



Swelling of electrochemically active polyelectrolyte multilayers

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ABSTRACT

This article is focused on the swelling of redox-active polyelectrolyte multilayers. Upon electrochemical stimulation, the influx of counterions and solvent molecules causes an increase of osmotic pressure in the film which results in a volumetric expansion. Motivated by potential biomedical and micromechanical applications, the current experimental and theoretical understanding of the process is described. Electroactive polyelectrolyte multilayers show a rich thermodynamic behavior which is dependent on both the properties of the polyelectrolytes, such as the pKa and the complexation enthalpy, and of the electrolyte solution, such as the pH and the type of counterions. Although, at present no complete theoretical description of the swelling phenomenon is available, a simple qualitative model can be used to explain the influence of various different external parameters on the swelling.

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1. Introduction

Stimuli-responsive polymer materials have received considerable attention in the last years due to their wide range of envisioned and actual applications [1–3]. These polymer films translate a large stimulus to a microscopic response and are therefore good candidates for actuators, coatings, or gating devices that change their physical properties on a nanometer scale. Electroactive thin films contain building blocks that can be oxidized and reduced in a reversible way. Upon oxidation/reduction, these films undergo a swelling/deswelling reaction that is caused by an ion and solvent exchange between the film and the liquid phase and by a subsequent relaxation of the polymer chains. In contrast to other activation methods, like pH or temperature induced swelling, an electrical potential can be varied continuously and thus a tunable response can be achieved. Common architectures of electrochemically active thin films include polymer monolayers, cross-linked polymer films, polymer brushes, hydrogels and polyelectrolyte multilayers assemblies [1,3,4].

Layer-by-layer assembly (LbL) of polyelectrolyte multilayers (PEMs) has been developed in the mid 1990s [5,6], and is nowadays widely established as an easy tool for preparing functionalized

surfaces [7]. In contrast to other architectures, PEMs have the advantage that they can easily be assembled on any kind of charged surface without the need of spin coating or elaborated surface chemistry. Not only polyelectrolytes can be assembled to LbL films but all kinds of charged molecules can be embedded in the film. In addition, its physicochemical properties can also be tuned by varying the deposition conditions (pH [8,9], solvent quality [10], temperature [11], etc.). Depending on the choice of the polyelectrolytes, linearly and exponentially growing PEM systems have been described. These two growth modes have different thermodynamics resulting in differences in the interdiffusivity of the polyelectrolytes in the film [12–14].

Overall, the high structural flexibility renders PEMs especially interesting for applications in the biomedical field [15,16] (e.g. for drug delivery [17–19], cell sheet engineering [20], or cell stimulation [21,22]).

Schlenoff's group began research on electroactive polyelectrolyte multilayers in 1997 with multilayers composed of poly(styrenesulfonate) (PSS) and poly(butanyl viologen) (PBV) [23,24]. The same year Hodak et al. constructed multilayers composed of poly(allylamine ferrocene) (PAH-FC) and glucose oxidase (GOx) [25]. Hodak's work pioneered the use of PEMs in amperometric biosensing. Polyelectrolyte multilayers offer the advantage that enzymes (e.g. GOx) as well as their mediators (e.g. ferrocene) can be integrated to the film. In fact, the field of electroactive PEMs is largely dominated by the effort to

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realize new amperometric biosensors [26]. Even though the electrochemical swelling of redox modified electrodes was already discussed in the 1980s [27–29], no attention was paid to this phenomenon for electroactive PEMs until Calvo's group described it in 2002 for several different polymer systems [30–32]. By now, redox-driven swelling has been characterized for a variety of PEM systems with different physicochemical properties, among them linear growing multilayers (poly(allylamine) derivatized with $\text{Os}(\text{bpy})_2\text{PyCl}^+$ (PAH-OS) and poly(vinyl sulfonate) (PVS) or poly(styrene sulfonate) (PSS) [32,33–37,38,39]), exponentially growing ones (ferrocyanide containing multilayers of poly(allylamine) hydrochloride (PAH) and poly(glutamic acid) (PGA) [40,41]) as well as multilayers containing enzymes (PAH-FC and GOx [31]) or Prussian Blue (PB) nanoparticles (with linear poly(ethylene imine) (LPEI) [42]). Usually the electroactive molecules are integrated into the PEM during the build-up. However, it is possible to incorporate ferrocyanide as electrochemically active molecule in multilayers composed of weakly-binding polyelectrolyte pairs after the build-up has been completed [40,41,43–46].

For potential applications, three different features of the electrochemical swelling process are of importance. The thickness change of the PEM upon swelling is typically between 5% and 25% [40,41,42]. As multilayers can be fabricated with a thickness of only a few tens of nanometers this enables actuation with nanometer precision. The swelling process also results in a change in Young's elastic modulus of the film [30,42]. This effect could be used to tailor cellular behavior since cell adhesion, locomotion, and differentiation are known to depend strongly on the viscoelastic properties of the adhesive substrate. Electrochemically-swallowable multilayers are also of interest for applications in ion filtration [47] and drug delivery [17–19]. The swelling of the multilayer causes a change of the permeability of the membrane for ions and small molecules. Electroactive PEMs were assembled in the form of hollow capsules that changed their permeability upon chemical oxidation and could be loaded with representative molecules [48] (see Fig. 1). The release from such

capsules could be triggered by different redox potentials that are present in different regions of the body.

In order to advance such applications, in depth understanding of the current research is necessary. In the following, we provide an overview of the characterization techniques commonly used for electroactive thin films followed by a brief introduction of the physical basis of the swelling process. The influence of external parameters on the swelling process is discussed in the last section.

2. Characterization

Electrochemical swelling of polyelectrolyte multilayers is usually characterized by complementary methods involving both electrochemical and surface sensitive techniques. Electrochemistry provides the external stimulus needed to regulate the swelling of polyelectrolyte multilayers by changing the oxidation state of the redox-active sites. With electrochemical characterization methods it is not possible to obtain information about the mechanical changes involved in the multilayer swelling. However, electrochemistry is used to determine parameters, which are needed to develop a thermodynamic picture of this process. Nernst plots, derived from controlled potential coulometry, showed coupling between mechanical and electrochemical thermodynamics and were used to estimate the mechanical energy consumed during the swelling [27–29]. Cyclic voltammetry with standard redox probes like hexacyanoferrate was applied and the Donnan potential of the multilayer films was calculated using the measured shift in apparent redox potential (see Fig. 2A) [32,38,41]. The Donnan potential is related to the number of fixed charges in the multilayer, and provides information if the film acts as a selective anion exchanger (positive Donnan potential) or a selective cation exchanger (negative Donnan potential) [32]. If all the redox sites in the film are accessible in the experimental time scale (by electron hopping or by physical diffusion), the concentration of electrochemically active sites in multilayer films can be estimated by the integration of half-waves

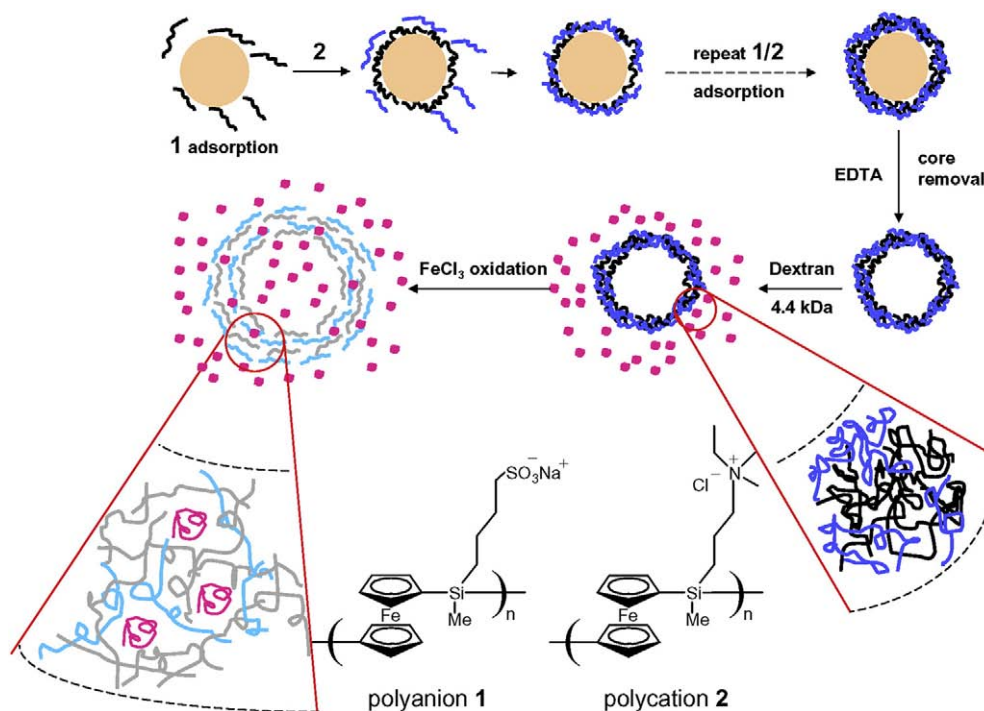


Fig. 1. Scheme illustrating the use of electroactive polyelectrolytes to control the permeability of multilayer capsules. Polyanions 1 (back lines) and polycations 2 (blue lines), both electroactive poly(silanes), are adsorbed stepwise on a colloidal core. After core removal the permeability of the obtained capsules can be tuned via chemical oxidation (e.g. using FeCl_3). While in the reduced state the capsule walls were impermeable for dextran (red bundles), they become permeable upon oxidation. Figure reproduced from reference [48] with permission.

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