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Multiple Membranes from “True” Polyelectrolyte Multilayers

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Ultrathin polymer membranes, fabricated on porous supports using the layer-by-layer assembly of oppositely charged polyelectrolytes,[1,2] exhibit high selectivity for the separation of charged[3] and vapor-phase[4] components. The flux of ion transport through these polyelectrolyte multilayers shows a strongly nonlinear dependence on solution ionic strength,[5] which is a consequence of efficient matching of internal charge between positive and negative polymer segments.[6] Certain limitations on the large-scale use of multilayer membranes are imposed by the requirement that they be fabricated on a porous support. For example, the films are inhomogeneous, with the area over the pores thinner than those directly covering the substrate. Here, we describe a method for producing isolated, free floating, and free-standing films in conjunction with a high-throughput alternating spray method for multilayer formation.[7]

The key to producing isolated membranes involves inserting weak points that are designed to decompose under specific conditions, in contrast to using a dissolvable substrate.[8] A variety of interaction mechanisms provide for multilayer buildup of polymers: in addition to the widely employed electrostatic ion pairing,[1,2] hydrogen bonding has been used,[9] as have charge-transfer interactions,[10] biocomplexation,[11] and stereocomplex formation.[12] Recent studies suggest possible strategies for introducing a programmed decrease of polymer−polymer interactions, depending on the interaction. Thus, Mendelsohn et al.[13] reported complete removal of a weak polyacid-containing multilayer from a substrate at low pH, where electrostatic interactions are eliminated by neutralizing the negatively charged polyelectrolyte.[14] Sukhishvili and Granick[15] describe the use of hydrogen bonding polymer complexes to make multilayers that are destabilized by a change in pH. We have recently shown that polyelectrolytes within multilayers may be dissociated by ion-exchange competition of salt ions for polymer/polymer ion pairs.[16] For example, poly(acrylic acid)/poly(diallyldimethylammonium), PAA/PDADMA, multilayers were quantitatively and rapidly removed at salt concentrations greater than 0.6 M.[16]

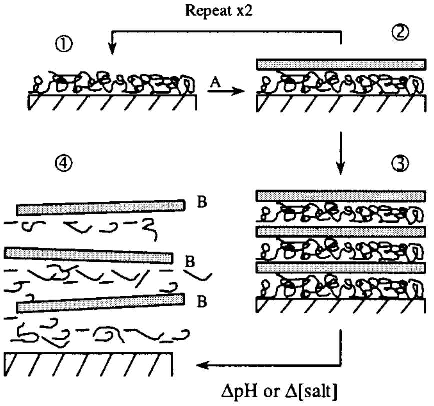

Figure 1. Method for producing multiple strata of membranes (shown as shaded rectangles) using release layers (shown as freehand lines). In steps 1 and 2, many layer pairs of dissociable polyelectrolytes are deposited on a substrate, followed by several layer pairs of nondissociable polymers. The process may be repeated to yield an “onionskin” stack of several strata, whereupon the individual membranes are delaminated by a change in pH or salt concentration.

To make free membranes, we use a multiple combination of polymers, deposited in several “strata.”[17] Selective decomposition of polyelectrolyte pairs, driven by changes in pH or salt concentration, affords controlled delamination of high-quality membranes. This general approach is summarized in Figure 1. Due to the extensive interpenetration of neighboring polyelectrolyte layers,[1,6,18−20] each stratum must be at least several layers thick.

An example, using an increase in salt concentration as a delamination stimulus, is provided by a multilayer made from 20 layers of PAA and PDADMA, followed by 20 layers of poly(styrene sulfonate)(PSS)/PDADMA. Multilayers made from the former combination of polymers increase in thickness with increasing salt concentration, reaching a maximum at about 0.4 M NaCl, whereupon they start to decompose.[16] Complete removal from the substrate is observed at salt concentrations greater than 0.6 M. In contrast, PSS/PDADMA multilayers are stable up to a salt concentration of ca. 3.5 M.[6] Thus, the PSS/PDADMA stratum is quickly released from the substrate intact on immersion in 1 M NaCl.

An alternative release layer employs a random copolymer of PAA (20%) and PDADMA (80%), bearing a net positive charge (PDADMA-*co*-PAA) and PSS as its negative partner. When deposited under conditions of low pH, the PAA units are protonated (uncharged). A PSS/PDADMA stratum is then deposited on top of this, also at low pH. Exposure of this thin film to pH >6 causes the PAA units to ionize, imparting a net negative charge to the release layer, and causing it to dissociate. Figure 2 depicts transmission FTIR of such a delamination scheme. Spectrum A is of the first PSS/PDADMA-*co*-PAA stratum. Signals from the sulfonates (960 to 1210 cm^{-1} region)[21] and the

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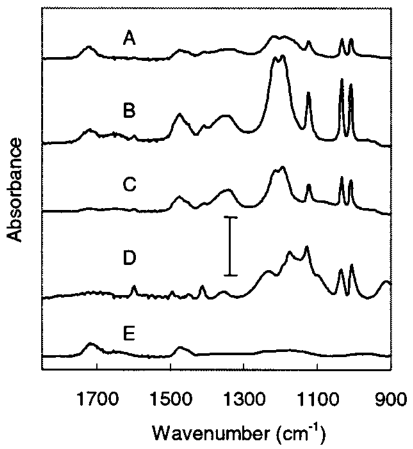

Figure 2. FTIR transmission spectra of (A) 10 layer pairs of PSS/PDADMA-*co*-PAA built on an Si wafer from 1 M NaCl at pH 2; (B) multilayer A plus 10 layer pairs of PSS/PDADMA from 1 M NaCl at pH 2; (C) membrane B, delaminated from the substrate by decomposing A in pH 11 solution, captured on a Si wafer and exposed to pH 2 HCl; (D) PSS reference spectrum; (E) PDADMA-*co*-PAA reference spectrum (pH 2). The scale bar is 0.05 AU for A, B, and C.

C=O stretch (protonated carboxylate, ca. 1720 cm^{-1}) are clearly observed. The sulfonate bands are enhanced when the PSS/PDADMA stratum is added (Spectrum B, PDADMA shows few discernible features in the frequency region presented[21]). At pH 11 the PSS/PDADMA stratum detaches (Spectrum C). Approximately 13% (equivalent to 2.6 layers) of the original carboxylic acid intensity is observed in Spectrum C, which is a consequence of interpenetration of the first and second strata.[20] Spectra D and E are of the pure PSS and PDADMA-*co*-PAA, respectively.

The copolymer/pH change approach to delamination is advantageous over the salt concentration change method because the former method tolerates higher salt concentrations[16] and thus yields thicker layers. It is possible to assemble many alternating strata, as in Figure 1. Dissociation of such a multistrata "onionskin" film yields multiple membranes. We have produced up to four stacked membranes in this fashion, each stratum having 20 layers of polyelectrolyte. (Assembly time is the major constraint here.) In the sense that composition modulation in the substrate normal direction is achieved, these "onionskins" are "true" multilayers, rather than amorphous, isotropic thin films, which are typically obtained from two complementary polyelectrolytes.[1,19,20]

When using PAA/PDADMA as the release layer, reduction of solution pH to eliminate electrostatic interactions is not as effective as the salt-competition method, since secondary interactions, such as hydrogen bonding and hydrophobic forces,[13,14,16] hold the neutralized PAA and PDADMA together at all but the lowest pH values. The driving forces for dissociation are probably entropic in nature. Each polymer repeat unit gains about 0.2 kT of configurational entropy when released to the solution,[22] in addition to the translation entropy of associated salt ions and water molecules. Hoogeveen et al.[23] estimate that a minimum charge density of about 20% is required to form stable multilayers. The critical point for multilayer decomposition does not require that all polymer/polymer contacts be broken, but a sufficient number must be removed for the multilayer to surrender to the entropic forces driving dissociation. Following decomposition, it is quite possible that the polyelectrolytes remain loosely associated, highly swollen complexes.[24]

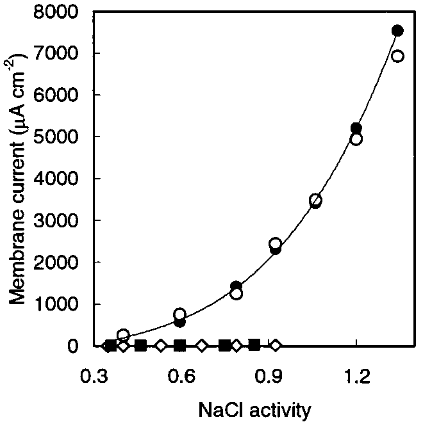

Figure 3. Ion flux, as current density, through multilayer membranes on the surface of a rotating disk electrode as a function of the activity of salt in solution. The solid line is a fit to the relationship: flux $\sim$ [salt]^3 (see ref 5). Open circles, 10 layer-pair free membrane of PSS/PDADMA fabricated as in Figures 1 and 2. Filled circles, 10 layer pairs of PSS/PDADMA deposited directly on the electrode surface from 1.0 M NaCl. Squares, 10 layer pairs of SPEEK/PDADMA deposited on PSS/PDADMA-*co*-PAA at pH 2 and released from the surface at pH 11. Diamonds, similar SPEEK/PDADMA multilayer deposited directly on the electrode.

The ion transport properties of released and as-deposited membranes were compared by measuring the flux of electrochemically active ferricyanide ion through them.[5] Figure 3 compares the current of a 20-layer PSS/PDADMA film grown directly on a platinum electrode with that of a 20 layer PSS/PDADMA film deposited on a 20 layer PSS/PDADMA-*co*-PAA release stratum, delaminated by immersion in pH ll, 1 M NaCl. The films had the same nominal thickness (2000 Å). Both samples showed the strong nonlinear dependence of ion flux on salt concentration peculiar to these intrinsically compensated systems.[5] For comparison, membranes from a more hydrophobic, therefore less permeable, sulfonated poly(ether ether ketone)(SPEEK)/PDADMA are shown. Currents for a particular membrane are the same, within experimental error, whether they are deposited directly on the electrode or whether they are floated off the surface with a release layer then recaptured on the electrode, indicating the latter to be of high quality and pinhole-free.

Using alternate spraying of polyelectrolytes[7] we were able to produce 600 cm^2 of continuous free-floating film 2000 Å thick. These films could be lifted from solution as elastic, workable sheets. When spread over an opening several square cemtimeters in area and allowed to dry, free-standing films were obtained, though they were very fragile due to their ultrathin morphology.

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