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Specific Immobilization of Electropolymerized Polypyrrole Thin Films Onto Interdigitated Microsensor Electrode Arrays

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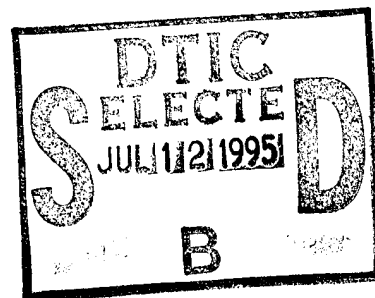
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Electroactive polypyrrole (PPy) thin films were grown by potentiostatic electropolymerization at chemically derivatized interdigitated microsensor electrodes (IMEs) of gold on borosilicate glass leading to specific adhesion of the electroconductive polymer film to the device. Films were grown to a constant electropolymerization charge density of 70 mC/cm^2 at 0.65 V vs Ag°/AgCl, 3 M Cl$^-$ from 1.0 M aqueous pyrrole solutions containing 5% poly(styrenesulfonic acid) (PSSA) and 1% dodecylbenzynesulphonate with the pH adjusted to 3.0 and the temperature maintained at 20°C. The interdigit space of the IME devices was chemically derivatized by chemical modification with 3-amniopropyltrimethoxysilane followed by direct linking of the 1° amine to the carboxylic acid of 3-(1-pyrrolyl)propionic acid using the heterobifunctional linker 1,3-diisopropylcarbodiimide enhanced with N-hydroxysulfosuccinimide in aqueous solution. The 3-(1-pyrrolyl)propionic acid was shown to be electroactive, electropolymerizable, and co-electropolymerizable with pyrrole monomer from aqueous solution.

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SPECIFIC IMMOBILIZATION OF ELECTROPOLYMERIZED POLYPYRROLE THIN FILMS ONTO INTERDIGITATED MICROSENSOR ARRAY ELECTRODES.

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ABSTRACT

Electroactive polypyrrole (PPy) thin films were grown by potentiostatic electropolymerization at chemically derivatized interdigitated microsensor electrodes (IMEs) of gold on borosilicate glass leading to specific adhesion of the electroconductive polymer film to the device. Films were grown to a constant electropolymerization charge density of 70 mC/cm^2 at 0.65 V vs Ag$^\circ$/AgCl, 3 M Cl$^-$ from 1.0 M aqueous pyrrole solutions containing 5% poly(styrenesulfonic acid) (PSSA) and 1% dodecylbenzynesulphonate with the pH adjusted to 3.0 and the temperature maintained at 20°C. The interdigit space of the IME devices was chemically derivatized by chemical modification with 3-aminopropyltrimethoxysilane followed by direct linking of the 1° amine to the carboxylic acid of 3-(1-pyrrolyl)propionic acid using the heterobifunctional linker 1,3-diisopropylcarbodiimide enhanced with N-hydroxysulfosuccinimide in aqueous solution. The 3-(1-pyrrolyl)propionic acid was shown to be electroactive, electropolymerizable, and co-electropolymerizable with pyrrole monomer from aqueous solution. Electroconductive PPy films grown on these ω-(1-pyrrolyl) derivatized IME devices were allowed to bridge the interdigit space and so be co-electropolymerized with ω-(1-pyrrolyl) moieties

specifically attached to the interdigit space of the device. This leads to specific adhesion of the PPy thin film to the device surface. Films grown in this way were compared to films similarly grown on unmodified devices, on IME devices rendered hydrophobic by chemical modification with dodecyltrichlorosilane, and on devices modified with 3-aminopropyltrimethoxysilane. Cyclic voltammetry revealed no significant difference in the electroactivity of PPy films grown on these various IME surfaces. Films were characterized by the time to adhesive failure using the Scotch® Tape test following immersion in PBS 7.2 buffer or after being maintained dry under vacuum and over desiccating molecular sieves. The time to adhesive failure in both test environments occurred in the order unmodified < dodecyl modified << 3-aminotrimethoxysilane modified << ω-(1-pyrrolyl) derivatized. The failure times were 3 days < 5 days << 27 days << 36+ days for films immersed in aqueous buffer and were 3 days < 36+ days << 36+ days << 36+ days for films stored dry under vacuum. The electrochemical and adhesion test evidence suggest that the PPy films are specifically immobilized to the ω-(1-pyrrolyl) derivatized IME devices and that this negates the hydrolytic instability of the PPy/glass interface that leads to poor adhesion under physiologic conditions.

INTRODUCTION

The development of chemical and biological sensor devices that are based on electroconductive polymers is an area that has attracted considerable recent attention[1-3]. Sensor devices that exploit the transducer-active responses of electroactive polymers such as polypyrrole, polyaniline, and polythiophene may be conductimetric[4] when they use the large change in electrical impedance[5-9] that accompanies oxidoreduction of the polymer, amperometric[10] when they use redox mediation and or electrocatalysis[11-13], or potentiometric[14-16] when they use the electrode potential change that accompanies changes in polymer redox composition. In general, these devices are formed from thin films of the electroconductive polymer fabricated on a pattern of microsensor electrodes formed on an insulating substrate. Electropolymerization provides a unique and convenient method of polymer film fabrication for such devices as it confers the following advantages: control of the location of the polymer film leading to micropatterning of the organic polymer on the device, direct association of the polymer with metallic or semiconductor electrodes for device interrogation and signal capture, precise control of polymer film thickness by control of the electropolymerization charge density[17], and convenient device functionalization by electrophoretic blending with other molecules[2] that confer chemical and biological specificity to the device. Such molecules may be of biological origin such as polypeptides[18], enzymes[2,19,20], cofactors[21], antibodies, or may be inorganic catalysts such as heteropolyanions[22], semiconductor particles[23] or metallic inclusions[24].

During potentiostatic electropolymerization, the PPy film is grown at a fixed potential selected to induce charge transfer initiation of the monomer as well as growth and deposition of the polymer film. However, since the polymer generally has an oxidation potential that is lower than that of its monomer, the polymer is consequently grown under continuously oxidizing conditions leading to incorportion of counteranions. One major technological limitation to the development of viable chemical and biological sensor devices based on electroconductive polymers has been the poor adhesion of electroconductive polymers to device surfaces. Recently, Nishizawa et al.[25] reported on the use of surface pretreatment to facilitate lateral growth of

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polypyrrole films onto and between gold microband electrodes. Yon-Him et al.[26] have also demonstrated the co-electropolymerization of 1-pyrrolyl functionalized glucose oxidase leading to specific attachment of active GOx within electropolymerized polypyrrole films. These works address scientific issues of technological significance to chemical and biosensor devices based on electroconductive polymers. In this paper we report on another such issue - the development of a simple chemical modification and derivitization scheme to promote specific adhesion of electropolymerized polypyrrole films formed on interdigitated microsensor array electrodes (IMEs) of gold on borosilicate glass and/or oxidized silicon. IMEs of 10 μm line and space dimensions were derivatized by chemical modification with 3-aminopropyltrimethoxysilane followed by direct linking of the 1° amine to the carboxylic acid of 3-(1-pyrrolyl)propionic acid using the heterobifunctional linker N-hydroxysulfosuccinimide enhanced 1,3-diisopropylcarbodiimide in aqueous solution. The use of termnally active silanes and heterobifunctional crosslinkers for specific immobilization is quite common[27].

The 3-(1-pyrrolyl)propionic acid is shown to be electroactive, electropolymerizable, and co-electropolymerizable with pyrrole under the conditions commonly used for the electropolymerization of pyrrole. Electroconductive PPy films grown on these ω-(1-pyrroyl) derivatized IME devices were allowed to bridge the interdigit space and so be co-electropolymerized with ω-(1-pyrrolyl) moieties specifically attached to the interdigit space of the device. This leads to specific attachement of the electropolymerized PPy film to the surface of the device. Films grown in this way were compared to films similarly grown on unmodified IME devices, on IME devices rendered hydrophobic by chemical modification with the the *n*-alkylsilane -- dodecyltrichlorosilane, and on devices modified with 3-aminopropyltrimethoxysilane - the precursor to ω-(1-pyrrolyl) derivatization. Films grown on ω-(1-pyrrolyl) derivatized IME devices show no difference in polymer film growth kinetics compared to the other surfaces. Films grown on ω-(1-pyrrolyl) derivatized IME devices and on 3-aminopropyltrimethoxysilane modified surfaces display some modest variation in electroactivity as measured by cyclic voltammetry but are otherwise the same. PPy films grown on ω-(1-pyrrolyl) derivatized IME devices display

significantly enhanced adhesion compared to films grown on any the other surfaces studied. Films readily pass the Scotch® tape test and did not disbond after six weeks of continuous immersion in PBS 7.2 buffer or when maintained dry under vacuum and over molecular seives. This is to be compared to unmodified IME devices and dodecylsilane derivatized IME devices from which the film fails the Scotch™ tape test and readily disbonded after 3 days and after 5 days of immersion in PBKCl pH 7.2 buffer respectively. The time to adhesive failure in both test environments occured in the order unmodified < dodecyltrichlorosilane modified << 3-aminotrimethoxysilane modified << ω-(1-pyrrolyl) derivatized. The failure times were 3 days < 5 days << 27 days << 36+ days for films immeresded in aqueous PBKCl pH 7.2 buffer and were 3 days < 36+ days << 36+ days << 36+ days for films stored dry and under vacuum. The combined electrochemical and adhesion test evidence suggest that the PPy films are specifically immobilized to the ω-(1-pyrrolyl) derivatized IME devices and that specific immobilization overcomes the hydrolytic instability of the PPy/glass interface under aqueous immersion conditions.

EXPERIMENTAL

Instrumentation

Potentiostatic electropolymerization of pyrrole was carried out using an EG&G PAR 173 Potentiostat/Galvanostat outfitted with a PAR 179 Digital Coulometer. Where needed, potentiodynamic sweeps were accomplished by interfacing the PAR 173 to a PAR 175 Universal Programmer and cyclic voltammograms were recorded on an Esterline Angus XYY' 540 Recorder. Cyclic voltammetric characterization of pyrrole monomer and electropolymerized polypyrrole films was carried out using an EG&G PAR Model 273 Potentiostat/Galvanostat interfaced to an ACER 486 33MHz PC outfitted with EG&G PAR's Model 270 data acquisition and instrument control software. Electropolymerized polypyrrole films fabricated on Interdigitated Microsensor Electrodes (IMEs) were also characterized by Electrochemical Impedance Spectroscopy (EIS) over the range 1 mHz to 100 KHz using a Schlumberger Solartron 1250 Frequency Response Analyzer (FRA) interfaced through the EG&G 273 Potentiostatic to a three electrode impedance cell. The FRA-Potentiostat combination was similarly interfaced to the ACER 486PC outfitted with EG&G PAR's Model M388 data acquisition and instrument control software. Electrical conductivity measurements were made directly on the interdigitated microsensor electrodes using the small amplitude discontinuoues DC pulse technique of EPSIS (EG&G PAR).

Materials

3-(1-Pyrrolyl)propionic acid was synthesized using a procedure based on a modification of Blume's[28] method. Pyrrole (Py) was supplied by Aldrich and was used after distillation under reduced nitrogen pressure. 3-Aminopropyltrimethoxysilane (Aldrich), N-hydroxysulfosuccinimide (sulfo-NHS) (Pierce), 1,3-diisopropylcarbodiimide (DIPC) (Chemical Dynamics) and ($\alpha\alpha\alpha$-trifluro-*p*-tolyl)acetic acid (Aldrich) were purchased and used as supplied. The solvents acetone, 2-propanol, acetonitrile, and Omnisolve triply distilled water were used as supplied. Phosphate buffered potassium chloride (PBKCl), pH 7.2, was prepared in the standard way[25]. Planar gold

(PME-Au), planar platinum (PME-Pt) and micro Ag°/AgCl 3 M Cl⁻ reference electrodes (Model RE803) were supplied by AAI-ABTECH. The saturated calomel electrodes (SCE) were supplied by Fisher. Electropolymerization of polypyrrole (PPy) was done on Interdigitated Microsensor Electrodes Model IME-1550-M-P (AAI-ABTECH) schematically illustrated in Figure 1. The IMEs are suitable for a wide variety of sensor development applications and for materials characterizations of polymer thin films. The IME is fabricated from 1,000 Å of magnetron sputtered gold over 100 Å of adhesion promoting Titanium/Tungsten (Ti/W) on a chemically resistant, electronics quality Schott D263 Borosilicate glass substrate. The array possesses lines and spaces that are 15 microns each and consists of 50 finger pairs. The total interdigit area of the IME 1550-M device was 0.15 cm² on a chip that was ca 1.0 cm². For XPS analysis, surface chemical modification, functionalization, and derivatization was performed on 1 cm x 1.75 cm plates of the chemically resistant, electronics quality borosilicate glass as well as on oxidized silicon.

Procedures

Surface Modification and Derivatization   IME 1550-M microsensor devices were cleaned in a Branson 1200 Ultrasonic Cleaner by sequential washing - first in acetone, followed by 2-propanol and finally in Omnisolve water. Prior to silanization, the devices were cleaned for 5 mins in a UV/ozone cleaner, UV_Clean™ (Boekel Industries, PA), to remove adventitiously adsorbed organics. The chemically cleaned device was then immersed for 10 mins in a freshly prepared solution of 2% 3-aminopropyltrimethoxysilane in 95% ethanol/5% water. The adsorbed and hydrogen bonded silanol layer was rinsed profusely with ethanol then cured at 110°C for 10 mins before being cleaned again in a Branson 1200 Ultrasonic Cleaner by sequential washing - first in heptane, followed by acetone, then 2-propanol and finally in Omnisolve water. Surface modification with dodecyltrichlorosilane was similarly performed from a 2% solution in anhydrous ethyl alcohol. The surface modified device was then derivatized by immersion into a freshly prepared *aqueous* solution containing N-hydroxysulfosuccinimide (Sulfo-NHS) (0.1 mg/ml), 1,3-

Diisopropylcarbodiimide (DIPC) (0.1 mg/ml) and 3-(1-pyrroyl)propionic acid (0.1 mg/ml). The device was stirred gently and allowed to incubate for 1 hr at 20°C to derivatize the surface. Where derivatization with ($\alpha\alpha\alpha$-trifluro-*p*-tolyl)acetic acid was needed, the 3-(1-pyrroyl)propionic acid was replaced with ($\alpha\alpha\alpha$-trifluro-*p*-tolyl)acetic acid of equivalent concentration. Following derivatization, the device was made the working electrode in a three electrode electrochemical cell in which a clean Pt mesh electrode served as the counter electrode and the micro Ag°/AgCl, 3 M Cl⁻ served as the reference electrode. Cathodic cleaning of the electrode was then carried out by repeatedly cycling between -1.2 V and -2.0 V vs Ag/AgCl, 3 M Cl⁻ for eight minutes in pH 7.2 PBKCl. The device was then rinsed in Omnisolve water before being transferred to the pyrrole electropolymerization solution.

Potentiostatic electropolymerization of polypyrrole films at the surface of unmodified, modified, and modified and derivatized IME 1550-M devices was carried out by applying a potential of +0.65 V vs Ag°/AgCl, 3 M Cl⁻ to the combined/shorted electrodes of the IME device so that the film grew on each electrode and also between the digits of the pair of electrodes. The electropolymerization bath was prepared to contain 1.0 M pyrrole, 5% poly(styrenesulfonic acid), 1% dodecylbenzenesulfonate (sodium salt) and 1 mg/ml poly(l-lysine) at a pH of 3.0 and maintained at a constant temperature of 20°C in an EG&G PAR Model K2064 water-jacketed micro-electrochemical cell. The constant temperature was produced using a Lauda K-2/T refrigerated constant temperature circulator. Films were electropolymerized to a total anodic electropolymerization charge density, Q_e, of 2.9×10^{-3} C/cm². At the end of each electropolymerization, the devices were removed, rinsed thoroughly in 0.1 M KCl and characterized by cyclic voltammetry (CV), EPSIS conductivity testing, AC Electrical Impedance Spectroscopy, and adhesion testing.

CV Characterization of electropolymerized polypyrrole films was done in deaerated 0.10 M KCl at 20°C by performing single scans at 50 mV/s over the range -1.0V to +1.00 V vs SCE. The anodic charge density (total anodic charge per unit area), Q_a, (mC/cm²), measured in this manner was used as the standard method for the characterization of electropolymerized polypyrrole films.

EPSIS™ Conductivity Testing was performed on freshly electropolymerized PPy films in aqueous PBKCl pH 7.2 buffer. EPSIS uses a nonpurtubating interrogation method of small amplitude (10 mV), discontinuous (50 ms pulse, 100 duty cycle), DC pulses superimposed on the open circuit potential of the electroconductive polymer film[5,9] This yields the electrical conductivity as a function of time following electrolysis at a particular potential or redox composition. Films were electrolysed for 3 mins at potentials corresponding to the $E^{o'}$ measured by CV analysis prior to interrogation and were interrogated for 10 cycles or 5.5 secs.

AC Electrical Impedance Spectroscopy of electropolymerized polypyrrole films was performed using small amplitude sine waves of 20 mV peak-to-peak voltage over the range 1 mHz to 100 KHz in deaerated 0.1 M KCl at 20°C. The offset potential was choosen as the $E^{o'}$ for each polymer film as determined by CV analysis. For these measurements, the pair of electrodes of the 1550-M device served as working and counter electrodes respectively, while the Ag°/AgCl, 3 M Cl⁻ served as a reference electrode in solution. The impedance measured in this way is therefore the impedance in the plane of the film. The goal of impedance measurements in this configuration is to monitor incipient hydrolytic destabilization of the polymer film/device interface.

X-ray Photoelectron Spectroscopic Analysis of the silanized and functionalized device surface was performed on a modified Hewlett Packard 5950A ESCA spectrometer using a monochromatized Al Kα radiation source at 1486.6 eV. The base pressure of the analyzer chamber was maintained below $5x10^{-9}$ torr during analysis. All spectra were charge compensated by using C1s at 285.0 eV as the energy reference. The spectra were smoothed by the Savitsky-Golay method at a degree of 9.

Adhesion Testing of electropolymerized polypyrrole films grown on interdigitated microsensor electrode devices was performed using the familiar Scotch® tape test. The test was performed by rubbing on a strip of Scotch® tape over the approximately 1 cm² area of the device and with a smooth and continuous motion lifting the tape off begining from one end. The adhesion of polypyrrole films to the various device surfaces was tested in this way under both wet and dry

conditions. Adhesion tests on each of the four types of surfaces studied were performed in lots containing triplicate samples for each of the two test environments. Duplicate lots were performed leading to a total of 48 samples tested.

Wet Adhesion Measurements: Following electropolymerization films were rinsed in omnisolve water and transferred to 0.1 M PBKCl 7.2 buffer and maintained under immersion at room temperature. Triplicate Scotch® tape tests of each surface variation were performed at time zero and repeated after 24 hour intervals until adhesive or cohesive failure occured in all three samples. Prior to performing the test, samples were sapped dry using lintfree paper towels.

Dry Adhesion Measurements: Following electropolymerization films were rinsed in omnisolve water and transferred to a vaccum dissicator and stored over indicating molecular sieves at room temperature. Triplicate Scotch® tape tests of each surface variation were performed at time zero and repeated after 24 hour intervals until adhesive or cohesive failure occured in all three samples.

Synthesis of 3-(1-pyrrolyl)propionic acid was accomplished using a procedure analogous to Blume's method[28] which was modified as follows: A dry, nitrogen purged flask equipped with an internal thermometer was charged with pyrrole (3.8 mL, 55.0 mmol) and benzyltrimethylammonium hydroxide (0.3 mL, 0.8 mmol, 40 wt % solution in methanol). To this solution was added acrylonitrile (2.9 mL, 55.0 mmol) without allowing the reaction temperature to rise above 40°C. After the addition was complete the reaction was stirred for 24 hours. The crude nitrile was then hydrolyzed by adding potassium hydroxide (4.0 g, 71.4 mmol) in 10 mL of water to the reaction mixture and heating to reflux for 2 hours. After allowing the reaction to cool to room temperature, the product was isolated by acidification with 6 N HCl followed by extraction with ether (4x). The combined organic extracts were dried over anhydrous sodium sulfate and the solvent removed *in vacuo* to give a product which was purified by distillation (127 °C/3 mm Hg) to afford 6.0 g (78%) of the title compound as a white solid -- Mp 59°-60° (lit. 59°-60° (xx)). FT-IR (KBr) 2964 (br), 1717 (br), 1497, 1441, 1405, 1364, 1333, 1282, 1251, 1210, 1169, 1087, 1061, 923, 733, 620 cm-1. ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.6. (t, J = 2.1 Hz, 2 H), 6.13 (t, J = 2.2 Hz, 2 H), 4.19 (t, J = 6.8 Hz, 2H), 2.82 (t, J = 6.8 Hz, 2 H).

RESULTS AND DISCUSSION

Interdigitated microsensor array electrodes (IMEs), suitable for the development of conductimetric chemical and biological sensors based on electroconductive polymers, were chemically modified to provide for the specific adhesion of electropolymerized polypyrrole thin films. To achieve specific adhesion of electropolymerized PPy films, the interdigit space of the IME device (Figure 2.a) was functionalized with an ω-(1-pyrrolyl) derivative. The ω-(1-pyrrolyl) derivatized interdigit spaces resulted from a simple two step modification and derivatization procedure in which the borosilicate glass surface was first modified via silanization with 3-aminopropyltrimethoxysilane and the primary amine of the siloxane monolayer directly linked to 3-(1-pyrrolyl)propionic acid using carbodiimide linking chemistry[29]. This yielded the derivatized interdigit space illustrated in Figure 2c. To compare the effectiveness of the specific adhesion promoter, similar devices were rendered hydrophobic by modification of their interdigit spaces with the long chain *n*-alkane dodecyltrichlorosilane (Figure 2d) or rendered hydrophilic by modification with 3-aminopropyltrimethoxysilane (Figure 2b) -- the ω-(1-pyrrolyl) precursor. To facilitate XPS analysis of the modified and derivatized surfaces and to permit determination of coverage and conversion efficiencies from XPS data, glass surfaces were also derivatized with (α αα-trifluro-*p*-toyl)acetic acid to yield the derivatized surface shown in Figure 2e. Figure 2 therefore summarizes the various steps used in the surface modification and derivatization of the IME devices.

X-ray Photoelectron Spectroscopic Analysis of Chemically Modified Surfaces

XPS analysis of the silanized and functionalized device surfaces was performed on a modified Hewlett Packard 5950A ESCA spectrometer using a monochromatized Al Kα radiation source at 1486.6 eV. The spectra were smoothed by the Savitsky-Golay method at a degree of 9.

Specific Immobilization Samples for XPS Analysis

Surface Modification	Silicon Surface	Glass Surface
Blank (no modification, same process steps)	Three (3) samples	Three (3) samples
3-Aminopropyltrimethoxysilane -- silanized	Three (3) samples	Three (3) samples
3-Aminopropyltrimethoxysilane -- silanized and linked to 3-(1-pyrrolyl)propionic acid -- functionalized	Three (3) samples	Three (3) samples
3-Aminopropyltrimethoxysilane -- silanized and linked to (α,α,α-Trifluro-*p*-tolyl) acetic acid -- functionalized	Three (3) samples	Three (3) samples

Samples in triplicate to be analyzed on both glass and silicon substrates:

Regions to be analyzed on each sample are the N_{1s}, C_{1s}, F_{1s}

Background analysis on blank samples.

Curve fit analysis for surface coverage of $-NH_2$ on 3-Aminopropyltrimethoxysilane --silanized.

Curve fit analysis for surface coverage of $-NH_2$ and N of ω-(1-pyrrolyl) and ratio of both.

Curve fit analysis for surface coverage of -F on α,α,α-Trifluro-*p*-tolyl) acetic acid -- functionalized.

Electroactivity and Electropolymerization 3-(1-Pyrrolyl)propionic acid

In order to effectively serve as a specific adhesion promoter, the immobilized ω-(1-pyrrolyl) moiety must be co-electropolymerized with pyrrole monomer drawn from solution and so form specific anchorage sites within the coherent and adherent polypyrrole layer on the IME device. The immobilized ω-(1-pyrrolyl) must therefore itself be electroactive and must be electropolymerizable under the conditions of electropolymerization established for pyrrole. The electroactivity of 3-(1-pyrrolyl)propionic acid was investigated to determine if it could be anodicly oxidized and so possibly participate in electropolymerization, whether on the surface or in solution. 3-(1-Pyrrolyl)propionic acid was shown to be electroactive by cyclic voltammetry at a planar gold electrode in aqueous 2.5 mM polystyrene sulfonate (PSSA)/2.5 mM dodecylbenzenesulfonate (DDBS) at pH 2.5. The supporting electrolyte of PSSA and DDBS has a pH of 3.0. The addition of 0.2 M 3-(1-pyrrolyl)propionic acid reduced the pH to 2.5. Figure 3 shows the first oxidation wave of pyrrole monomer, 3-(1-pyrrolyl)propionic acid monomer, and a 50 mole % mixture of pyrrole monomer and 3-(1-pyrrolyl)propionic acid, each compared to the blank background electrolyte. CV scans were recorded over the range 0.0 V to 1.1 V *vs* SCE at a scan rate of 50 mV/sec using a 1.18 cm^2 planar gold electrode in aqueous PSSA/DDBS solutions at 20°C. At a concentration of 0.2 M, pyrrole solutions (pH = 3.4), 50 mole % pyrrole and 3-(1-pyr olyl)propionic acid solutions (pH = 2.8), and the supporting electrolyte (pH = 3.0) were individually pH adjusted to a pH of 2.5 by the addition of HCl.

A single irreversible oxidation peak commencing at ca. 0.5 V *vs* Ag°/AgCl, 3 M Cl⁻ can be seen in all three cases, thus confirming the electroactivity of 3-(1-pyrrolyl)propionic acid and 50 mole % mixtures of pyrrole and 3-(1-pyrrolyl)propionic acid. The pyrrole monomer does however show a considerably higher oxidation current compared to 3-(1-pyrrolyl)propionic acid and to the 50 mole % mixture of pyrrole and 3-(1-pyrrolyl)propionic acid. This may in part be due to more efficient adsorption of pyrrole monomer at the gold electrode. Interestingly, the 50 mole % mixture exactly mimics the electroactivity of 3-(1-pyrrolyl)propionic acid of equivalent concentration and the anodic current density of both is approximately half that of pyrrole

monomer of equivalent concentration.

The electropolymerizability of 3-(1-pyrrolyl)propionic acid monomer and the 50 mole % pyrrole and 3-(1-pyrrolyl)propionic acid mixture were also investigated and compared to the well established electropolymerizability of pyrrole[30]. When held at a potential of 0.65 V *vs* Ag°/AgCl, 3 M Cl⁻, the solution of 3-(1-pyrrolyl)propionic acid and the 50 mole % pyrrole and 3-(1-pyrrolyl)propionic acid mixture, like pyrrole, each produced a coherent black polymer film at a planar gold electrode. This confirmed the ability of 3-(1-pyrrolyl)propionic acid to the electropolymerized and further suggests that it may be readily co-polymerized with pyrrole. Films of the various polymers were grown from aqueous 0.25 mM PSSA/0.25 mM DDBS solutions at 20°C to a total electropolymerization charge, Q_e, of 70 mC/cm². Linear sweep cyclic voltammetry (CV) at a 10 mV/s sweep rate over the potential range -1.00 V to 0.00 V *vs* Ag° /AgCl, 3 M Cl⁻ was performed in deaerated 0.10 M KCl and was used as a standard method to characterize these various electropolymerized polypyrrole films. The integrated anodic current obtained in a single sweep over this range served to establish the anodic charge density, Q_a (mC/cm²), of the film. The anodic charge density, Q_a, obtained in this way was used to evaluate and compare the electroactivity of the various polypyrrole films formed from the various monomer solutions. Figure 4 shows the cyclic voltammograms of the various potentiostatically electropolymerized polypyrrole films obtained under these standard conditions. Films display the expected oxidation and reduction half waves[30] associated with polypyrrole. The characteristic anodic charge density, Q_a (mC/cm²), is shown as the shaded area of Figure 4. Table 1 summarizes key electrochemical characteristics of these various polymer films.

Poly(3-(1-pyrrolyl)propionic acid) films of equivalent electropolymerization charge density required electropolymerization times as much as ca. 3.5 times as long compared to polypyrrole films. Under these conditions the poly(3-(1-pyrrolyl)propionic acid) films were very poorly adhered to gold or to platinum electrodes at either neutral or at low pH and they lacked the physical integrity of polypyrrole films or of the copolymer films. The poly(3-(1-pyrrolyl)propionic acid) film rapidly disbonded during any attempt to obtain the anodic charge density via cyclic

voltammetry. Films formed from 50 mole % pyrrole and 3-(1-pyrrolyl)propionic acid required only slightly longer electropolymerization times but contained approximately half the charge density of polypyrrole films, had a more positive $E^{o'}$ suggesting a larger overpotential for oxidation, and displayed a larger ΔE_p suggesting a greater influence of the 3-(1-pyrrolyl)propionic acid monomer on the diffusion of potassium ions into and out of the film.

Electropolymerization of Polypyrrole Films on Surface Modified IME Devices

Having established the electroactivity and electropolymerizability of 3-(1-pyrrolyl)propionic acid, and the co-electropolymerizability of 3-(1-pyrrolyl)propionic acid with pyrrole it was possible to approach with confidence the electropolymerization of polypyrrole films onto surface modified IME devices. Polypyrrole (PPy) films were potentiostatically electropolymerized from pyrrole monomer at 0.65 V *vs* Ag°/AgCl, 3 M Cl⁻ from aqueous 0.25 mM PSSA/0.25 mM DDBS solutions at 20°C. Films were grown to a constant predetermined electropolymerization charge density, Q_e, of approximately 70 mC/cm². The time required to discharge each PPy film is a measure of the electropolymerization kinetics of polymer film growth on that device. The chemical surface modification of the interdigit space of the device had only a modest influence on the electropolymerization kinetics. PPy films grown on unmodified glass surfaces required the longest electropolymerization time of ca. 23 mins. Films grown on aminopropyltrimethoxysilane-modified surfaces required the shortest electropolymerization time of ca 16 mins. The electropolymerization time for the polypyrrole films grown on the various surfaces was observed to occur in the order; unmodified surface (23.17 mins) >> dodecyltrichlorosilane-modified surface (17.98 mins) > ω-(1-pyrrolyl) derivatized surface (17.17 mins) > 3-aminotrimethoxysilane-modified surface (16.10 mins). It is arguable that there is essentially no difference in the polymerization kinetics arising from the various substrate surface chemistries. Films were electropolymerized such that they completely bridged the interdigit space and formed a fully contiguous layer over the active device surface. In this way electrochemical, electrical, and adhesion measurements could be made on the film.

Electrochemical Characterization of PPy Films on IME Devices

Linear sweep cyclic voltammetry (CV) at a 10 mV/s sweep rate over the potential range -1.00 to 0.00V *vs* Ag°/AgCl, 3 M Cl⁻ in deaerated 0.10 M KCl held at 20°C was used as a standard method to characterize the electropolymerized polypyrrole films. The integrated anodic current obtained in a single sweep over this range served to establish the anodic charge density, Q_a (mC/cm²), of the film. The anodic charge density, Q_a, obtained in this way was used to evaluate and compare the electroactivity of the PPy films formed on the various interdigitated microsensor array electrodes. Figure 5 shows cyclic voltammograms of potentiostatically electropolymerized polypyrrole films grown over these chemically modified surfaces and obtained under these standard conditions. Films display the expected oxidation and reduction half waves[30] typical of polypyrrole with $E_{pa}^{1/2}$ centered around -0.42 V and $E_{pc}^{1/2}$ centered around -0.73 V *vs* Ag°/AgCl, 3 M Cl⁻. Films grown on unmodified surfaces and on dodecyltrichlorosilane-modified surfaces do however display a small shoulder in the cathodic half wave around 0.6 V *vs* Ag° /AgCl, 3 M Cl⁻. Table 2 summarizes important electrochemical characteristics of the polypyrrole films grown on these various chemically modified surfaces.

The anodic charge density, Q_a, of the polypyrrole films appears unaffected by the nature of the surface chemistry of the interdigit space over which the film is grown. Polypyrrole films grown on the various chemically modified surfaces all display a Q_a value of ca. 21 mC/cm2 with a conversion efficiency in each case of ca 30%.

In reviewing the electrochemical characteristics of polypyrrole films grown on these various chemically modified surfaces, the differences among them emerge as two distinct blocks -- The unmodified and purely hydrophobic dodecyltrichlorosilane-modified surface and the polar ω-amine surface of the 3-aminopropyltrimethoxysilane-modified and 3-(1-pyrrolyl)propionic acid derivatized surfaces. In addition to the shoulder at 0.6 V *vs* Ag°/AgCl, 3 M Cl⁻ on the cathodic half wave of the polypyrrole films grown on unmodified and purely hydrophobic dodecyltrichlorosilane-modified surfaces, these films also display the smallest ΔE_p values. The

most striking difference occurs between the purely hydrophobic dodecyltrichlorosilane-modified surface and the hydrophilic ω-amine surface of the 3-aminopropyltrimethoxysilane-modified surface. The dodecyltrichlorosilane-modified surface has a ΔE_p = 0.302 V which is smallest of all the surfaces examined. By contrast the ω-amine surface of the 3-aminopropyltrimethoxysilane-modified devices has a ΔE_p = 0.330 V which is largest of all the surfaces examined.

Electrical Characterization of PPy Films on IME Devices

The electrical conductivity of freshly electropolymerized PPy films were measured in aqueous PBKCl 7.2 buffer using the small amplitude (10 mV) discontinuous (50 ms pulse, 100 duty cycle) DC pulse method of EPSIS™. This nonpurtubating method[5,9] of electroconductive polymer interrogation gives the electrical conductivity as a function of time following electrolysis at a particular potential, and hence redox composition. Films were electrolysed for 3 mins at potentials corresponding to the E°' measured by CV analysis. The electrical conductivity was measured within 1 ms following electrolysis and the E°'.

PPy films fabricated on ω-(1-pyrrolyl) derivatized and on 3-aminotrimenthoxy silane functionalized device surfaces demonstrated a higher initial electrical conductivity compared to those films fabricated on the reference surfaces. Purely hydrophobic devices functionalized with dodecyltrichlorosilane and unmodified devices showed similar electrical conductivities.

The AC electrical resistance of electropolymerized PPy films was dertermined at 1 KHz with a peak-to-peak voltage of 20 mV RMS.

Adhesion of PPy Films to Chemically Modified IME Devices

Electropolymerized polypyrrole films grown on ω-(1-pyrrolyl) derivatized IME devices showed no disbondment when subjected to the Scotch™ tape test. There was no evidence of cohesive failure or adhesive failure of the films. This was true for films that were still wet following electropolymerization as well as for films that were dried over desiccant for 48 hours prior to testing. On the other hand, electropolymerized polypyrrole films grown on unmodified

devices as well as on dodecyltrichlorosilane-modified devices all failed the Scotch tape test. Both films showed clear adhesive failure as the films appeared to cleanly disbond onto the tape. Similarly prepared devices were immersed in aqueous PBS 7.2 buffer at room temperature and the time to spontaneously disbond noted. Devices were checked twice daily for evidence of liftoff. The PPy films display significantly enhanced adhesion to the ω-(1-pyrrolyl) derivatized IME devices. Films readily passed the Scotch™ tape test and did not spontaneously disbond after six weeks of continuous immersion in PBS 7.2 buffer. This is to be compared to unmodified IME devices and dodecylsilane derivatized IME devices from which the films fail the Scotch tape test and disbonded after 6-8 hours and after one day respectively.

Wet Adhesion Measurements: Rinse in omnisolve water. Soak in 0.1 M PBKCl 7.2 buffer at room temperature. Perform Scotch tape test after 24hrs. Repeat Scotch taspe test after further 24 hr periods until adhesive or cohesive.

Dry Adhesion Measurements: Rinse in omnisolve water. Place in a vaccum dissicator over indicating molecular sieves at room temperature. Perform Scotch tape test after 24hrs. Repeat Scotch tape test after further 24 hr periods until adhesive or cohesive failure.

Films were characterized by the time to adhesive failure using the Scotch® Tape following immersion in PBS 7.2 buffer or maintained dry under vacuum and over molecular seives. The time to adhesive failure in both test environments occured in the order unmodified < dodecyl modified << 3-aminotrimethoxysilane modified << ω-(1-pyrrolyl) derivatized. The failure times were 1 day < 3 days << 2 weeks << 6 weeks for films immeresded in aqueous buffer and were 1 day < 3 days << 4 weeks << 8 weeks for films stored dry under vacuum.

SUMMARY AND CONCLUSIONS

Acknowledgements

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Table 1. Electrochemical characteristics of various electropolymerized polypyrrole films formed on planar gold electrodes from 0.25 mM PSSA/0.25 mM DDBS at 20°C and electroanalysed by CV in 0.1 M KCl at 20°C over the range -1.0 V to +0.2 V vs SCE at a scan rate of 10 mV /sec.

	Pyrrole	50 mole % Pyrrole/3-(1- Pyrrolyl) propionic acid	3-(1-Pyrrolyl)propionic acid
Electropolymerization Time (min)	21.42	23.18	71.57
Electropolymerization Charge Density, Q_e, (mC/cm^2)	70.03	70.03	69.74
CV Anodic Charge Density, Q_a, (mC/cm^2)	61.14	33.34	-.
$E_{pa}^{1/2}$ (mV); $i_{pa}^{1/2}$ (mA)	-394 ; 1.219	-292 ; 0.740	-
$E_{pc}^{1/2}$ (mV); $i_{pc}^{1/2}$ (mA)	-662 ; -1.541	-652 ; -0.853	-
ΔE_p (mV)	268	360	-
$E^{0'}$ (mV)	-528	-472	-

Table 2. Electrochemical and electrical properties of electropolymerized polypyrrole films formed on various surface modified IME devices and electroanalysed by CV in 0.1 M KCl at 20°C over the range -1.00 V to +0.00 V *vs* Ag°/AgCl, 3 M Cl⁻ at a scan rate of 10 mV /sec.

	Surface Chemical Modification of the IME Interdigit Space			
	Unmodified	Dodecyl-trichlorosilane	3-Aminopropyl-trimethoxysilane, 3-(1-pyrrolyl) proprionic acid	3-Aminopropyl-trimethoxysilane
Electropolymerization Time (min)	23.17	17.98	17.17	16.10
Electropolymerization Charge Density, Q_e, (mC/cm^2)	69.98	70.01	69.97	69.94
CV Anodic Charge Density, Q_a, (mC/cm^2)	21.13	20.48	21.30	21.96
$E_{pa}^{1/2}$ (mV); $i_{pa}^{1/2}$ (mA)	-416 ; +0.415	-410 ; +0.432	-422 ; +0.421	-408 ; +0.437
$E_{pc}^{1/2}$ (mV); $i_{pc}^{1/2}$ (mA)	-725 ; -0.494	-712 ; -0.509	-740 ; -0.570	-738 ; -0.569
ΔE_p (mV)	309	302	318	330
$E^{0'}$	-571	-561	-581	-573
DC Resistance WET (Ω)				

Table 3. Time to adhesive failure using the Scotch tape test on electropolymerized polypyrrole films grown on the various chemically modified and derivatized IME surfaces.

Surface Modification	Dry Adhesion	Wet Adhesion
Blank (no modification, same process steps)	1day	1 day
Dodecyltrichlorosilane	3 days	3 days
3-Aminopropyltrimethoxysilane -- silanized	7 days	7 days
3-Aminopropyltrimethoxysilane -- silanized and linked to 3-(1-pyrrolyl)propionic acid -- functionalized	8 weeks	6 weeks

List of Figures

ELECTRODE 1
ELECTRODE 2

INTERDIGIT AREA

INSULATING SUBSTRATE

DELRIN STEM WITH
LEADWIRE CONNECTIONS

EPOXY ECAPSULANT

IME DEVICE

Fig. 1.

Fig. 2.

Py

3PyPA

Py/3PyPA

Blank

6

5

4

3

2

1

0

-1

I (mA)

-0.2   0.0   0.2   0.4   0.6   0.8   1.0   1.2

E (V) vs. SCE

Fig. 3.

File: CVA25.spg

PME118-Au-PPy/2.5mM PSSA-DdBSA-0.2M Py/pH2.5/10

Legend: —— PPY2510.DAT   - - - - - P2PA2510.DAT

Y-axis: I (mA)
X-axis: E (V) vs. SCE

Fig. 4.

A:\CVAPGE\

Blank
Unmodified
ASi
SiPy
DdSi

I (mA)
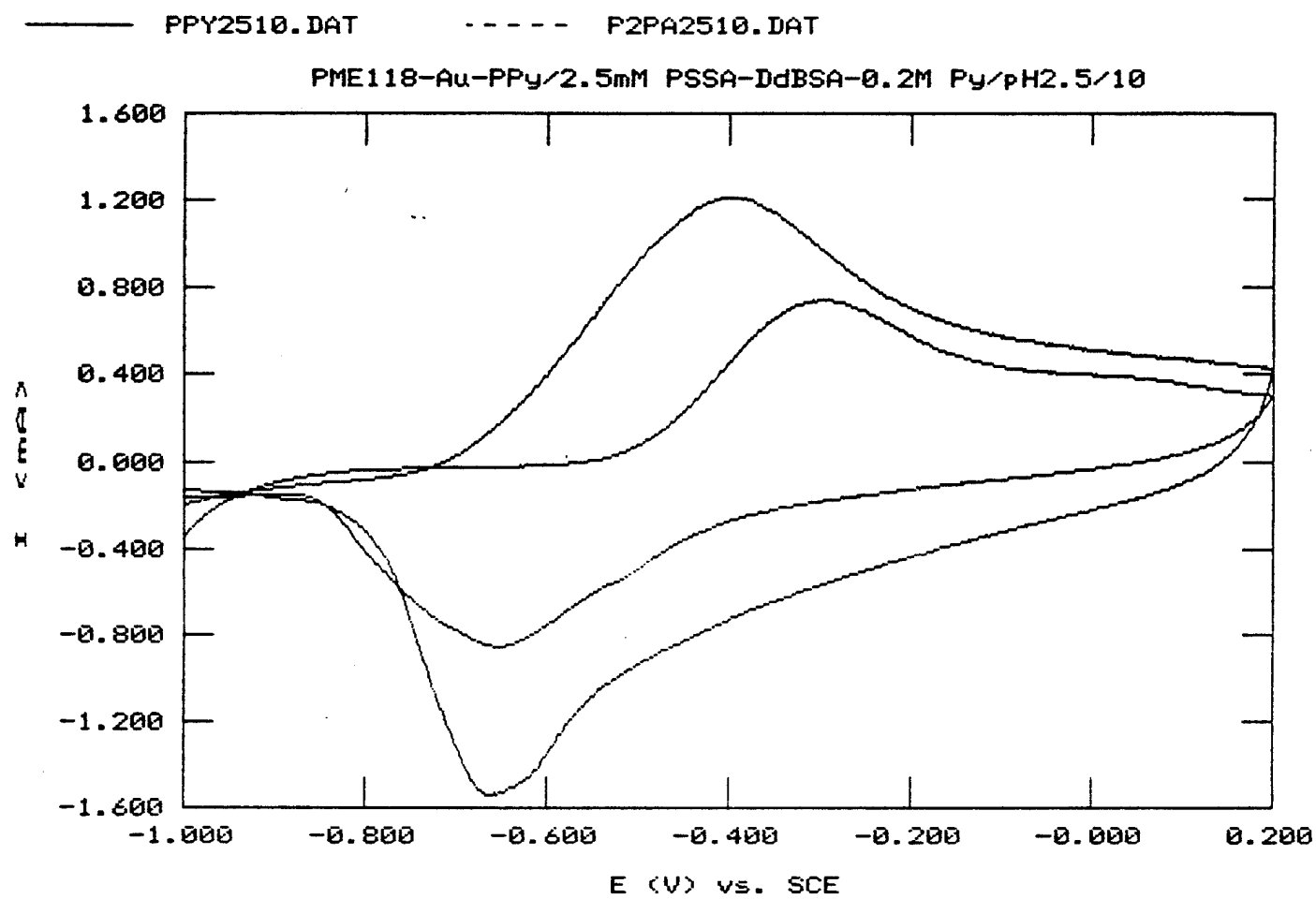
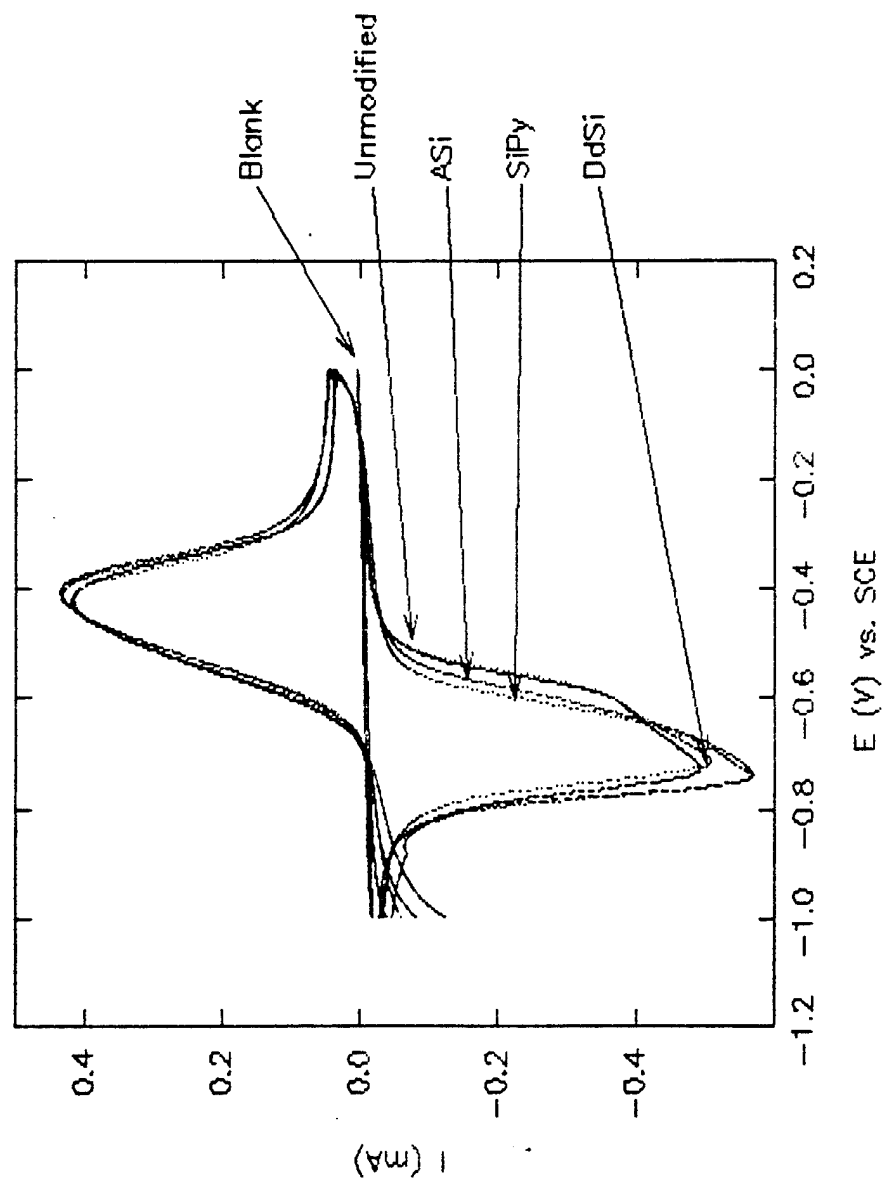0.4   0.2   0.0   -0.2   -0.4

-1.2   -1.0   -0.8   -0.6   -0.4   -0.2   0.0   0.2

E (V) vs. SCE

File: DatAna.spg

Fig. 5.