376a Layer-by-Layer Film Formation Kinetics under an Applied Electric Potential Measured by Optical Waveguide Lightmode Spectroscopy

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Layer-by-Layer (LbL) thin film assembly occurs via the alternate adsorption of positively and negatively charged macromolecular species. We investigate here the control of LbL film growth through the electric potential of the underlying substrate. We employ optical waveguide lightmode spectroscopy (OWLS) to obtain in situ kinetic measurements of poly(allylamine hydrochloride)/poly(sodium 4-styrenesulfonate) (PAH/PSS) and poly(L-lysine)/dextran sulfate (PLL/DXS) multilayer film formation in the presence of an applied voltage difference (DV) between the adsorbing substrate, an indium tin oxide (ITO) coated waveguiding sensor chip, and a parallel platinum counter electrode. We find initial layer adsorption to be significantly enhanced by an applied potential for both polyelectrolyte systems: the mass and thickness of (positively charged) PAH and PLL layers on ITO are about 60% and 500% larger, respectively, at DV = 2 V than at open circuit potential (OCP), in apparent violation of electrostatics. A kinetic analysis reveals the initial attachment rate constant to decrease with voltage, in agreement with electrostatics. To reconcile these results, we propose a more coiled and loosely bound adsorbed polymer conformation at higher applied potential. Following 10 adsorption steps, the mass and thickness of a PAH/PSS film grown under DV = 2 V are about 15% less than those of a comparable film grown under OCP, reflecting a lower degree of complexation between adsorbing polyanions and more highly coiled adsorbed polycations. Following 14 adsorption steps, the mass and thickness of a PLL/DXS film grown under DV = 2 V are about 70% greater than those of a comparable film grown under OCP, reflecting the increased charge overcompensation in the initial layer. We find the scaling of film mass with the number of adsorption steps to be linear in the PAH/PSS system and exponential in the PLL/DXS system, irrespective of applied voltage. We observe the exponential factor to decrease with applied voltage and to exhibit a cross-over to a smaller value upon the addition of the fifth layer. Extrapolation reveals PLL/DXS multilayer films to be suppressed by increased voltage in the limit of a large number of layers: the mass of films grown at OCP and DV = 1 V would surpass that of a film grown under DV = 2 V at about the 23rd and 18th adsorption steps, respectively. The formation kinetics of PLL/DXS, but not PAH/PSS, change qualitatively under voltage: PLL adsorption is slow to reach a plateau, possibly due to the formation of secondary structure, and a decrease in film mass occurs toward the end of each DXS adsorption step, suggesting a spontaneous removal of some PLL/DXS complexes from the film.