayer thickness of MEEP/PAA films as a function of assembly pH. The maximum bilayer thickness is greater than 200 nm/bilayer at the lowest assembly pH values, and is significantly reduced down to 50 nm/bilayer at the assembly pH 3.5. Large bilayer pair thicknesses are commonly observed in hydrogen-bonded multilayer thin films because of the looser network formed between weakly associative groups; furthermore, the potential for dimerization between PAA side groups increases the chance of greater amounts of film deposited with each cycle.

Because the MEEP/PAA system relies on hydrogen bonding to build the film, the degree of ionization in PAA greatly affects the bond attractions and like-charge repulsion between the polymer chains. At low pH, the ethylene oxide side chains of MEEP are paired with the carboxylic acid groups of PAA to create enough hydrogen bond cross-links between polymer layers to stabilize the resulting film. By changing the pH of the assembly baths, this cross-linking attraction can be varied, thus changing the stability of the film and allowing tuning of the final thickness. At higher pH values, the adsorbed PAA layer becomes increasingly thinner, as hydrogen bonding between PAA side chains (acid−acid dimerization) is decreased. The LbL film growth is suppressed at assembly pH values above pH 3.5 because of the more highly ionized PAA, which introduces large electrostatic repulsion, and limits the hydrogen-bonding interaction between MEEP and PAA.

Figure 1 also shows the tunability of the ionic conductivity of MEEP/PAA films by varying the assembly pH. In-plane conductivity was measured at fully humidified conditions at 25 °C using platinum wires one centimeter apart on the surface of a 50 bilayer MEEP/PAA film. By increasing the assembly pH, the bulk proton conductivity increases from 1×10^{-4} S cm^{-1} at assembly pH 2.0 up to 7×10^{-4} S cm^{-1} at assembly pH = 3.5. This increase could be partially attributed to the higher ionization of PAA (more anionic sites for ion transport); however, the effect of ionization on proton conductivity is small as verified by the values obtained from pristine PAA films (spun coat from aqueous solutions, see Table S1 in the Supporting Information), and cannot account for the 7-fold increase observed for the LbL assembled films. Therefore, the observed enhancement of conductivity is due to the changes in the effective hydrogen bond network and/or composition in the films built at higher pH values, and resulting differences in ion and water transport. We hypothesize that the average number of transient hydrogen bonds per unit volume should undergo an overall decrease with these small increases in pH. The observed trend is consistent with the conductivity trend observed for the previously assembled LbL PEO/PAA systems, with MEEP/PAA values consistently being higher than the PEO/PAA values obtained at 100% RH.[16] The LbL films assembled at high pH values yield higher values because of a more favorable, loose polymer network for ion and water transport, which would facilitate ion conduction via Grotthuss and carrier mechanisms.

To determine the impact of ambient humidity on the ionic conductivity, 25 bilayers of MEEP/PAA films are assembled on patterned ITO/Glass substrates followed by thermal gold evaporation on top of the film to yield an 8-cell ITO | MEEP/PAA | Au configuration. Through-plane conductivity measurements are then carried out by connecting the ITO and gold ends to the impedance analyzer. Figure 2 shows the ionic conductivity values of MEEP/PAA multilayers assembled at pH 2.5 (circles) and pH = 3.0 (triangles) as the %RH is decreased from 60% down to 0%. It is important to note that the difference in ionic conductivity between these two films becomes systematically less pronounced at drier conditions. For example, at %RH values less than 20%, the

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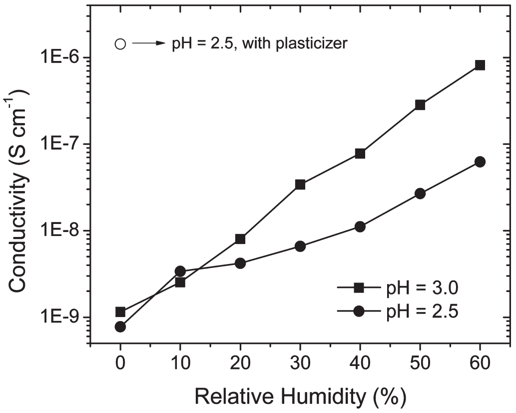

Figure 2. Relative humidity dependence of ionic conductivity of MEEP/PAA films assembled at pH 2.5 and pH 3.0. Also shown is the conductivity enhancement of a dry film upon addition of a small molecule plasticizer (propylene carbonate).

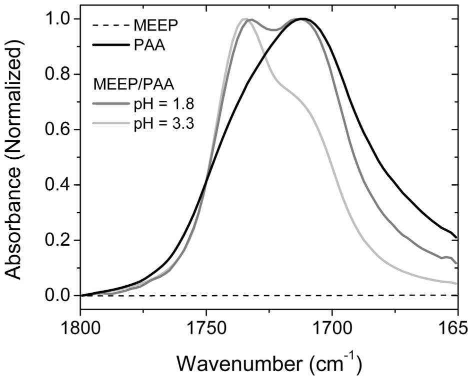

Figure 3. FTIR spectra of the carboxylic acid region of MEEP/PAA multilayers assembled at pH 1.8 and 3.3 on IR-transparent ZnSe substrates. The relative intensity of peak at 1710 cm^{-1} appears to decrease as assembly pH increases.

ionic conductivities converge in the dry state to the value of 10^{-9} S cm^{-1}. We attribute this behavior to the crucial role of water in ion transport of hydrated systems and the impact of its relative uptake in the films on the mobility of the ionic species, a phenomenon extensively discussed in the following section. As the films approach the dry state, the differences in hydrogen-bond networks become irrelevant; the rate determining factor for these systems in the dry state is the inherent mobility of the ethylene oxide chain segments in the matrix. The dry conductivity values (0% RH) obtained from LbL assembled MEEP/PAA films can be compared to those reported for PEO/PAA films examined under the same conditions, for which the dry state conductivity was 3×10^{-10} S cm^{-1}.[17]

Finally, to observe the effect of a small molecule plasticizer in a water-free environment, a drop of propylene carbonate was added onto a dry MEEP/PAA film (assembly pH 2.5) placed in a glovebox. The ionic conductivity rapidly increased by 3 orders of magnitude to reach 1.43×10^{-6} S cm^{-1} (Figure 2, empty circle) because of the more favorable liquid-like medium for ion transport. However, it is important to note that this value is still much lower than that of a film in fully humidified conditions, indicating the crucial impact of water on proton transport through hydrated hydronium ions.[18]

FTIR Analysis. To better understand the type and extent of hydrogen bonding versus acid ionization at different assembly pH values, we have assembled two MEEP/PAA multilayer films on IR transparent ZnSe substrates at low pH (1.80) and at high pH (3.30), as well as pristine films of MEEP and PAA. Figure 3 shows the carboxylic acid region of the FTIR spectra, where the hydrogen-bonding characteristics of LbL films are investigated. As expected, pristine MEEP does not have any absorption in this region. Pristine PAA, on the other hand, has a strong peak centered at 1711 cm^{-1}, indicative of intramolecular hydrogen bonding of COOH groups via acid−acid dimerization.[17,19] For the LbL films of MEEP/PAA, another peak centered at 1740 cm^{-1} is observed in addition to the peak at 1711 cm^{-1}, confirming the partial disruption of PAA's acid-dimerization and the presence of intermolecular hydrogen bonding between the acidic groups of PAA and the ether lone pair electrons of MEEP. The relative intensity of the 1711 cm^{-1} peak decreases as assembly pH increases from 1.80 to 3.30, suggesting a decrease in the extent of COOH groups participating in intramolecular hydrogen bonding. This is primarily attributed to the higher degree of ionization of PAA, because the equilibrium between pH dependent groups ($\mathrm{COOH} \Leftrightarrow \mathrm{COO^-} + \mathrm{H^+}$) favors the ionized groups at higher assembly pH values. This decreases the number of COOH neighbors available for self-dimerization, and increases hydrogen bond interactions of remaining COOH groups with MEEP. Also of interest is the $\mathrm{COO^-}$ region (~1550 cm^{-1}), which is indicative of changes occurring in the ionization of the carboxylic acid groups in PAA. Differences between the spectra of the PAA and MEEP/PAA films are minimal and difficult to observe in this region, because of the weakness of the ionized acid peak at low pH, and the fact that the degree of ionization varies by a fairly small fraction (approximately 5% ionization at pH 3.5, see Figure S2 in the Supporting Information).

Bulk Characterization of Free-Standing Films. To analyze the thermal and mechanical characteristics, we deposited MEEP/PAA films on low-surface-energy polystyrene substrates and gently peeled them off with tweezers as previously described by our group.[20] The resulting films appear amber-colored and transparent, indicating a homogeneous blend with minimal surface roughness. Figure 4 shows a DSC thermogram for a peeled-off MEEP/PAA film assembled at pH 2.5, along with spuncast films of neat PAA and MEEP (inset) from water. Multiple heating/cooling cycles are performed on each sample to remove bound water from the film and ensure

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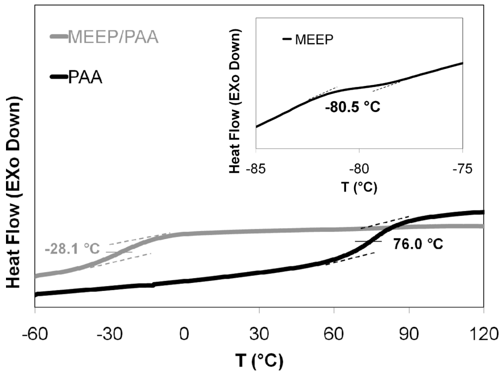

Figure 4. DSC thermogram for a free-standing MEEP/PAA film assembled at pH 2.5, along with neat PAA and MEEP (inset). All MEEP/PAA LbL films displayed one T_g indicative of a homogeneous blend.

accurate T_g values are observed. The measured T_g values of pristine PAA and MEEP are found to be 76.0 °C and −80.5 °C, respectively.

All MEEP/PAA LbL films exhibit a single T_g between that of neat MEEP and PAA, which is indicative of a truly homogeneous blended film, and is consistent with earlier reports of DSC analysis on PEO/PAA LbL films.[17] Interestingly, the observed T_g of MEEP/PAA LbL systems show little variation when the pH of the assembly solutions was varied from 1.8 to 2.5. Both MEEP/PAA samples assembled at pH values 1.8 and 2.5 exhibited a T_g of -28.0 ± 2.0 °C (see Figure S3 in the Supporting Information). By use of the Fox equation, a T_g of −28.0 °C corresponds to a composition of 52 wt % MEEP or 21 mol % MEEP.[21] The lack of variation between assembly pH and T_g of the resulting MEEP/PAA blend differs from a similar study on PEO/PAA LbL films, where the T_g of PEO/PAA films varied from ~60 °C when assembled below pH 2.0 to ~25 °C at assembly pH values ≥3.0.[17] The variation in T_g of PEO/PAA films at different assembly pH values were due to different film compositions caused by the degree of ionization of PAA and its ability to form intramolecular versus intermolecular hydrogen bonds, thus leading to decreased adsorption of PAA relative to PEO at higher pH. For the MEEP systems, the changes in intra- versus intermolecular hydrogen bonding also seem to be responsible for changes in conductivity; however, this is not because of significant changes in relative MEEP content based on our DSC results. This difference between PEO and MEEP may be due in part to structural differences; the ethylene oxide groups attached as side chains to MEEP are very short, and would not undergo significant conformational changes to yield dense, loopy arrangements of PEO during the adsorption cycle. In this case, less PAA adsorbed in the first adsorption cycle of the LbL assembly leads to lowered MEEP adsorption in the second. It is also noted that the relative increase in ionic conductivity with pH is also more moderate than observed with PEO/PAA, indicative of the smaller differences in the composition and structure of the films with pH. The primary reason for the observed increases in conductivity is therefore likely to be due to the decrease in the number of hydrogen bonds acting as effective physical cross-links in the network, yielding a “looser” network and increased ion mobility.

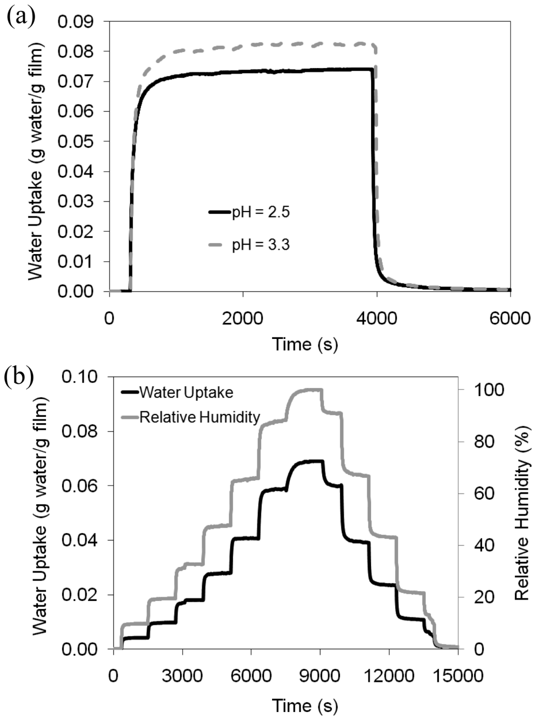

Figure 5. (a) Water vapor uptake and desorption as a function of time for MEEP/PAA LbL films assembled at pH 2.5 and pH 3.3 at 30 °C. A step change in the sample chamber relative humidity from 0 to 100% occurs at t = 300 s, whereas a step change from 100 to 0% occurs at t = 3900 s. (b) Water vapor sorption isotherm at 30 °C for a MEEP/PAA film assembled at pH 2.5.

A major concern for polymer electrolytes with low glass transition temperatures is their gumlike nature, which prohibits them from qualifying as truly solid-state electrolytes. To demonstrate the mechanical advantage of LbL assembled systems compared to pristine films of MEEP, we have tested the indentation response of MEEP/PAA films on glass as well as the pristine MEEP and PAA films for comparison. To minimize the substrate interference, we have assured that the thickness of the polymer film is at least ten times greater than that of the indentation distance. Preliminary results show that a typical MEEP/PAA film (~6 μm) yields an elastic modulus value of 690 ± 57 MPa at ambient conditions, over an order of magnitude higher than a pristine MEEP film (56 ± 5 MPa). We are currently further investigating these differences in mechanical properties by measuring the tensile modulus and strength of free-standing LbL films.

Water Transport. We utilized a recently developed approach to determine the water uptake and transport of MEEP/PAA LbL films with a quartz crystal microbalance (QCM).[22,23] This QCM method has been used to determine the permeability of various gases through polymer thin films, coatings and powders. QCMs measure the change in mass per unit area of a sample by

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Table 1. Diffusion Coefficients, Solubilities, And Permeabilites of Water in MEEP/PAA Films Assembled at pH 2.5 and pH 3.3, Along with Neat MEEP, PAA, and LbL Assembled PEO/PAA films (T = 30°C)

polymer	H_2O uptake (g H_2O/g film)	D (cm^2/s)	S (cm^3 H_2O/cm^3 film cm Hg)	P (Barrer)[a]
MEEP	0.027	1.31×10^{-13}	17.5	10.0
PAA	0.111	3.72×10^{-13}	70.6	0.03
MEEP/PAA (pH = 2.5)	0.066	1.72×10^{-11}	41.7	7.17
MEEP/PAA (pH = 3.3)	0.081	4.84×10^{-10}	52.8	255
PEO/PAA (pH = 2.5)[23]	0.090[b]	1.3×10^{-11}	28.1	36

[a] Barrer = 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$. [b] 70% RH.

measuring the variation in frequency of a quartz resonator due to absorption and diffusion of the permeating species, in this case water, in the films. Permeability is defined as

$$P = \frac{J \cdot l}{\Delta p} = SD \qquad (1)$$

where J, l, and Δp are the flux, film thickness, and partial pressure difference across the film, respectively. Analyzing water permeation through a film involves both an equilibrium thermodynamic property, solubility (S), and a kinetic property, the diffusion coefficient (D). Both parameters, S and D, can be obtained from mass uptake experiments using the QCM. The ability to control the relative humidity of the QCM sample chamber allows the study of the relationship between water transport in MEEP/PAA films and the dependence of humidity on ionic conductivity.

To investigate the water uptake characteristics, MEEP/PAA films (5−10 bilayers, 0.5−2.1 μm) were assembled on quartz crystals and equilibrated at 30 °C under a dry nitrogen atmosphere until there is no longer a loss in moisture from the film, as determined by QCM. The films were then exposed to a step change to 100%RH while monitoring the changes in oscillation frequency. Figure 5a shows the water uptake of two MEEP/PAA films upon exposure to a fully humidified environment followed by a step change back to dry nitrogen and the corresponding water loss. Water uptake as a function of incremental step changes in humidity is shown in Figure 5b. The kinetic data from the single-step experiment allows for the calculation of the diffusion coefficient through use of a simplified model of one-dimensional diffusion of water into a slab, which has been previously described.[24,25]

The linear sorption isotherm from the multistep experiment yields the films' solubility. The permeability of the film is simply calculated from eq 1 as the product of solubility and the diffusion coefficient. It is important to note that while deviations from the Sauerbrey equation can exist for highly hydrated films, these deviations are minimal for thin films studied at the QCM's fundamental frequency (5 MHz).

The solubility values, diffusion coefficients, and permeability values of water in MEEP/PAA LbL films, along with neat, spun-cast MEEP and PAA films, are given in Table 1. PAA has a water uptake value of 0.111 g of H_2O/g of PAA, which corresponds to 0.32 water molecules per PAA repeat unit, while MEEP uptakes 0.027 g of H_2O/g of MEEP or 0.38 water molecules per MEEP repeat unit. The water transport properties of PAA are in agreement with the literature;[23,26] however, the water uptake of MEEP is lower than previously reported values and may be attributed to differences in film processing. The water uptake of the MEEP/PAA LbL films is between that of MEEP and PAA, which is expected because the LbL films are homogeneous blends of the two polymers. MEEP/PAA films assembled at pH 3.3 absorb 22.7% more water on a gravimetric basis than pH 2.5 films, most likely due the increased charge on the incorporated PAA at pH 3.3. Overall, in the case of MEEP/PAA LbL systems, films assembled at higher pH values have larger diffusion coefficients and solubilities. For example, MEEP/PAA films assembled at pH 3.3 have diffusion coefficients approximately 30 times larger and solubility values about 25% larger than films assembled at pH 2.5; thus, films assembled at pH 3.3 have water permeability values 35 times higher than films assembled at pH 2.5. The increase in water transport properties at higher pH values is consistent with the increase in ionic conductivity values of MEEP/PAA films at higher pH values, especially under humidified conditions.[27,28] Regardless of the mechanism of ion transport through a polymer electrolyte, an increase in the water transport properties will result in higher ionic conductivities when the membrane is humidified.[29] Thus, the increase in ionic conductivity values of MEEP/PAA films assembled at higher pH values is attributed to better water transport, which is improved by a looser hydrogen-bond cross-linked network and the increased presence of some ionized PAA groups.

The water transport in MEEP/PAA LbL films and previously assembled PEO/PAA LbL films (both assembled at pH 2.5) compares quite closely,[23] with MEEP/PAA having a slightly higher permeability value, indicating more favorable water transport characteristics. While the functional groups of MEEP and PEO are the same, the water transport properties might also be influenced by the nature of the hydrogen bonded network

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formed in each case by LbL assembly. MEEP, which presents ethylene oxide groups as side chains, may form a relatively stronger LbL hydrogen-bonded network as compared to the ethylene oxide groups contained in the backbone of PEO.

Summary and Perspective

In conclusion, we have demonstrated the layer-by-layer assembly of MEEP/PAA thin films by utilizing the hydrogen bonding between these two polymers. The ionic conductivity of these films is tuned by changing the assembly pH of initial polymer solutions and thereby controlling the hydrogen bonding characteristics. The growth rate of these films can be tuned over the range of < 50 nm/bilayer up to > 200 nm/bilayer, which is quite large for an LbL assembled system. At fully humidified conditions, the ionic conductivity of MEEP/PAA is over 1 order of magnitude higher than previously studied hydrogen bonded LbL systems ($\sim 7 \times 10^{-4}$ S cm^{-1} for MEEP/PAA versus 6×10^{-5} S cm^{-1} for PEO/PAA). This improvement in conductivity is attributed to both MEEP's superior ion transport properties and the high water transport of these blends. Using the LbL technique to tune the properties of the film is promising to obtain stable and high performance solid state electrolytes for various electrochemical energy applications. At fully dry conditions, ionic conductivity values of these films show little variation with respect to assembly conditions possibly due to the films' similar composition, as suggested by the DSC thermograms of free-standing films. Indentation experiments show that the elastic modulus of MEEP/PAA is more than an order of magnitude higher than neat MEEP, which is critical for the applications of solid polymer electrolyte systems. Finally, the water transport characteristics are quantified by gradually changing the environment's relative humidity and monitoring the weight gain/loss of thin films through a QCM technique. The kinetic and thermodynamic data obtained allows for a full characterization of water solubilities, diffusion coefficients, and permeability. MEEP/PAA films assembled at higher pH values have enhanced water uptake and transport properties, which play a key role in increasing ion transport within the films at humidified conditions.

Acknowledgment. This work was supported by NSF and the MIT Energy Initiative (MITEI). We thank Ilke Kalcioglu of the Van Vliet group in the Department of Materials Science and Engineering for her assistance with indentation measurements. We also thank Allan Smith of MassCal Corporation for all of his help understanding the QCM technique.

Supporting Information Available: Growth curves for LbL assembled MEEP/PAA films. Ionic conductivity of pristine MEEP and PAA films. FTIR spectra (carboxylic acid region) of PAA and MEEP/PAA films. DSC curves of LbL assembled MEEP/PAA films (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.