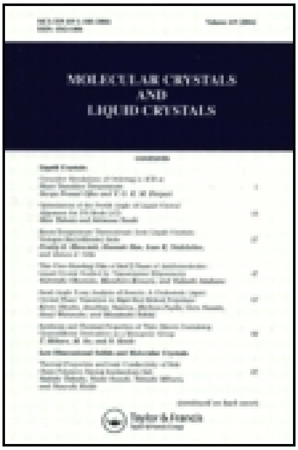

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# Electrochemical Quartz Crystal Microbalance Study of the Self-assembled Multilayered Poly(aniline N-Butansulfonate) Film

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# Electrochemical Quartz Crystal Microbalance Study of the Self-assembled Multilayered Poly(aniline N-Butansulfonate) Film

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Electrochemically active multilayers of self doped polyaniline films were prepared by the ionic interaction between poly(aniline N-butanesulfonate) (PANBUS) and polyethylene imine. Kinetic constant and free energy of the PANBUS adsorption were calculated to be 2.3 /M·sec and -5.4 kcal/mole, respectively from the analysis of QCM. The prepared film showed the characteristic cyclic voltammogram of polyaniline and EQCM study of the multilayered film indicated that the mass change during oxidation and reduction was independent on the cations and anions of the used electrolytes.

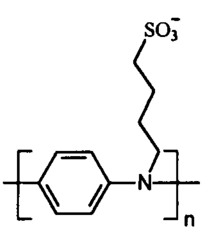
Keywords self-assembly; multilayer; polyaniline; EQCM

## INTRODUCTION

Ultrathin film with electrochemical activity may find its use on the molecular scale electronic devices such as sensors, diodes etc.[1, 2] It has been reported that the self-assembled films can be fabricated using partially doped polyaniline by means of electronic interaction[3] and hydrogen-bonding interactions[4]. However, the poor solubility and solution stability of the partially doped polyaniline make the processing very difficult.

We reported the synthesis of a water soluble self-doped poly(aniline N-butanesulfonate) (PANBUS) and observed that the electrochemically grown film was electrochemically stable after $10^6$ redox cycles.[5] This water soluble self-doped polyaniline seems a good candidate for the self-assembled multilayer system. In this study, we report fabrication of the multilayered film from PANBUS and examination of the adsorption kinetics and redox properties using an electrochemical quartz crystal microbalance (EQCM).

## EXPERIMENTALS



SCHEME

PANBUS was prepared by electrochemically oxidative polymerization according to the previously reported method. The structure of the PANBUS is shown in scheme.

The self-assembled film was prepared by ionic interactions between negatively charged PANBUS and positively charged gold electrode surface which was modified with 11-aminoundecylthiol. Multilayered film can be obtained by the sequential dipping of the modified gold electrode in polycation and PANBUS solutions. The adsorption kinetics was followed by the observation of the frequency change during the adsorption of PANBUS and poly(ethyleneimine)(PEI) on the electrode surface.

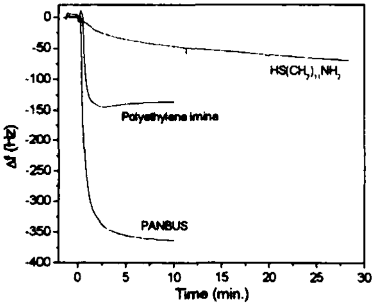
The redox behavior of the ultrathin films was investigated by cycling the electrode potential between –0.2 and 0.45 V against Ag/AgCl reference with a 50 mV/sec sweep rate.

## RESULTS AND DISCUSSION

First, adsorption of 11-aminoundecylthiol on to the gold electrode was examined using QCM. The adsorption of the alkanethiol onto the gold surface is observed as the decrease of frequency (Fig. 1). The 68.5 Hz frequency decrease was calculated to surface coverage of 7.10 x $10^{14}$ molecules/$cm^2$ (with surface roughness 1.2) which is reasonable value for the monolayer formation.

After modifying the electrode surface with amine, the electrode was alternatively dipped into PANSBUS and polyethylene imine(PEI) solution to build up multilayer. The polymer adsorbed very quickly even though the solution was quite diluted (less than 0.2wt%) and more than 99% of polymer adsorption took place within 4 min (Fig. 1). The adsorption curve of PANBUS was simulated by Langmuir isotherm to give the adsorption kinetic constant $k_a$ = 2.3 $M^{-1}$·$sec^{-1}$ and adsorption free energy of −5.4 kcal/mole.

In Fig 2, the cyclic voltammograms of the self-assembled



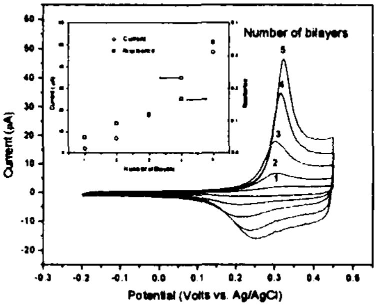


FIGURE 1 Time dependence of the frequency change of the 11-aminoundecylthiol on gold and PANBUS and polyethylene imine onto a substrate precoated with 2 bilayers of the PANBUS/PEI.

FIGURE 2 Cyclic voltammogram of the self-assembled PANBUS films as the increase of the number of bilayers in 1M HCl.

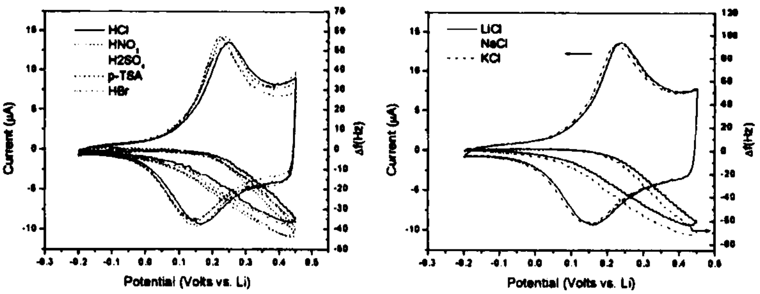


FIGURE 3 EQCM study of the self-assembled PANBUS film with changing of a) anions and b) cations. (sweep rate = 50mV/s)

PANBUS/PEI are shown. The peak current of PANBUS was linearly increased as number of bilayers increased. The multilayered PANBUS film was electrochemically reversible and $E_{1/2}$ was almost constant.

In Fig. 3a) and b) show CV's and frequency change with variation of anions and cations, respectively. It was found that the mass change during the redox cycle was not dependent on the cations or anions used in the electrolytes. Thus, the mass change during the redox cycle was interpreted as the water adsorption and desorption in the polymer film.

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