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On the anodic deposition of poly-L-lysine on indium tin oxide

Sara Nilsson, Nathaniel D. Robinson*

Transport and Separations Group, Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

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ABSTRACT

We provide and discuss electrochemical quartz crystal microbalance (EQCM) measurements confirming previously-reported observations that poly-L-lysine films deposited from solution under anodic conditions grow at a constant deposition rate for extended periods of time. Compared to our previous results using Pt, we find that indium tin oxide (ITO) offers an effective surface for film growth where water oxidation is sufficiently suppressed to allow uniform films to be deposited. The fact that the previous results on ITO have been reproduced is positive for the study of polyelectrolyte film creation, and has implications for the use of these films to increase the biocompatibility of hard conducting materials used as electrodes.

1. Introduction

Poly-L-lysine (PLL) and similar polyelectrolytes are often proposed for passivating surfaces of "incompatible" electronic conductors such as metals and metal oxides to make them more "biocompatible." [1,2] Relatively few conducting or semi-conducting materials offer a surface that biomolecules and biological cells recognize or accept, and coating them with materials like PLL increases the likelihood that cells or biomolecules will interact [3] with (or ignore) the treated surface much as they would any surface in their usual physiological environment [4,5]. PLL has a net positive charge at pH near 7, limiting the density and thickness of the coating that can be achieved simply by immersing an electrode material in a PLL solution. Recent studies have reported peculiarities in the anodic deposition of PLL onto conducting Indium Tin Oxide (ITO) under a positive bias, namely that the deposition rate is reported to be largely independent of the concentration of PLL in the electrolyte and that the deposition can continue at a constant rate for extended time periods as measured via optical waveguide light spectroscopy (OWLS) [6,7]. We have previously attempted to reproduce and study this process using Pt electrodes in a quartz crystal microbalance (QCM), and showed that PLL can indeed be deposited, but electrolytic oxidation of water to oxygen competes with the deposition, limiting the information that can be collected and the value of the method for coating Pt surfaces [8]. We have repeated this study with ITO-coated QCM sensors.

The relative rates of competing electrochemical reactions are typically studied and discerned via techniques such as cyclic voltammetry (CV) or linear-sweep voltammetry (LSV). However, the anodic deposition of PLL, while clearly dependent on potential, does not itself follow a simple electrochemical process. As such, voltammetric techniques must be combined with e.g. gravimetric techniques capable of monitoring the deposition of the polymer. The simultaneous voltammetric or chronoamperometric measurement of electrochemical reactions with a 3-electrode cell in conjunction with QCM, often referred to as EQCM, is an example of a combination of instruments capable of achieving this goal [8,9]. Our previous work demonstrated that the deposition of PLL onto Pt can, with considerable effort, be discerned from the electrochemical removal (etching) of the Pt and gas evolution at the electrode. The gas evolution we observed seemed to contradict previous reports that PLL could be anodically deposited without observable gas evolution on ITO [6]. We attributed this contradiction to the difference in electrode material, particularly since Pt is often cited as one of the better surfaces for electrolytic oxidation of water. Here, we reproduce our EQCM measurements, this time using ITO-coated QCM sensors, under identical conditions and can confirm the results of Ngankam and van Tassel [6].

2. Experimental

2.1. Chemicals

HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), Sigma-Aldrich) buffer (10 mM containing 0.1 M NaCl, Sigma Aldrich) and PLL (mol. wt. 70000–150000, Sigma–Aldrich, 0.4 g

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* Corresponding author. Tel.: +46 13 28 2212.
E-mail address: natro@ifm.liu.se (N.D. Robinson).

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l^{-1} in 10 mM HEPES) were prepared from deionized water (18.2 MΩ cm) obtained from a Milli-Q system and used in all experiments. Prior to use, HEPES and PLL were filtered and deoxygenated with N_2.

2.2. Quartz crystal microbalance and sensors

ITO-coated QCM sensors (ITO coated on quartz, Microvacuum, Hungary) were cleaned according to this procedure: The sensors were immersed in a solution of 2% Sodium Dodecyl Sulfate (SDS, BDH Laboratory Supplies, England) in Milli-Q water (18.2 MΩ cm) for 30 minutes at room temperature. Thereafter, the sensors were rinsed thoroughly with Milli-Q water, dried with N_2 gas and finally air-plasma-treated for 10 minutes at 100 W in a Pico plasma reactor below 0.01 mbar (Diener Electric, GmbH, Germany). After the washing procedure, each sensor was placed in an electrochemical flow cell (QEM 401, Q-Sense AB, Sweden) in a QCM E1-system (Q-Sense AB). The resonance frequencies of the crystal were then obtained for harmonics n = 1, 3, 5, 7, 9, 11, 13 while the cell was dry. HEPES buffer, adjusted to pH = 7.4 by adding HCl (1 M, Fluka Analytical), was introduced into the cell via a peristaltic pump at a flow rate of 10 μl min^{-1}. All the harmonics followed the same trends in the experiments, but for convenience only the scaled change in frequency for the seventh harmonic Δf_7 and the respective change in dissipation ΔD_7 are shown. Other substrates that were tested include Q-sense sensors with an Au electrode (on top of a Ti adhesion layer), and the Au on Ti stack coated with ITO. They were all treated in the same manner as the crystals from Microvacuum. The QCM sensors used respond with -17.7 ng Hz^{-1} cm^{-2}.

2.3. Electrochemical measurements

CV and CA experiments were carried out using a Potentiostat (μautolab type II, Metrohm Autolab B.V., The Netherlands) in combination with GPES software (version 4.9.007, Metrohm Autolab B.V.) connected to the QCM E1-system. The QCM-sensors in the three-electrode setup functioned as the working electrode (WE) in conjunction with a WPI Dri-REF™ Ag/AgCl reference electrode (RE) and a plate of Pt (which is also the ceiling of the QCM flow cell) as the counter electrode (CE). The vertex potentials in the CV sweeps were 1 and 1.3 V vs. Ag/AgCl and, during the CA measurements, the applied potential was 1.3 V vs. Ag/AgCl. The open-circuit potential (OCP) for all experiments was 0.23 V +/− 10 mV.

3. Results

3.1. PLL adsorption without applied potential

At the OCP, a thin layer of PLL deposits onto ITO in a matter of seconds after the polyelectrolyte solution (0.4 g l^{-1}) is introduced into the flow cell. The QCM measures a change in resonance frequency Δf of about 5 Hz over 20 seconds, corresponding to a (wet) mass of 90 ng cm^{-2}, as seen in Fig. 1. The QCM detects a barely significant change in ΔD, almost certainly due to the viscosity of the PLL + HEPES solution, which is higher than the viscosity of the HEPES buffer without PLL.

3.2. Cyclic voltammetry

Starting with a saturated ITO QCM sensor under 0.4 g l^{-1} PLL at OCP and initiating cyclic voltammetry between 1.0 V and 1.3 V vs. Ag/AgCl results in nearly monotonic deposition of PLL onto the sensor surface, as shown in Fig. 2. The rapid temporary increase in Δf observed during each cycle for similar experiments on Pt [8], which we attributed to oxygen gas generation, are here on ITO only significant in the first cycle. Instead, on ITO, each voltage cycle deposits a clear but decreasing amount of PLL onto the sensor (resulting in a decrease in Δf). Similarly, the peak current observed during each subsequent cycle decreases. No significant change in ΔD is observed. The corresponding experiment using only the HEPES buffer (without PLL) resulted in a peak current of 15 μA and no discernible change in Δf or ΔD (See Fig. A.1 in the SI).

Figs. 3 and A.2 show the 2nd and 3rd cycles of the data in Figs. 2 and A.1, respectively, vs. the applied voltage rather than time (voltammograms). The voltammograms make it very clear that the largest change in Δf occurs when the potential reaches its upper vertex (1.3 V) and continues for almost half of the return cycle.

3.3. PLL adsorption at a constant anodic potential (chronoamperometry)

As shown in Fig. 4, the rate of deposition of PLL (0.4 g l^{-1}) from solution increases rapidly from the open-circuit saturation level ($\Delta f = 0, t < 0$) when a constant potential of 1.3 V vs. Ag/AgCl is applied

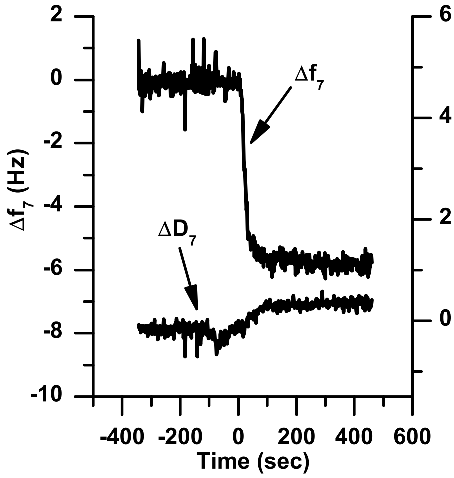

Fig. 1. QCM measurement of PLL adsorption at the open-circuit potential (0.2 V vs. Ag/AgCl) onto an ITO-coated sensor. Change in the resonance frequency (as recorded using the 7th overtone) and corresponding change in dissipation as a function of time as recorded by the QCM. The solution flowing through the cell was changed from HEPES to HEPES with PLL at 0 seconds.