

The degradation of pinhole free poly (1,3-dihydroxybenzene) films in sodium hydroxide for the production of microelectrode ensembles

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Abstract

The degradation of poly (1,3-dihydroxybenzene) films in the presence of sodium hydroxide has been studied. It is found that films of poly (1,3-dihydroxybenzene) when grown electrochemically under certain conditions are pinhole free. Concentrations of sodium hydroxide as low as 10 mM lead to pore formation in the polymer layer in a controlled manner. Microelectrode ensembles can be produced using this technique. An impedance model has been developed that characterises the behaviour of these thin-layer, porous polymer films. © 2007 Published by Elsevier B.V.

Keywords: Hydroxide; Pinhole; Thin-layer; Impedance; Microelectrode ensemble

1. Introduction

A number of strategies have been developed for the fabrication of microelectrode arrays/ensembles. The first method employed for the construction of microelectrode arrays was lithography [1–4]. This method of preparing the arrays is reliable and reproducible. However, there are considerable costs involved in the production of arrays in this manner, mainly the expense of the equipment. Another strategy used is the use of Self Assembled Monolayers (SAMs) to form microelectrode ensembles through the formation of defective monolayers upon adsorption of the molecules. Sabatani et al. [5,6] formed microarrays in their investigation of mixed monolayers of *n*-octadecyl trichlorosilane and *n*-octadecyl mercaptan. Finklea et al. [7] have studied octadecane thiol SAMs and have found that the pinholes in these SAMs lead to the SAM covered gold electrode behaving as a rough microarray. They treat the microarray problem as being analogous to that of the coupling of an electron transfer reaction with preceding and following chemical reactions (based on the work of Amatore et al.

[8] and Tokuda et al. [9]). Recently Diao et al. [10] have applied the same models to the microarrays they fabricated by adsorbing octadecanethiol onto gold surfaces. By varying the time of adsorption they were able to vary the surface coverage of the thiol molecule and thus were able to vary the number of microelectrodes in the microarray. Campuzano et al. [11] have studied pure and mixed monolayers of 3-mercaptopropionic acid and 11-mercaptoundecanoic acid. They found that an electrode modified with a monolayer of 3-mercaptopropionic acid behaves like a microarray due to pinhole defects in the monolayer acting as individual microelectrodes. Gao and Siow [12] formed microarray electrodes by forming mixed SAMs of poly(3-dodecylthiophene) and 3-dodecylthiophene.

Another approach has been to use Carbon Nano Tubes (CNTs) to fabricate microarrays (or more accurately Nano Electrode Arrays (NEAs)). These CNTs have been used [13–15] for electroanalytical purposes but the arrangement of these arrays was haphazard and the response generated was indistinguishable from that of a macroelectrode. Recently Koehne et al. [16] have produced ordered NEAs using CNTs and microlithography. Appropriately sized nickel nano particles were sputtered onto chromium coated silicon wafers. Vertically aligned Multi-Walled Carbon

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Nanotubes (MWCNTs) were grown on these nickel catalyst particles using Plasma Enhanced Chemical Vapour Deposition (PECVD). Chemical Vapour Deposition (CVD) of tetraethylorthosilicate encapsulated the MWCNTs in silicon dioxide. The microarray surface was then polished flat. They were able to control the inter electrode separations and thus fabricate NEAs with a lower density of electrodes. This lower density of electrodes ensured that the NEAs incorporated the enhanced mass transport at each individual CNT and the lower charging currents associated with microelectrodes. Tu et al. [17] fabricated NEAs in quite a similar manner. They electrochemically deposited nickel nanoparticles onto similar chromium coated silicon wafers and grew the CNTs using PECVD. They encapsulated the CNTs in an epoxy resin using a spin coating technique, which after curing was polished flat. Fletcher and Horne [18] describe the fabrication and electrochemical response of random assemblies of microdisks (RAM™). These microelectrode assemblies are constructed by setting carbon fibres in an epoxy resin and connecting each individual carbon fibre to a current collector. The electrode surface is polished so that the microelectrodes and epoxy sit in the same plane.

Madigan et al. [19] describe the formation of microelectrode arrays on poly (1,2-phenylenediamine) coated glassy carbon electrodes. This was achieved by subjecting the polymer-coated electrode to ultrasonics. This treatment produced a random ensemble of cavities in the polymer surface, which exposes the underlying conducting surface. These cavities are formed due to localised heating of the sonication solution at the polymer surface. This produces vapour bubbles, which violently explode and ablate the polymer films. Barton et al. [20] also describe the production of microelectrode arrays at poly (1,2-phenylenediamine) coated gold electrodes in this manner. They claimed that their polymer layer is ca. 40 nm and showed it to passivate a gold electrode to redox reaction of ferri/ferro cyanide. Myler et al. [21,22] working in the same group have developed a glucose biosensor and other sensors for the detection of pesticides using this same sonication technique.

In this paper, the degradation of electropolymerised poly (1,3-dihydroxybenzene) films is studied, which leads to the production of microelectrode ensembles. The films were treated with sodium hydroxide solutions. It is shown that initially the films are pinhole free and that AC impedance is a useful technique for studying the emergent pinhole defects in these coatings [23]. It is shown in this paper that AC impedance characteristics of the electrode are substantially different for the pinhole free and pinholed films even at high levels of polymer coverage. This is not always as evident from cyclic voltammograms.

2. Experimental

All electrochemical experiments were carried out in a three-electrode glass cell. A Solartron SI-1287 potentiostat

was used throughout the course of the work. The monomer 1,3-dihydroxybenzene was electropolymerised onto gold electrodes (see below) from pH neutral aqueous solutions. This was accomplished by sweeping the potential of the working electrode between 0 and 1 V vs. Ag/AgCl at 5 mV s^{-1} for five sweeps of potential (see Fig. 1). 1,3-Dihydroxybenzene (99%) was supplied by Sigma–Aldrich. Ultra pure water (resistivity: $18.2 \text{ M}\Omega \text{ cm}$) was used to make up all aqueous solutions. The films were exposed to sodium hydroxide (100 mM, 50 mM and 10 mM) for varying time periods. The time dependant cyclic voltammetry response and AC impedance response of the poly (1,3-dihydroxybenzene) modified electrodes was then ascertained.

For both the cyclic voltammetry and impedance experiments solutions of 20 mM $\text{Fe}_3(\text{CN})_6/\text{Fe}_4(\text{CN})_6$ (99.99%, Aldrich) in 0.5 M potassium chloride (99.99%, Aldrich) in ultra pure water were used. A sweep rate of 20 mV s^{-1} was used for the cyclic voltammetry experiments and the potential of the working electrode was switched between 0.2 and 0.7 V vs. Ag/AgCl. The working electrode used was a Teflon shrouded Au disk electrode ($A = 0.07 \text{ cm}^2$) supplied by Metrohm.

The impedance response was obtained when an AC potential of amplitude 5 mV was imposed on a DC potential of 0.265 V vs. Ag/AgCl. The frequency of the AC signal varied from 1 Hz to 5 kHz utilizing a Solartron SI 1260 Impedance/Gain Phase Analyser. Certain impedance spectra (Figs. 3a and b) were fitted to simple equivalent circuits using ZView 2 (Scribner Associates Inc.). Electrodes of evaporated gold on silicon (100) (gold chip electrodes) were used for the AC impedance work. These gold chip electrodes were constructed in-house using an Edwards E306A coating system. It was necessary to lay down a 9 nm adhesion layer of titanium prior to evaporating the

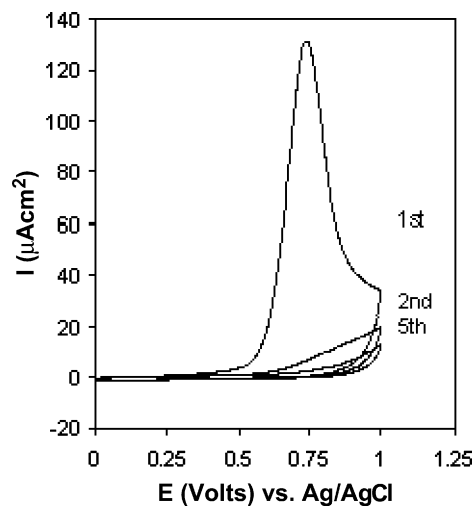


Fig. 1. Polymerisation of 0.1 M 1,3-dihydroxybenzene from an aqueous solution (pH 7) containing 0.1 M KCl between 0 and 1 V vs. Ag/AgCl. The working electrode was gold. The sweep rate employed was 5 mV s^{-1} . Sweeps 1, 2 and 5 are shown.

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