

Biomaterial Interfaces

Room: 317 - Session BI+AS+MN+NS-TuM

Biosensors

Moderator: Graham Leggett, University of Sheffield

8:20am **BI+AS+MN+NS-TuM2 An Inductive-Capacitive Sensor for Real-time Biofilm Growth Monitoring**, *Ekaterina Tolstaya, Y.W. Kim, S. Chu, K.D. Gerasopoulos, W.E. Bentley, R. Ghodssi*, University of Maryland, College Park

We present a real-time biofilm monitoring device based on inductive-capacitive (LC) sensing principles. Bacterial biofilms cause severe infectious diseases and environmental contamination. The bacterial biofilm's complex structure and composition, as well as its ability to exchange genetic information, result in a high tolerance for antimicrobial agents. As a result, established biofilms on implanted or external biomedical devices, such as catheters, are difficult to treat. Traditional antibiotic therapies for biofilm infections often require doses 500-5000 times larger than for non-biofilm infections [1]. Moreover, biofilm growth in environmental and industrial facilities causes contamination and corrosion of equipment due to the toxins generated by biofilms. Therefore, early detection of biofilm growth is critical to facilitate treatment of severe infections and prevent equipment contamination.

In this work, an LC sensor was fabricated using conventional lithography and metal deposition via E-beam evaporation (Cr/Au, 15 nm/200 nm) (Figure 1). The resonant frequency of the sensor was approximately 16 MHz in air at room temperature. A device sensitivity of 1140 Hz/dielectric was demonstrated using a known dielectric material (deionized water) (Figure 2). *Escherichia coli* W3110 biofilms were grown for 48 hours over the LC sensor and the resonant frequency of the sensor was measured every 80 seconds using a spectrum analyzer (Figure 3). As the biofilm grew over the device, an increase in the resonant frequency of the LC sensor was observed. This is due to the lower dielectric permittivity of the biofilm compared to that of the growth media (Luria Broth, $\epsilon \sim 80$), which results in decrease in the capacitance of the sensor. In control experiments with water and air as the media, a slight decrease in the resonant frequency was observed. The resonant frequency shift over time is in good agreement with the natural trend of biofilm growth (Figure 4) [2, 3]. The results validate the use of LC sensing for continuous monitoring of biofilm growth. This sensitive and reliable detection scheme, as well as the capability for flexible substrate integration and wireless interfacing, can serve as a foundation for the development of microsystems for real-time biofilm monitoring for both clinical and environmental applications.

8:40am **BI+AS+MN+NS-TuM3 The Interplay of Electrode Materials and Biomaterials in a Catechol-Modified Chitosan-Based Sensor for Clozapine Detection**, *Robert Dietrich, T.E. Winkler, H. Ben-Yoav, S.E. Chocron, E. Kim*, University of Maryland, College Park, *D.L. Kelly*, University of Maryland School of Medicine, *G.F. Payne, R. Ghodssi*, University of Maryland, College Park

We present a study of atomic layer-deposited TiN and electroplated Pt black (PtB) as candidate electrode materials to replace Au in a catechol-modified chitosan redox cycling system (Fig. 1) for the electrochemical detection of the antipsychotic clozapine (CLZ). In complex biological fluids like blood, interference from other electrochemically active species is a major challenge. The choice of electrode material is critical in addressing this challenge, as surface morphology and composition may produce a stronger and more reproducible CLZ signal, while shifting that signal away from potential interferents and improving the signal-to-noise ratio. Our electrochemical characterization results indicate that TiN is superior to Au as a sensor material, with a 2.6 times higher CLZ signal and a 3.2-fold lower variability.

Identifying electrode materials with high CLZ signal-to-noise ratio will greatly aid in translating our detection approach into a point-of-care monitoring system. Such a device will reduce the burden currently associated with CLZ due to safety and efficacy monitoring requirements [1], thereby improving the quality of life for people affected by schizophrenia. Our previous work [2] has relied on gold electrodes as a substrate for our catechol-modified chitosan films. These 5×5 mm² micro-fabricated planar gold electrodes serve as controls, which we further modified here with: TiN for its inert properties; and PtB for its high surface area and potential electrocatalytic activity (Fig. 2).

The fabricated electrodes were characterized using cyclic voltammetry. Bare Au yields an oxidative CLZ peak signal of 1.06 ± 0.20 μ A, compared to 5.20 ± 2.26 μ A when coated with chitosan-catechol (Fig. 3). TiN electrodes

produce a signal of 2.00 ± 0.26 μ A bare, and 13.7 ± 0.7 μ A when modified. The combination of higher signal and lower variability with the TiN is likely due to its inert chemical properties which also propagate more repeatable biomaterial modification. We observed a secondary peak with gold as well as bare TiN electrodes, likely due to interference related to chloride or oxygen. Modified TiN revealed only a single, CLZ-related peak. Results show that, as expected, signals from the bare PtB electrodes were 3370 times higher than from Au. However, they exhibited large variation between experiments, indicating the need for electroplating optimization. Testing the PtB electrodes with the chitosan-catechol film should increase both CLZ signal and resolution. Ongoing work is also focused on glassy carbon electrodes, which are expected to yield high repeatability by eliminating potential interfering oxygen signals in the redox cycling system.

9:00am **BI+AS+MN+NS-TuM4 Characterization of an Amperometric Glucose Sensor on a Flexible Polyimide Substrate for Continuous Glucose Monitoring and Insulin Delivery through Single Device**, *X. Du, J.R. Motley, A.K. Herman, Liney Arnadottir, G.S. Herman, X. Tan, J.F. Conley, Jr.*, Oregon State University, *W.K. Ward, R.S. Cargill, J.R. Castle, P.G. Jacobs*, Pacific Diabetes Technologies

Type 1 diabetes affects over one million people and every year more than 30,000 children and adults are diagnosed with type 1 diabetes in the United States alone. Patients with type 1 diabetes cannot produce their own insulin and depend upon glucose sensors to monitor their blood glucose and adjust insulin levels either by injection or an insulin pump. The continuous monitoring of glucose blood levels and automatic insulin release by an artificial pancreas is a promising alternative to current treatment options, and can significantly improve the comfort and quality of life for the patient. Here we introduce a flexible catheter with an integrated glucose sensor capable of both continuously measuring glucose levels and deliver insulin through a single catheter. The amperometric glucose sensor includes multiple Pt indicating electrodes, Ag/AgCl reference electrode, electrohydrodynamic jet (e-jet) printed glucose oxidase enzyme layers, and permselective membrane for optimal glucose response from the interstitial tissue. The compact design is integrated on a flexible polyimide substrate and requires high durability for all the components due to the small radius of curvature of the catheter. The e-jet printing provides digital patterning flexibility and highly precise deposition of the enzyme layer, which allows improved uniformity and accuracy of the glucose sensor. Here we will discuss characterization and optimization of the indicating and reference electrodes using electrochemical methods, scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), and time of flight secondary ion mass spectrometry. XPS was used to confirm full glucose oxidase coverage of the indicating electrode. Electrochemical testing indicates that e-jet printed glucose oxidase inks are still active towards glucose oxidation after printing and subsequent deposition of the permselective membrane. The operation and characterization of a fully functional glucose sensor integrated onto a catheter will also be discussed.

9:20am **BI+AS+MN+NS-TuM5 Chemically Modifying Graphene for Biosensing and Interfacing with Biology**, *Paul Sheehan*, Naval Research Laboratory, *S.C. Hernandez*, National Research Council, *N. Long*, Nova Research, *S.P. Mulvaney, J. Robinson*, Naval Research Laboratory, *R. Stine*, Nova Research, *C.R. Tamana, S.G. Walton*, Naval Research Laboratory

INVITED

Graphene has many properties that are highly suited for biological studies. For instance, its atomic thinness, high electrical conductivity, and simple production methods are ideal for biosensing. As another example, graphene can be attached to arbitrary substrates to lend them the chemical flexibility of carbon while adding only an ultrathin coating. For both biosensing and biofunctionalization, it is critical to produce high quality films that are precisely modified with the desired chemistry. For biosensing, the sensor must be functionalized for specific receptor-ligand recognition such as DNA-DNA or antibody-antigen binding. We will discuss our strategies for functionalization and the successful detection of specific DNA hybridization biologically-active field-effect transistors (BioFETs) based on chemically modified graphene. We will then discuss our use of graphene to interface biology with materials ranging from polymers to dielectrics to semiconductors. Graphene's incredible thinness enables its inclusion in more traditional sensing platforms as a non-intrusive functionalization layer, discreetly lending its chemical flexibility to other, more inert materials without otherwise impacting the sensing device.

11:00am **BI+AS+MN+NS-TuM10 Bioresorbable Sensors and Electronics**, *John Rogers*, University of Illinois at Urbana Champaign
INVITED

A remarkable feature of the modern integrated circuit is its ability to operate in a stable fashion, with almost perfect reliability. Recently developed classes of electronic materials create an opportunity to engineer the opposite outcome, in the form of devices that dissolve completely in water, with harmless end products. The enabled applications range from 'green' consumer electronics to bio-resorbable medical implants – none of which would be possible with technologies that exist today. This talk summarizes recent work on this physically 'transient' type of electronics and sensors, from basic advances in materials chemistry, to fundamental studies of dissolution reactions, to engineering development of complete sets of device components, sensors and integrated systems.

11:40am **BI+AS+MN+NS-TuM12 Surface Chemistry Enhanced Microbial Bioelectrocatalysis**, *Kateryna Artyushkova, C. Santoro, S. Babanova, J. Cornejo, L. Ista, A. Schuler, P. Atanassov*, University of New Mexico

Bioelectrochemical oxidation carried out by bacteria attached on a solid electrode is capturing the attention of scientists all over the world. Different species of bacteria have been shown as electroactive and being able to oxidize organic compounds releasing electrons that can be transferred to a conductive solid support. If the oxidation reaction is coupled with the oxygen reduction reaction (ORR), the degradation of organics could lead to a production of useful electricity and water. Those related aspects are currently utilized in the development of alternative and cost effective bioelectrochemical systems (e.g. microbial fuel cell (MFC)) for simultaneous organics removal and electricity production. Understanding the bioelectrocatalytic nature of organics dissimilation by bacteria and the subsequent internal and external electron transfer is of a high importance for the further development of these systems and a key moment in their future application.

In this work, an artificial approach for enhanced microbial bioelectrocatalysis was explored along with study of the parameters promoting bacteria external electron transfer. This approach consisted of artificial modification of electrode surfaces having, as a result, different surface chemistries. Mixed bacterial culture development, biofilm growth and electrochemical performance have been studied. Smooth gold surfaces were modified with organic thiols to form self assembled monolayers (SAMs) with various functional groups (-CH₃, -OH, -N(CH₃)₃ and -COOH).

Power curves and single electrode polarization curves have been taken to evaluate the performance of the MFC as a whole and of the electrodes separately. XPS analysis of electrodes was used to study the effect of chemistry on the performance. Confocal and SEM microscopy was used to study the bacteria biomass and biofilm development was tracked over time .

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