

Molecular Composite Coatings on Nafion Using Layer-by-Layer Self-Assembly

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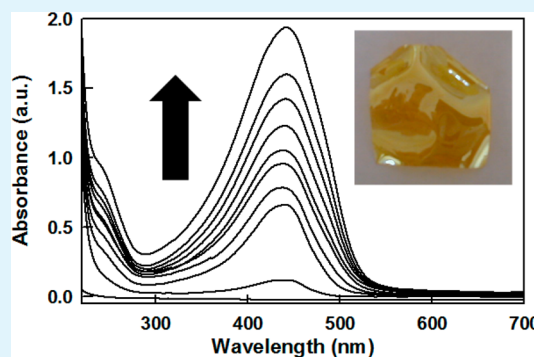
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S Supporting Information

ABSTRACT: Controlled growth of nanometer-scale multilayered coatings of negatively charged sulfonated poly(benzobisimidazole) (SPBI), complexed with positively charged poly(2-vinylpyridine) (P2VP) on quartz, and Nafion membrane as substrates has been explored. Both polymers, SPBI and P2VP, possess a net charge in methanol as a result of the dissolution of SPBI by complexation with triethylamine (TEA) and the protonation of P2VP with HCl, respectively, and thereby can form a multilayered molecular composite of alternating anionic SPBI and cationic P2VP via an electrostatic layer-by-layer (LbL) self-assembly. UV-vis absorption spectrophotometry was used to monitor the buildup and growth rate of such SPBI/P2VP multilayer films. Atomic force microscopy (AFM) was used to determine the roughness and thickness of the resulting SPBI/P2VP multilayers. As a result, it was found that a steady-state linear growth regime for the LbL self-assembled SPBI/P2VP multilayer films and coatings onto quartz and Nafion membranes was observed after completion of the first few deposition cycles, indicating the successful formation of the SPBI/P2VP multilayered assembly in methanol solutions. In addition, the SPBI/P2VP multilayer films in the perpendicular direction (flat view) demonstrated isotropic orientation distribution on the Nafion membrane, while the SPBI/P2VP multilayer films examined by X-ray scattering in the parallel direction (edge view) revealed anisotropic orientation, the combined observations indicating confinement of SPBI rods to the plane of the coating. We further found that the SPBI/P2VP multilayer coated Nafion possesses good thermal stability, as indicated by isothermal gravimetric analysis at 310 °C, and it was further observed that SPBI/P2VP multilayer coatings using the LbL self-assembly technique on Nafion membrane significantly increased the membrane stiffness, despite the small coating thickness employed.

KEYWORDS: layer-by-layer, multilayers, adsorption, molecular composite, complexation, membranes



INTRODUCTION

In recent years, significant attention has been given to the microfabrication and micropatterning techniques of nanostructured materials using the layer-by-layer (LbL) self-assembly technique. The LbL assembly technique is a relatively straightforward and versatile technique for the preparation of functionalized polyelectrolyte multilayer films with well-defined structure and thickness.^{1–5} In LbL processing, substrates are alternately exposed to dilute aqueous solutions containing oppositely charged (cationic or anionic) polyelectrolytes. It is commonly accepted that the electrostatic interaction between oppositely charged polyelectrolytes is the main driving force for the multilayer assembly as well as the main factor for its stability,^{2,5} indicating the formation of a physically cross-linked network structure. The charge density of polyelectrolytes and

the ionic strength of the surrounding medium are reported to be of main importance in controlling the structure of the multilayers.⁶ Thus, the physicochemical properties (stability,⁷ permeability,⁸ and stiffness⁹) as well as porosity and roughness of the multilayers can be varied through composition, salt addition, and pH adjustment.^{10–16} While electrostatic LbL self-assembly techniques have been well established for polyelectrolytes in aqueous solution, comparatively little attention has been paid to the polymers soluble in organic solvents. Here, we attempt to investigate the application of the LbL technique to nonaqueous polymer solutions, motivated by a technical

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motivation to do so for LbL adsorption on a water-swellaible polymer. The long-term goal driving this work is to apply the developed method to the processing of proton exchange membranes (PEMs) of fuel cell devices with balancing of such properties as thermal stability, durability, proton conductivity, and methanol crossover, noting that limited attention has yet been given to such an approach.¹⁶

Perfluorosulfonated ionomer (PFSI) membranes were first developed for applications as separators in chloroalkali electrolyzers,^{17–19} and the first PFSI membrane was commercialized by DuPont de Nemours under the trade name Nafion, this polymer consisting of a fluorocarbon backbone with long pendant perfluorosulfonated ionic pendant groups. The exceptional properties of these membranes derive from their chemical, mechanical, and thermal stabilities afforded by the perfluorinated backbone as well as the ion-exchange properties provided by the highly acidic pendant sulfonated groups.

On the other hand, in order to develop high performance portable direct methanol fuel cells, dramatic improvements to such proton exchange membranes (PEMs) are needed beyond the state-of-the-art Nafion materials.^{20–29} In particular, ion-exchange membranes for direct methanol PEM fuel cells must possess a combination of properties, including high proton conductivity for $T > 100$ °C, low methanol permeability (“crossover”), and thermal/mechanical/chemical stability. To improve the elevated-temperature performance of PEMs, it is not surprising that polymer scientists have adopted the two most common approaches used for any “high” temperature application of polymers; namely, (i) the use of heterocyclic repeating units in the polymer backbone and (ii) the intimate incorporation of inorganic phases via sol–gel chemistry. Specifically, because of their outstanding physical and mechanical properties, rigid-rod polymers are attractive materials for use in high-performance structural applications, including aircraft components, fire protection garments, and as constituents of both traditional (e.g., fiber-reinforced) and molecular composites.³⁰ In addition to its advantageous mechanical characteristics, past attempts to use heterocyclic or rigid-rod polymers for ionic conductivity at high temperatures have included: (i) lithium-doped sulfonated Kevlar,²⁷ (ii) sodium-doped sulfonated poly(benzobisthiazole)s,²⁸ (iii) acid-doped polybenzimidazole,²⁹ and (iv) lithium propanesulfonate-derivatized sulfonated poly(*p*-phenylenebenzobisimidazole).³¹

In previous studies in our group, we have successfully prepared sulfonated poly(*p*-phenylenebenzobisimidazole)/poly(2-vinylpyridine) (SPBI/P2VP) molecular composites in which the rigid rod-like SPBI polymers act as reinforcing elements that can be dispersed within a flexible coil matrix at the molecular scale.^{32,33} In this case, to achieve homogeneous molecular dispersion without the self-aggregation of the rigid rod-like SPBI polymers, it has been necessary to introduce specific interactions between the rigid-rod reinforcement and the matrix, such as hydrogen bonding and ion–ion and ion–dipole interactions. Introduction of such interaction is a way to improve the miscibility of the molecular composites through favorable mixing enthalpy. This concept of ionic interaction between negatively charged SPBI and positively charged P2VP in methanol may be also applied to the LbL technique involving common polyelectrolytes in aqueous media. The most interesting reports have been based on the work^{30,31} on a variety of sulfonated rigid-rod polymers such as SPBI and their derivatives whose synthesis was developed at Air Force

Research Lab (AFRL). These polymers were found to possess high ionic (including proton) conductivity that was quite anisotropic, with higher values in the plane of the film than across the film thickness. This was proven to be connected with the distribution of rod orientation in the films which were also quite planar. SPBI-P2VP LbL-coated Nafion membranes can be expected to have reduced methanol crossover for DMFC fuel cells due to the physical (ionic) cross-links inherent to the SPBI-P2VP molecular composite system. Enhanced barrier properties in terms of reduced methanol permeability have been described in sulfonated poly(ether ketone ketone) (SPEKK) systems with ionic cross-links³⁴ as well as in acid–base polymer blends involving SPEEK–poly(vinylpyrrolidone).³⁵ An added advantage of the incorporation of the SPBI system is due to the unique hydration (moisture retention) capability of the benzimidazole system³⁶ that can potentially enhance the fuel cell performance of Nafion at temperatures >80 °C; it is well-known that Nafion shows poor proton conductivity at high temperatures owing to a sudden loss of hydration from the membrane. Thus, with the SPBI-P2VP-modified Nafion system, the potential for both enhanced high temperature proton conductivity and lower methanol permeability can be realized.^{37–39}

In this paper, we are primarily focused on the fabrication of nanometer-dimensioned multilayered coatings of SPBI with P2VP via an LbL self-assembly technique on both quartz and Nafion membrane as substrates and investigate their physicochemical properties, including thermal and mechanical properties by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) and the microstructure by wide-angle X-ray scattering (WAXS).

■ EXPERIMENTAL SECTION

Materials. Sulfonated poly(*p*-phenylenebenzobisimidazole) (SPBI) was supplied by researchers from the U.S. Air Force Research Laboratories, Wright-Patterson Air Force Base, Dayton, OH, following a previously published protocol.⁴⁰ The intrinsic viscosity of SPBI used was 8.9 dL/g in methanesulfonic acid at 30 °C, indicating that the rod-like SPBI is a high molecular weight polymer.³³ Poly(2-vinylpyridine) (P2VP, $M_w = 500$ kDa) was purchased from Specialty Polymer Products and used as received. Nafion 117 perfluorinated membrane films used in this work, manufactured by Dupont, were obtained from Aldrich Chemical Co., Inc. The membrane has a nominal equivalent weight of 1100 and a thickness of ca. 178 μm . Methanol and triethylamine (TEA) were dried over anhydrous MgSO_4 and CaH_2 , respectively, and then distilled prior to use. A low molecular weight poly(ethylenimine) (PEI, CAS No. 025987068) was purchased from Aldrich and used as received. All chemicals of analytical grade were used without further purification. The procedures for producing a fully charged polymer were as follows. Negatively charged SPBI solution was prepared by dissolving SPBI and TEA in methanol at a molar ratio of 1:4 (based on the repeat unit of SPBI), followed by vigorously stirring the mixture and then refluxing under nitrogen in the temperature range of 70–80 °C until the solution was observed to be clear and homogeneous. Positively charged P2VP solution was prepared by treating it with equimolar amounts of hydrochloric acid (based on the repeat unit of P2VP) in methanol. The concentration of both polymer solutions was controlled to be 10^{-3} mol/L based on the repeating unit of each polymer. Quartz (1 in. diameter \times 1/16 in. thick) discs (Chemglass) were used as the substrate for the preparation of multilayered films by charged polymer spin assembly.

Multilayer Buildup on Quartz via Layer-by-Layer Polyelectrolyte Spin Coating Assembly (LbL-SCA). Quartz substrate for the LbL-SCA process was treated with piranha solution (70:30 v/v, $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) (Caution: Piranha solution is extremely corrosive, and special care must be taken during handling of the solution.) at 80 °C

for 1 h, followed by sonication for 15 min. Substrates were then rinsed multiple times in ultrapure deionized water (Milli-Q, $\rho > 18 \text{ M}\Omega\cdot\text{cm}$) and dried. After rinsing, the quartz substrate was further treated in a base solution (1:1:5, $\text{NH}_3/\text{H}_2\text{O}_2/\text{H}_2\text{O}$) at 50°C for 1 h, followed by rinsing in ultrapure deionized water (Milli-Q, $\rho > 18 \text{ M}\Omega\cdot\text{cm}$) for 15 min. Next, to achieve uniform surface charges for the successive depositions of oppositely charged polymers, a layer of low molecular weight poly(ethylenimine) (PEI) (25 wt % solution in methanol) was deposited on the substrate by spin coating at 3000 rpm for a duration of 8 s, followed by rinsing with pure methanol three times under the same spinning conditions to remove the loosely adsorbed PEI and obtain a uniform, positively charged layer on the quartz substrate. For the growth of multilayers using LbL-SCA, the positively charged quartz substrate was spin-coated with negatively charged SPBI solution (10^{-3} M) as polyanion at 3000 rpm for 8 s, followed by rinsing at least twice with pure methanol. Afterward, the negatively charged substrate was spin-coated with the positively charged P2VP solution (10^{-3} M) as polycation at 3000 rpm for 8 s, followed by two rinsing cycles. The SPBI and P2VP adsorption steps were repeated to build multilayers on the quartz substrate until the desired number of bilayer was reached.

Multilayer Coating on Nafion Membrane via Layer-by-Layer Dip-Coating Assembly (LbL-DCA). For effective LbL procedures in methanol, the Nafion membranes were first swollen in fresh methanol for 12 h, achieving an equilibrium swollen state (degree of swelling, $q \sim 0.4 \text{ g/g}$). The rubbery, durable membrane was then used for LbL multilayer buildup as a substrate.⁴¹ The SPBI/P2VP multilayer coatings on Nafion were prepared as follows. Each methanol-swollen Nafion membrane as a substrate was pretreated with a methanol solution of low molecular weight poly(ethylenimine) (PEI) (25 wt % in methanol) to achieve uniform surface charges for the successive depositions of oppositely charged polymers according to the same strategy. The sequential adsorption on Nafion membrane of SPBI (10^{-3} M) and P2VP (10^{-3} M) for 20 min for each step with an intervening rinse step was carried out, followed by a rinsing step with fresh methanol for 2 min in order to remove the weakly adsorbed polymers. By repetition of this process, we could build an LbL multilayer of SPBI/P2VP on both sides of the Nafion membrane.

Methods. UV–Vis Spectroscopy. UV–vis spectra of the multilayer assembly were collected using a PerkinElmer Lambda 6 UV–vis spectrophotometer at a scanning speed of 120 nm/min. A clean quartz disk with the same thickness was used as a reference in the case of the LbL-SCA process, while in the case of the LbL-DCA process using Nafion membrane, the Nafion membrane swollen in methanol was used as a reference.

Thermogravimetric Analysis (TGA). Thermal stabilities of the Nafion membranes before and after LbL multilayer coating were analyzed using a TA Instruments TGA Q500 under a continuous nitrogen purge of 20 mL/min. The samples were heated from room temperature to 800°C with a heating rate of $10^\circ\text{C}/\text{min}$.

Atomic Force Microscopy (AFM). Surface morphology, roughness, and thickness measurements of the multilayers were obtained from the height images collected with contact-mode using model 1520-00 tips atomic force microscopy (AFM) (Topometrix TMX 2000 Scanning Probe Microscope). Measurements were performed on the dried multilayered films formed on the quartz substrate after deposition of the desired number of bilayers of SPBI and P2VP. Several images were recorded from different areas, and representative images are being reported. AFM images were taken as $10 \mu\text{m} \times 10 \mu\text{m}$ scans on the multilayer film on quartz substrate, and roughness calculations were then performed over $5 \mu\text{m} \times 5 \mu\text{m}$ areas of the scan. AFM-based thickness measurements were performed by first etching a portion of the film using the sharp edge of a razor blade that penetrates to the quartz substrate (but no further).⁴² AFM scans of $50 \mu\text{m} \times 50 \mu\text{m}$ were performed on a region including the bare quartz, and the thickness was determined by the average height difference between the areas with and without the multilayered films. The analysis of AFM images was done by the Topometrix imaging software.

Wide-Angle X-ray Scattering (WAXS). Wide-angle X-ray scattering (WAXS) experiments were performed on multilayer films using a Bruker AXS instrument at room temperature equipped with a

chromium X-ray source ($\lambda = 2.291 \text{ \AA}$), a power source delivering 40 mA and 40 kV, and the exposure time was 120 min. The data were gathered and analyzed via a General Area Detector Diffraction System (GADDS) software version 3.317. The scattering patterns were collected on a HiStar area detector with the distance of the sample to detector set to 6.0 cm.

Dynamic Mechanical Analysis (DMA). TA Instruments DMA 2980 was run in tensile mode at an oscillation frequency of 1 Hz, a static force of 10 mN, an oscillation amplitude of $10 \mu\text{m}$, and an automatic tension setting of 110%. Temperature ramps were conducted at $4^\circ\text{C}/\text{min}$ over the range of $35^\circ\text{C} < T < 225^\circ\text{C}$. Sample sizes (length \times width \times thickness) in mm: pure Nafion membrane ($22.03 \times 4.37 \times 0.17$) and LbL Nafion membrane coated with 9 bilayers of SPBI and P2VP ($5.63 \times 0.83 \times 0.16$).

RESULTS AND DISCUSSION

Multilayer Buildup and the Morphologies of SPBI/P2VP on Quartz. We have investigated the capability for building up SPBI/P2VP multilayers on quartz as a substrate and in methanol as the organic medium, taking advantage of the known solubilization of SPBI as its triethylammonium salt in methanol.³³ It is thus interesting to explore the possibility of LbL self-assembly of SPBI and P2VP via an electrostatic interaction in methanol. We note here that the electrostatic force, $F_e = (1/4\pi\epsilon)(q_1q_2/r^2)$, varies inversely with the dielectric constant (for instance, water: $\epsilon_w = 78.54$; methanol: $\epsilon_m = 32.6$) of the medium. Therefore, we expected that the LbL self-assembly technique through an ion–ion interaction in methanol might work well, as long as the polymers used are completely soluble and also have an electric charge for the LbL multilayer deposition. Moreover, it is expected that this method may improve the Nafion membrane (Nafion 117, Dupont) performance, in terms of its thermal and mechanical properties as well as its low methanol crossover required for a high temperature PEMFC, specifically.

The UV–vis absorption spectra from methanol solutions of SPBI and P2VP, as their triethylammonium and hydrochloride salts, respectively, are shown in Figure 1. Insets show their chemical structures. It was observed that SPBI shows a strong absorbance intensity at $\lambda_{\text{max}} = 450 \text{ nm}$ corresponding to a characteristic strong absorption band of the imidazole ring $\pi \rightarrow$

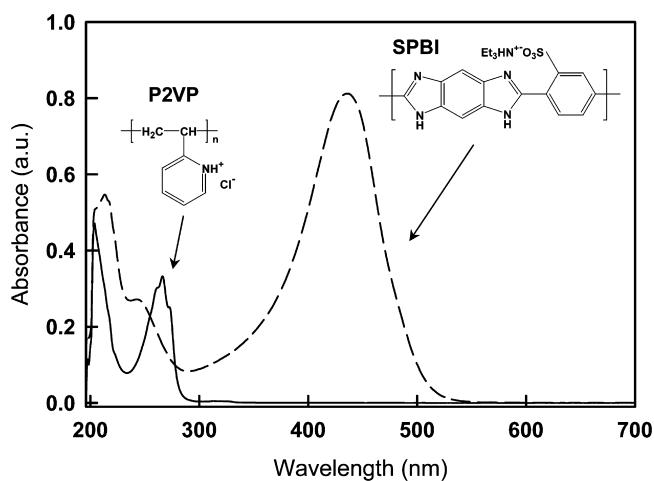


Figure 1. UV–vis absorption spectra of SPBI (as its triethylammonium salt) and P2VP (as its hydrochloride) solutions in methanol. The concentrations of SPBI and P2VP solutions were 0.2×10^{-4} and $1.0 \times 10^{-4} \text{ M}$, respectively, based on the repeating unit of each polymer. Insets show the chemical structures of SPBI and P2VP, as labeled.

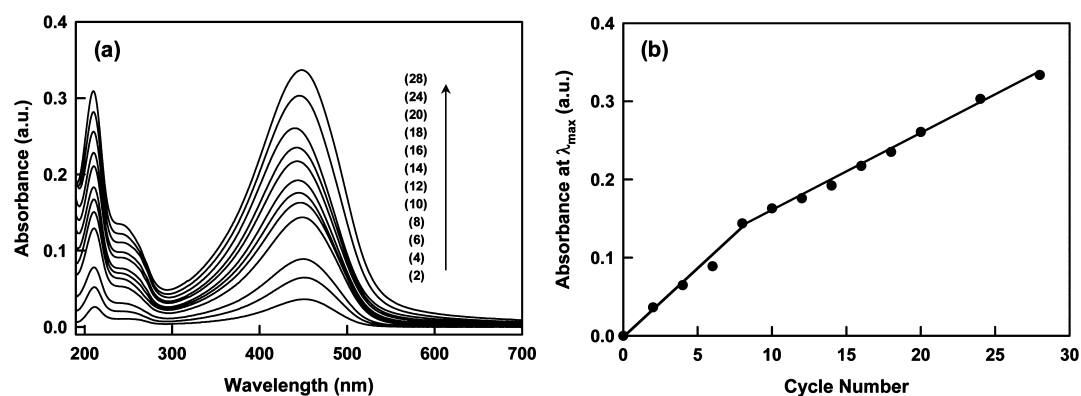


Figure 2. UV-vis absorption spectra versus wavelength for SPBI/P2VP multilayers deposited (on the quartz substrate by spin coating at 3000 rpm for a duration of 8 s) by layer-by-layer spin-coating assembly (LbL-SCA) for different number of bilayers, shown in parentheses (a). (b) Absorbance intensity (at $\lambda_{\max} = 450$) versus the number of bilayers for the same assembly. The spectra were obtained after the number of cycles from 2 to 28 bilayers. The concentration of both polymer solutions was controlled to be 10^{-3} M based on the repeating unit of each polymer.

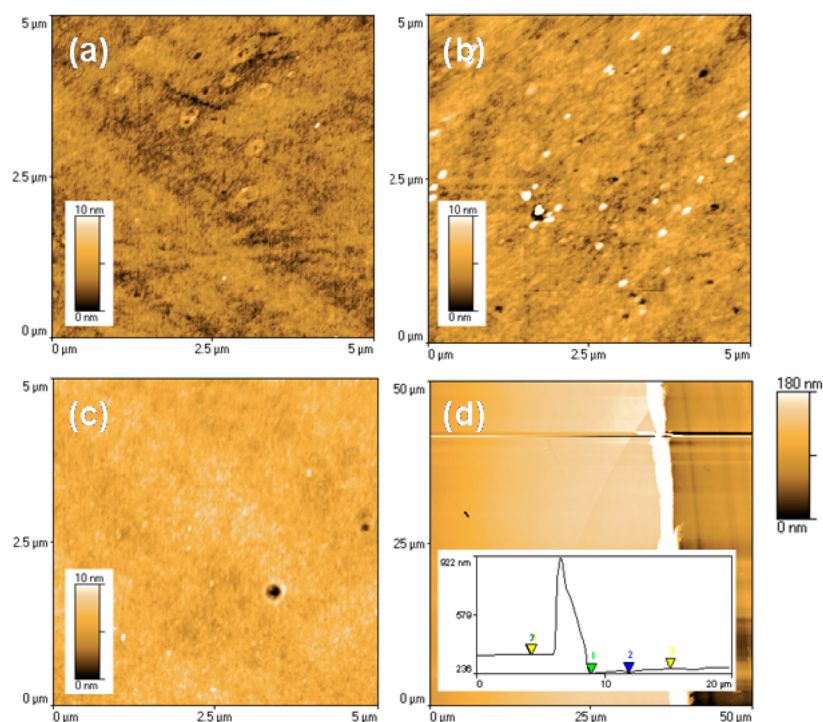


Figure 3. Atomic force microscopy (AFM) images at different numbers of bilayers of SPBI and P2VP on the quartz substrate, (a) 10 bilayers, (b) 20 bilayers, and (c) 28 bilayers at the spinning rate of ca. 3000 rpm; (d) an illustration for measuring the thickness, which is calculated from the height difference between the substrate side and the multilayer film (28 cycles). Inset shows height profile after scratching (28 cycles deposited layer), allowing determination of the average coating thickness.

π^* transition peak while P2VP shows a weak absorption ($\lambda_{\max} = 280$ nm) in the UV-vis spectrum. The multilayer SPBI/P2VP growth by LbL-SCA on quartz substrates was monitored by measuring the absorbance intensity of the distinct SPBI band at 450 nm. Both polymers, SPBI and P2VP, possess a net charge in methanol as a result of the dissolution of SPBI by complexation with TEA and the protonation of P2VP with HCl, respectively, and thereby can form the multilayered molecular composite of alternating anionic SPBI and cationic P2VP via an electrostatic LbL self-assembly. The SPBI/P2VP multilayers were first constructed on a quartz support in order to characterize their LbL growth. Figure 2a shows the representative evolution of the absorbance spectra for the SPBI/P2VP multilayers deposited with an increase in the

number of deposition cycles. The absorbance (the peak amplitude) at 450 nm with respect to cycle number shows a linear growth after completion of eight deposition cycles (see Figure 2b), indicating a successful buildup of the SPBI/P2VP multilayers from methanol solutions. For the first few layers, the absorbance grows with a different initial slope compared to the later stage which represents a steady-state regime. This is consistent with the previously reported paper,¹² wherein molecular dynamics simulations revealed that a steady-state linear growth regime is usually observed in the experiments after completion of the first few deposition cycles in the case of LbL assembly.^{43,44} The growth rate difference at early stages is believed to result from the difference in surface charge density

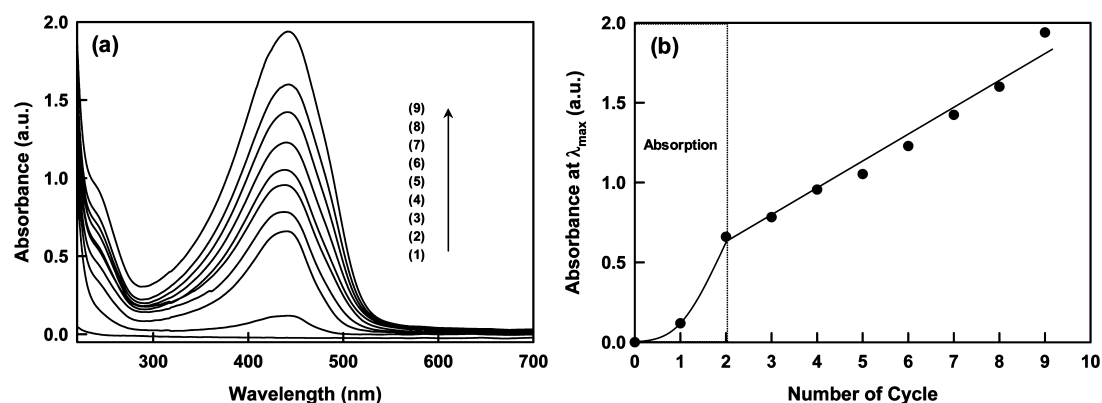


Figure 4. UV-vis absorption spectra versus wavelength for SPBI/P2VP multilayers deposited on Nafion membrane by the layer-by-layer dip-coating assembly (LbL-DCA) for a different number of bilayers, shown in parentheses (a). (b) Absorbance intensity (at $\lambda_{\max} = 450$ nm) versus the number of bilayers for the same assembly.

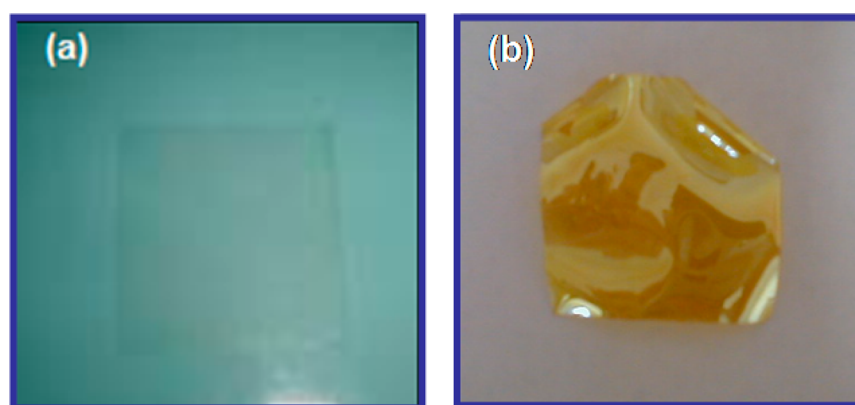


Figure 5. Photographs of (a) pure Nafion membrane and (b) LbL Nafion membrane coated with 9 bilayers of SPBI and P2VP. The size of each membrane was 4 cm \times 4 cm (width \times length).

of the substrate compared to the natural overcharging at the steady-state regime.

The surface morphology, roughness, and thickness of the formed SPBI/P2VP multilayered films were investigated by using AFM. Figure 3 shows the surface topography obtained by AFM at different numbers of bilayers of SPBI and P2VP, (a) 10 bilayers, (b) 20 bilayers, and (c) 28 bilayers at a spinning rate of ca. 3000 rpm. It was observed that all SPBI/P2VP multilayered films, regardless of the number of deposition cycles, are quite smooth, with a root-mean-square (RMS) roughness value equal to 0.9–1.3 nm. The thickness of the SPBI/P2VP multilayered films was obtained in profilometry after scratching the surface with a sharp razor blade before scanning it with AFM. This procedure is illustrated in Figure 3d, where the vertically oriented dark region in the image corresponds to the substrate with the removal of the film by a sharp razor blade. The very bright region is an artifact induced due to scratching. That is, the thickness of the SPBI/P2VP multilayered films is calculated from the height difference between the substrate side and the multilayer film (see inset, Figure 3d). The total thickness of multilayers of 28 bilayers of SPBI and P2VP is found to be 89.90 nm with a standard deviation of 12.75 nm, corresponding to the thickness of approximately 3.2 nm per bilayer. As a result, we could successfully fabricate the LbL self-assembled SPBI/P2VP molecular composite films.

Multilayer Coating and Their Morphologies of SPBI/P2VP on Nafion Membrane. Having demonstrated the

potential to grow the LbL self-assembled SPBI/P2VP multilayer films on quartz from charged polymers in methanol solutions by a LbL-SCA method, the LbL self-assembly technique was further extended to allow similar SPBI/P2VP multilayered coatings on Nafion membranes, here using the dipping technique. This was selected over spin-coating due to the need to preserve the Nafion membranes in their methanol-swollen state throughout processing. By sequential dipping of a Nafion membrane into oppositely charged polymeric solutions (anionic SPBI and cationic P2VP), we were able to build up SPBI/P2VP multilayers on Nafion membrane. Figure 4a shows UV-vis absorption spectra versus wavelength for the SPBI/P2VP multilayer films deposited on Nafion membrane using the layer-by-layer dip-coating assembly (LbL-DCA) method for a different number of bilayers. The LbL growth was characterized by the plot of absorbance intensity at $\lambda_{\max} = 450$ nm versus the number of bilayers for the multilayer films. Interestingly, an abrupt increase of absorbance intensity in the first two deposition cycles was observed (see Figure 4b), probably due to the diffusion of SPBI solution (absorption) into the bulk regime of Nafion membrane driven by a chemical potential gradient.

Indeed, such an increase of absorbance intensity at early stages is much higher compared to the SPBI/P2VP multilayers deposited on the quartz substrate. Afterward, as the number of dipping cycles further increases, a linear increase in absorbance at the λ_{\max} value with each cycle was observed, indicating a

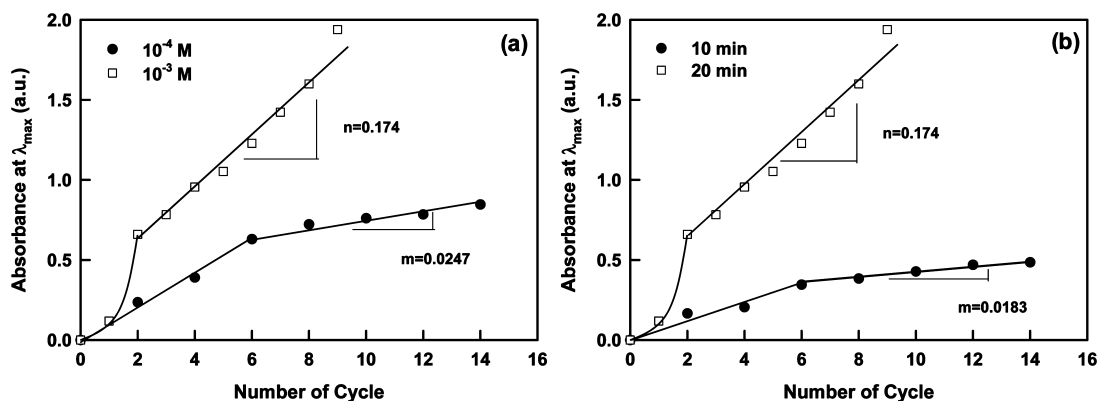


Figure 6. Dependence of (a) SPBI concentration (10^{-4} M: ●; 10^{-3} M: □) and (b) dipping time (10 min: ●; 20 min: □; concentration: 10^{-3} M) on SPBI/P2VP multilayer growth as examined via absorbance intensity of SPBI at 450 nm.

linear growth of the SPBI/P2VP multilayer films (see Figure 4b). It was therefore found that the formation of the SPBI/P2VP multilayers on Nafion membrane follows a two-step process: (1) absorption via a diffusion behavior of polymer solutions at an early stage, followed by (2) surface deposition of SPBI/P2VP multilayers via an LbL self-assembly. It is possible that the absorption of SPBI and P2VP into the Nafion bulk (step 1 of LbL) will adversely impact proton conductivity.

Figure 5 shows photographs of (a) pure Nafion membrane and (b) LbL Nafion membrane coated with the 9 bilayers of SPBI and P2VP. It is seen that the SPBI/P2VP multilayer-coated Nafion membrane exhibits a shiny, foil-like surface. Further, we found the coated membranes to be noticeably stiffer than the uncoated Nafion membrane. Moreover, the SPBI/P2VP multilayer coated Nafion membranes were quite environmentally durable, with no visible changes upon exposure to boiling water. In order to get a better understanding of the surface morphology of the SPBI/P2VP multilayer coated Nafion membrane, contact mode AFM was conducted on both pure Nafion membrane and LbL Nafion membrane coated with the 9 bilayers of SPBI and P2VP, respectively. It was found that the surface of the SPBI/P2VP multilayer coated Nafion membrane is smoother than that of the pure Nafion membrane. The surface roughness of LbL Nafion membrane coated with the multilayers of 9 bilayers of SPBI and P2VP and that of pure Nafion membranes was found to be 6.88 and 15.82 nm, respectively. Specifically, the SPBI/P2VP multilayer-coated Nafion membrane did not reveal any pinholes or open pores (data not shown), which implies that the SPBI/P2VP multilayer coatings are even and homogeneous.

The effects of SPBI concentration and dipping time on the SPBI/P2VP multilayer growth on Nafion membranes were also explored, anticipating that increases in either would lead to an increased rate of deposition per bilayer. Figure 6a shows the dependence of SPBI/P2VP multilayer growth on SPBI concentration (using only two concentrations) as examined via monitoring the absorbance intensity of SPBI at 450 nm. It was observed that the SPBI/P2VP multilayers grow in a two-step process similar to that of the SPBI/P2VP multilayer buildup on quartz substrate (see Figure 2b). Also, at the decreased SPBI concentration of 10^{-4} M, we did not observe the dramatic increase of absorbance at an early stage (less than 2 bilayers) that had been observed for 10^{-3} M and attributed in that case to higher bulk absorption. Thus, the concentration of SPBI solution has a profound impact on the growth rate and growing pattern of the SPBI/P2VP multilayers. For the lower

concentration of SPBI solution (10^{-4} M), the SPBI/P2VP multilayers were found to grow gradually until 6 dipping cycles and then eventually slowed down, with a reduction in quantity of polymer deposited per cycle. Specifically, the 10-fold decrease in polymer concentration led to a 7-fold decrease in the growth rate of multilayers (see Figure 6a). The effect of concentration is evidently kinetic in origin, since a similar decrease in the adsorption rate is observed when decreasing the dipping time with polymer solutions. Figure 6b shows the influence of the dipping time on the SPBI/P2VP multilayer growth. Similar to the effect of SPBI concentration, the dipping time of SPBI solution has a similarly strong influence on the SPBI/P2VP multilayer growth. That is, in the case of a shorter dipping time, the growth rate became smaller than that corresponding to the longer dipping time. The decrease in dipping time of a factor of 2 led to a 9.5 decrease in growth rate (see Figure 6b).

Microstructure Analysis. Like other ionomers, the microstructure of Nafion is complex. Although the exact structure is not known, several models have been proposed since the early 1970s to describe ways in which ionic groups aggregate within the material. Such structural models have been proposed for the interpretation of scattering patterns and dynamic mechanical data.⁴⁵ In small-angle X-ray scattering (SAXS), these membranes were shown to be characterized by a microphase separation between the ionic domains and the polymer matrix, that gives rise to a small-angle scattering maximum (interplanar distance d -spacing = 40 Å), commonly called the “ionomer peak”. The SAXS curves generally exhibit scattering maxima at $q = (4\pi/\lambda)\sin(\theta)$, approximately equal to the inverse of cluster size. On the basis of both SAXS and WAXS (as well as DMA), it has been proposed that Nafion membranes exhibit network structures with interconnected reverse micelle-like ionic clusters.^{46–49} Along these lines, it is interesting to investigate the multilayered microstructures composed of rod-like SPBI and coil-like P2VP coated on Nafion membrane. To understand the microstructures of the SPBI/P2VP multilayered coatings, we acquired WAXS patterns in two different beam orientations: X-ray beam (I) perpendicular (flat view) and (II) parallel (edge view) to the plane of the SPBI/P2VP multilayer coating layer. Figure 7 shows the two-dimensional WAXS patterns of pure Nafion membranes (a: perpendicular; b: parallel) and SPBI/P2VP multilayer coated Nafion membranes (c: perpendicular; d: parallel) under these two experimental conditions.

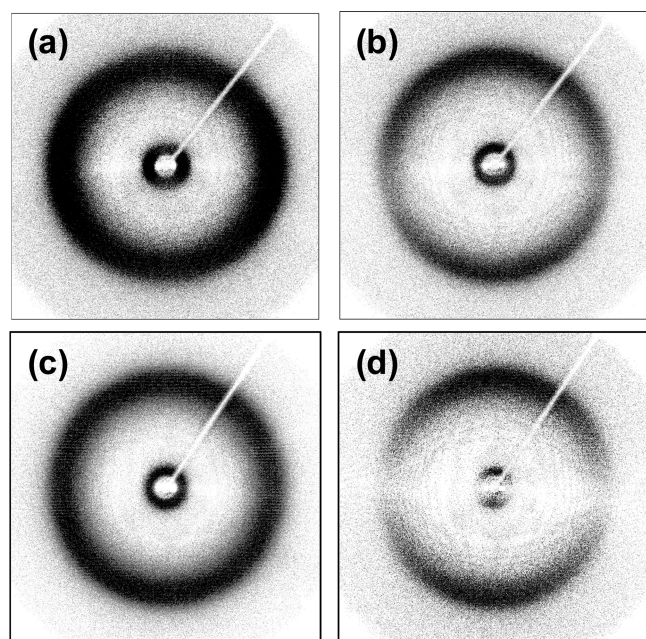


Figure 7. Two-dimensional WAXS patterns of pure Nafion membranes (a: through-thickness; b: edge-on) and a SPBI/P2VP multilayer-coated Nafion membrane (c: through-thickness; d: edge-on) under two experimental conditions. For (b) and (d), the film normal was vertically oriented relative to the patterns shown.

For both pristine and SPBI/P2VP multilayer coated Nafion membranes, a large amorphous halo at $2\theta = 25^\circ$ (d -spacing of 5.3 Å), which is attributed to the interchain spacing in the amorphous component of the PTFE-like structure, was observed.⁴⁴ We could also observe another peak at $2\theta = 5^\circ$ (d -spacing = 35 Å), commonly attributed to scattering from ionic clusters present in the Nafion membrane and, in this case, coincidentally corresponding to the layer-by-layer multilayered orderings.^{50,51} That is, the probing X-ray photons transmitted through the thickness “see” only cluster-based electron density fluctuations, which are isotropically distributed in the plane of the coating. However, the intensity of the long-range peak at 35 Å features contributions from two structures: one is a function only of ionic clusters present in Nafion, and the other is the number and stratification degree of the SPBI/P2VP multilayers (Supporting Information, Figure S1). Accordingly, the intensity of this peak in the parallel direction increases dramatically compared to pure Nafion, due to a presence of the LbL multilayers coated on Nafion. On the other hand, as seen in Figure 7b, the 2-D scattering pattern of pure Nafion in the parallel direction shows obvious orientation of the large angle halo, indicative of residual orientation from manufacturing, but no orientation of the ionomer peak. In addition, the SPBI/P2VP multilayer films caused no alteration of the scattering pattern in the perpendicular direction (through-thickness view) due to its isotropic ordering on Nafion (see Figure 7c). In contrast, Figure 7d shows evidence for orientation in the plane of LbL molecular composite microstructures coated on Nafion membrane in the parallel direction (edge view), which contributes positively to the anisotropic scattering at low angles. This is expected to further increase by increasing the number of the SPBI/P2VP multilayers. A schematic representation of the anisotropy evident in the LbL molecular composite coatings is provided in the Supporting Information, Figure S2.

Thermal and Mechanical Properties. In the direct methanol fuel cell (DMFC), the important requirements for the proton exchange membrane (PEM) are high thermal stability, high mechanical properties, high proton conductivity, and low methanol crossover. We studied the thermal stability of the SPBI/P2VP multilayer coated Nafion membrane by thermogravimetric analysis (TGA). It was observed that the thermal decomposition of pure Nafion and SPBI/P2VP multilayer coated Nafion membranes proceeded in two distinct stages (Supporting Information, Figure S3). The first modest decomposition of both samples starts in the temperature region of 300–400 °C, which is commonly attributed to the loss of $-\text{SO}_3\text{H}$ groups.⁵² Afterward, the SPBI/P2VP multilayer coated Nafion and pure Nafion start to decompose at the same rate after 450 °C. Figure 8 shows the isothermal TGA data at 310

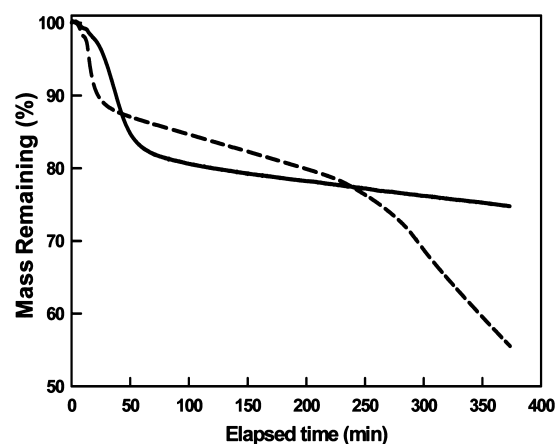


Figure 8. Isothermal thermogravimetric analysis (Iso-TGA) at 310 °C for (dotted line) pure Nafion membrane and (solid line) LbL Nafion membrane coated with the 9 bilayers of SPBI and P2VP under N_2 (60 mL/min).

°C for pure Nafion and SPBI/P2VP multilayer coated Nafion membranes. It can be seen that the LbL coated Nafion presents a somewhat better thermal stability under isothermal conditions for more than 6 h, evidenced by a lower weight loss over that period of time. To determine the level of mechanical reinforcement caused by the molecular composite coating, we performed dynamic mechanical analysis (DMA) for pure Nafion and SPBI/P2VP multilayer coated Nafion membranes. Figure 9 shows the plots of the tensile storage modulus (E') and $\tan \delta$ versus temperature using an oscillation frequency of 1 Hz. It can be seen that the storage modulus of pure Nafion membrane decreases dramatically around 80 °C, presumably indicative of a T_g , whereas the tensile storage modulus of the SPBI/P2VP multilayer coated Nafion membrane decreases gradually with temperature in this region and then starts to drop only after reaching $T = 160$ °C. Also, the initial storage modulus of the SPBI/P2VP coated Nafion membrane was higher than that of the untreated Nafion. Thus, the pure Nafion membrane was substantially reinforced with SPBI/P2VP multilayer coatings on its surface. In particular, the SPBI/P2VP multilayer coated Nafion had a nearly constant tensile storage modulus from 850 MPa at 35 °C to 670 MPa at 100 °C, while the bare Nafion storage modulus decreased drastically from 563 MPa at 35 °C to 48 MPa at 100 °C. Moreover, we observed that, by increasing the number of SPBI/P2VP multilayer cycles from 9 to 14 at the same solution

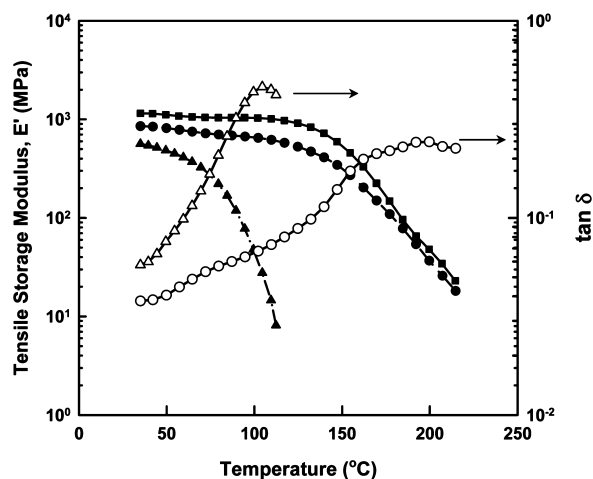


Figure 9. Temperature dependence of the tensile storage modulus (E') and $\tan \delta$ for the pure Nafion membrane (E' : ▲; $\tan \delta$: Δ) and LbL Nafion membrane coated with 9 bilayers of SPBI and P2VP (E' : ●; $\tan \delta$: ○). E' of LbL Nafion membrane coated with 14 bilayers of SPBI and P2VP was also measured (■).

concentration of 10^{-3} M, a significant increase of modulus near room temperature was obtained. Specifically, the modulus at $T = 35$ °C was found to increase by 21% from 851 MPa for 9 cycles to 1027 MPa for 14 cycles. With all of these factors considered, such SPBI/P2VP multilayer coated Nafion membranes might be used as promising PEMs for a high temperature DMFC.

CONCLUSIONS

We have reported on a LbL technique for the deposition of SPBI/P2VP molecular composite multilayers for enhancing the properties of proton exchange membranes (PEMs) such as Nafion, in particular aiming at the improvement of the thermal and mechanical properties of PEMs for direct methanol fuel cells. It was found that a steady-state linear growth regime for the LbL self-assembled SPBI/P2VP multilayer films and coatings onto quartz and Nafion membranes was successfully achieved after completion of the first few deposition cycles, indicating a successful buildup of the SPBI/P2VP multilayers in methanol solutions, as evidenced by UV-vis spectroscopy. WAXS studies revealed stratification of the LbL coatings with orientation of the layers parallel to the surface and with a length scale overlapping with the ionomeric nanostructure of the Nafion membrane. From isothermal TGA experiments at 310 °C under nitrogen, it was found that the SPBI/P2VP multilayer-coated Nafion exhibited higher thermal stability for more than 4 h. Moreover, it was also observed that pure Nafion membranes were rendered mechanically tougher and stronger after the deposition of SPBI/P2VP multilayer coatings of Nafion membrane using the LbL self-assembly technique. From DMA experiments, it was evident that the SPBI/P2VP multilayer coating by the LbL technique enhanced the thermo-mechanical properties of the Nafion membrane. The multilayer-treated Nafion showed a distinctly higher and stable storage modulus in the temperature range in which the storage modulus of Nafion decreased drastically. Besides the enhancement of thermo-mechanical properties, potential also exists for the Nafion membranes to exhibit increased proton conductivity at higher temperatures due to the strong hydration (moisture retention) capabilities of SPBI as well as decreased methanol

crossover (permeability) due to the ionic (physical) cross-links inherent in the SPBI/P2VP molecular composite system. Although methanol permeability measurements have not yet been performed, preliminary studies of thermal stability and mechanical property show large improvements of the physical properties of such membranes in comparison to pure Nafion membranes. Detailed studies with regard to the measurement of proton conductivity and methanol permeability of such membranes should be performed in the future. Finally, the high controllability of the LbL process gives the potential for fine-tuning of the end-use properties of the processed membranes for a high performance portable direct methanol fuel cells application.

ASSOCIATED CONTENT

Supporting Information

X-ray scattering data, X-ray scattering microstructure schematics, and TGA data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01371.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Decher, G. Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites. *Science* **1997**, *277* (5330), 1232–1237.
- (2) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. Ultrathin Polymer Coatings by Complexation of Polyelectrolytes at Interfaces: Suitable Materials, Structure and Properties. *Macromol. Rapid Commun.* **2000**, *21* (7), 319–348.
- (3) Mendelsohn, J. D.; Barrett, C. J.; Chan, V. V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. Fabrication of Microporous Thin Films from Polyelectrolyte Multilayers. *Langmuir* **2000**, *16*, 5017–5023.
- (4) Hammond, P. T. Form and Function in Multilayer Assembly: New Applications at the Nanoscale. *Adv. Mater.* **2004**, *16*, 1271–1293.
- (5) Dubas, S. T.; Schlenoff, J. B. Swelling and Smoothing of Polyelectrolyte Multilayers by Salt. *Langmuir* **2001**, *17*, 7725–7727.
- (6) Patel, P. A.; Dobrynin, A. V.; Mather, P. T. Combined Effect of Spin Speed and Ionic Strength on Polyelectrolyte Spin Assembly. *Langmuir* **2007**, *23*, 12589–12597.
- (7) Hoogeveen, N. G.; Stuart, M. A. C.; Fleer, G. J.; Bohmer, M. R. Formation and Stability of Multilayers of Polyelectrolytes. *Langmuir* **1996**, *12*, 3675–3681.
- (8) Antipov, A. A.; Sukhorukov, G. B.; Mohwald, H. Influence of the Ionic Strength on the Polyelectrolyte Multilayers' Permeability. *Langmuir* **2003**, *19*, 2444–2448.
- (9) Kim, B. S.; Lebedeva, O. V.; Kim, D. H.; Caminade, A. M.; Majoral, J. P.; Knoll, W.; Vinogradova, O. I. Assembly and Mechanical

Properties of Phosphorus Dendrimer/Polyelectrolyte Multilayer Microcapsules. *Langmuir* **2005**, *21*, 7200–7206.

(10) Fery, A.; Schoeler, B.; Cassagneau, T.; Caruso, F. Nanoporous Thin Films Formed by Salt-Induced Structural Changes in Multilayers of Poly(acrylic acid) and Poly(allylamine). *Langmuir* **2001**, *17*, 3779–3783.

(11) Wang, D.; Caruso, R. A.; Caruso, F. Synthesis of Macroporous Titania and Inorganic Composite Materials from Coated Colloidal Spheres – A Novel Route to Tune Pore Morphology. *Chem. Mater.* **2001**, *13*, 364–371.

(12) Angelatos, A. S.; Radt, B.; Caruso, F. Light-Responsive Polyelectrolyte/Gold Nanoparticle Microcapsules. *J. Phys. Chem. B* **2005**, *109*, 3071–3076.

(13) Rmaile, H. H.; Farhat, T. R.; Schlenoff, J. B. pH-Gated Permeability of Variably Charged Species through Polyelectrolyte Multilayer Membranes. *J. Phys. Chem. B* **2003**, *107*, 14401–14406.

(14) Sui, Z.; Schlenoff, J. B. Controlling Electroosmotic Flow in Microchannels with pH-Responsive Polyelectrolyte Multilayers. *Langmuir* **2003**, *19*, 7829–7831.

(15) Ghostine, R. A.; Jisr, R. M.; Lehaf, A.; Schlenoff, J. B. Roughness and Salt Annealing in a Polyelectrolyte Multilayer. *Langmuir* **2013**, *29*, 11742–11750.

(16) Farhat, T. R.; Hammond, P. T. Designing a New Generation of Proton-Exchange Membranes Using Layer-by-Layer Deposition of Polyelectrolytes. *Adv. Funct. Mater.* **2005**, *15* (6), 945–954.

(17) Coulter, M. O. *Modern Chlor-Alkali Technology*; Ellis Horwood, Ltd.: Harlow, Essex, 1980; Vol. 1, p 290.

(18) Eisenberg, A. *Perfluorinated Ionomer Membranes*, 1st ed.; American Chemical Society: Washington DC, 1982; p 500.

(19) Schlick, S. *Ionomers: Characterization, Theory, and Applications*; CRC Press: Boca Raton and New York, 1996; p 320.

(20) Kerres, J.; Zhang, W.; Jorissen, L.; Gogel, V. Application of Different Types of Polyaryl-Blend-Membranes in DMFC. *J. New Mater. Electrochem. Syst.* **2002**, *5*, 97–107.

(21) Kerres, J. A. Development of Ionomer Membranes for Fuel Cells. *J. Membr. Sci.* **2001**, *185*, 3–27.

(22) Tazi, B.; Savadogo, O. Parameters of PEM Fuel-Cells Based on New Membranes Fabricated from Nafion(R), Silicotungstic Acid and Thiophene. *Electrochim. Acta* **2000**, *45*, 4329–4339.

(23) Fontanella, J. J.; Wintersgill, M. C.; Wainright, J. S.; Savinell, R. F.; Litt, M. High Pressure Electrical Conductivity Studies of Acid Doped Polybenzimidazole. *Electrochim. Acta* **1998**, *43*, 1289–1294.

(24) Wang, J. T.; Savinell, R. F.; Wainright, J.; Litt, M.; Yu, H. A H-2/O-2 Fuel Cell Using Acid Doped Polybenzimidazole as Polymer Electrolyte. *Electrochim. Acta* **1996**, *41*, 193–197.

(25) Savinell, R. F.; Litt, M. H. *Proton Conducting Polymers Used as Membranes*. U.S. Patent 5525436, 1996.

(26) Savinell, R. F.; Litt, M. H. *Proton Conducting Polymers Prepared by Direct Acid Casting*. U.S. Patent 5716727, 1998.

(27) Asensio, J. A.; Borros, S.; Gomez-Romero, P. Proton-Conducting Polymers Based on Benzimidazoles and Sulfonated Benzimidazoles. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3703–3710.

(28) Hasiotis, C.; Deimede, V.; Kontoyannis, C. New Polymer Electrolytes Based on Blends of Sulfonated Polysulfones with Polybenzimidazole. *Electrochim. Acta* **2001**, *46*, 2401–2406.

(29) Nakajima, H.; Nomura, S.; Sugimoto, T.; Nishikawa, S.; Honma, I. High Temperature Proton Conducting Organic-Inorganic Nano-hybrids for Polymer Electrolyte Membrane - Part II. *J. Electrochem. Soc.* **2002**, *149*, A953–A959.

(30) Arnold, F. E.; Arnold, F. E. Rigid-Rod Polymers and Molecular Composites. *High Perform. Polym.* **1994**, *117*, 257–295.

(31) Spry, R. J.; Alexander, M. D.; Bai, S. J.; Dang, T. D.; Price, G. E.; Dean, D. R.; Kumar, B.; Solomon, J. S.; Arnold, F. E. Anisotropic Ionic Conductivity of Lithium-Doped Sulfonated PBI. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 2925–2933.

(32) Wu, J.; Kim, G. M.; Mather, P. T.; Venkatasubramanian, N.; Arnold, F. E.; Dang, T. D. Rheology and Morphology of Molecular

Composites from Sulfonated Rigid-Rods. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43*, 1051–1052.

(33) Venkatasubramanian, N.; Dean, D. R.; Dang, T. D.; Price, G. E.; Arnold, F. E. Solvent Cast Thermoplastic and Thermoset Rigid-Rod Molecular Composites. *Polymer* **2000**, *41*, 3213–3226.

(34) Gasa, J. V.; Weiss, R. A.; Shaw, M. T. Ionic Crosslinking of Ionomer Polymer Electrolyte Membranes using Barium Cations. *J. Membr. Sci.* **2007**, *304*, 173–180.

(35) Wu, H. L.; Ma, C. C. M.; Kuan, H. C.; Wang, C. H.; Chen, C. Y.; Chiang, C. L. Sulfonated Poly(ether ether ketone)/Poly(vinylpyrrolidone) Acid-Base Polymer Blends for Direct Methanol Fuel Cell Application. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 565–572.

(36) Tomlin, D. W.; Fratini, A. V.; Hunsaker, M.; Adams, W. W. The Role of Hydrogen Bonding in Rigid-Rod Polymers: The Crystal Structure of a Polybenzobisimidazole Model Compound. *Polymer* **2000**, *41*, 9003–9010.

(37) Mader, J. A.; Benicewicz, B. C. Sulfonated Polybenzimidazoles for High Temperature PEM for Fuel Cells. *Macromolecules* **2010**, *43*, 6706–6715.

(38) Argun, A. A.; Ashcraft, J. N.; Hammond, P. T. Highly Conductive Methanol Resistant Polyelectrolyte Multilayers. *Adv. Mater.* **2008**, *20*, 1539–43.

(39) Fu, Y.; Bai, S.; Cui, S.; Qiu, D.; Wang, Z.; Zhang, X. Hydrogen-Bonding Directed Layer-by-Layer Multilayer Assembly: Reformation Yielding Microporous Films. *Macromolecules* **2002**, *35*, 9451–9458.

(40) Dang, T. D.; Arnold, F. E. Water-Soluble Benzobisazole Rigid-Rod Copolymers. *MRS Online Proc. Libr.* **1993**, 49–58.

(41) Yoo, D.; Rubner, M. F. Layer-by-Layer Modification of Surfaces through the Use of Self-Assembled Monolayers of Polyions. *ANTEC 95 - The Plastics Challenger: A Revolution in Education, Conference Proceedings, Vols I–III: Vol I: Processing; Vol II: Materials; Vol III: Special Areas*; **1995**, pp 2568–2570.

(42) Lefaux, C. J.; Zimmerlin, J. A.; Dobrynin, A. V.; Mather, P. T. Polyelectrolyte Spin Assembly: Influence of Ionic Strength on the Growth of Multilayered Thin Films. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 3654–3666.

(43) Schlenoff, J. B.; Dubas, S. T. Mechanism of Polyelectrolyte Multilayer Growth: Charge Overcompensation and Distribution. *Macromolecules* **2001**, *34*, 592–598.

(44) Advincula, R.; Aust, E.; Meyer, W.; Knoll, W. In Situ Investigations of Polymer Self-Assembly Solution Adsorption by Surface Plasmon Spectroscopy. *Langmuir* **1996**, *12*, 3536–3540.

(45) Yeo, S. C.; Eisenberg, A. Physical-Properties and Supramolecular Structure of Perfluorinated Ion-Containing (Nafion) Polymers. *J. Appl. Polym. Sci.* **1977**, *21*, 875–898.

(46) Gebel, G.; Loppinet, B. Colloidal Structure of Ionomer Solutions in Polar Solvents. *J. Mol. Struct.* **1996**, *383*, 43–49.

(47) Longworth, R.; Vaughan, D. J. Physical Structure of Ionomers. *Nature* **1968**, *218*, 85–87.

(48) Fujimura, M.; Hashimoto, T.; Kawai, H. Small-Angle X-ray-Scattering Study of Perfluorinated Ionomer Membranes I. Origin of 2 Scattering Maxima. *Macromolecules* **1981**, *14*, 1309–1315.

(49) Gierke, T. D.; Munn, G. E.; Wilson, F. C. The Morphology in Nafion Perfluorinated Membrane Products, as Determined by Wide-Angle and Small-Angle X-ray Studies. *J. Polym. Sci., Part B: Polym. Phys.* **1981**, *19*, 1687–1704.

(50) Arys, X.; Laschewsky, A.; Jonas, A. M. Ordered Polyelectrolyte “Multilayers”. I. Mechanisms of Growth and Structure Formation: A Comparison with Classical Fuzzy “Multilayers”. *Macromolecules* **2001**, *34* (10), 3318–3330.

(51) Arys, X.; Fischer, P.; Jonas, A. M.; Koetse, M. M.; Laschewsky, A.; Legras, R.; Wischerhoff, E. Ordered Polyelectrolyte Multilayers. Rules Governing Layering in Organic Binary Multilayers. *J. Am. Chem. Soc.* **2003**, *125*, 1859–1865.

(52) Surowiec, J.; Bogoczek, R. Studies on the Thermal-Stability of the Perfluorinated Cation-Exchange Membrane Nafion-417. *J. Therm. Anal.* **1988**, *33*, 1097–1102.