An EQCM Study of the Effect of Potential on Fibrinogen Adsorption at Gold and Polypyrrole Surfaces.

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The adsorption of proteins and/or cells occurs on the surfaces of implanted devices and may lead to rejection of the device by the body. Consequently, a simple and rapid means for detecting the initial stages of the adsorption process on a surface foreign to the body would be of considerable value in biocompatability studies. The mass change that accompanies the adsorption process is one general method that responds to all adsorption processes, and a few in vitro studies with the Quartz Crystal Microbalance (QCM) have been reported[1,2].

QCM studies in solution correspond to open circuit electrochemical conditions, and occur at ill-defined, varying electrode potentials. This is not the case with the electrochemical quartz crystal microbalance (EQCM) where the electrode potential can be controlled. This distinction is an important one in the case of adsorbates that may be electroactive, as is the case for many biological species. Thus, it is remarkable that we have not been able to identify, in the literature, fibrinogen adsorption studies using the EQCM.

Here we demonstrate the utility of the EQCM for such adsorption studies. We chose to study the adsorption of fibrinogen because it plays a key role in the process by which the adhesion of cells and protein adhesion starts on surfaces[3]. Our studies were carried out on the evaporated gold surface supplied with the 10 MHz AT Cut quartz resonator we used, and on this gold surface modified with polypyrrole (PPY) in oxygen-free phosphate buffer saline (PBS, pH=7.4). Potentiostatic conditions were used, at applied potentials vs. SCE of 0.25 V, 0.01V and -0.50 V. The adsorption behavior at an open circuit was also determined for reference purposes.

Gold surfaces are thrombogenic[4]. In contra-distinction, PPY is one of the recognized, promising candidates for surface modification because it is shown to be biocompatible[5] when "doped" with particular counter anions. Note that determining the adsorption of fibrinogen at these two surfaces and their potential dependence represents a classical EQCM adsorption experiment[6].

Results and Discussion.

Figure 1 presents the experimental adsorption results as a plot of mass change/microscopic area (areal mass density change) vs. time on the bare gold electrode. The solid line represents saturation coverage for fibrinogen as calculated using averaged value of width (D domain 11.8 ± 1.7nm)[7] in an upright oriented direction[8]. The two horizontal dashed lines bracketing the solid line that represents the average on different surfaces are the extreme range of monolayer coverages that we calculated from Sit and Marchant[7] assuming an upright structure.

Figure 2 gives the results obtained at the PPY-tosylate modified gold electrode. Under comparable conditions, the change in areal mass is similar at the gold and the PPY modified gold surfaces.

A detailed interpretation of our results requires considering not only the charge[9] and redox state of the fibrinogen but also the electrode's surface composition as well its rugosity. We will present a rationalization of our results based on these factors.

References

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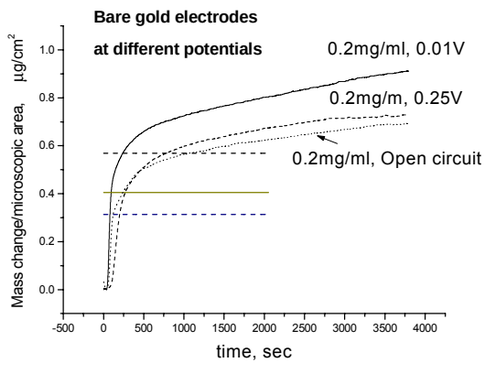

Figure 1. Fibrinogen adsorption on bare gold electrodes in PBS, pH=7.4, solutions. The concentration of fibrinogen is 0.2mg/ml. The potential was held at 0.01V, 0.25V and open circuit potential for each electrode. Adsorption quickly reached a saturation level followed by a continued, slow, almost linear mass increase. The roughness factor (oxygen atom method) ranged from 3.12 to 3.29.

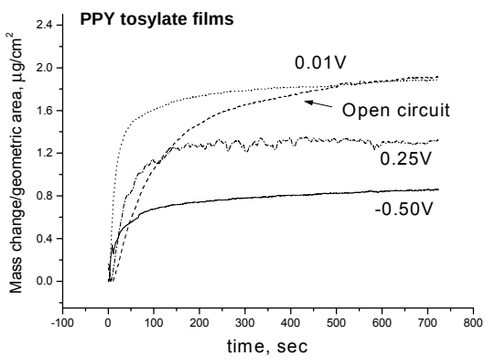

Figure 2. Fibrinogen adsorption on PPY modified gold electrodes in PBS, pH=7.4, solutions. The concentration of fibrinogen is 0.2mg/ml. Potential was held at 0.01V, 0.25V, -0.50V, and open circuit potential for each electrode.