ELECTROCATALYSIS OF OXYGEN USING WATER SOLUBLE METAL Porphyrins and Chemicals. (U) Ohio State University Research Foundation Columbus, T. Kuwana 01 Nov 83

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ELECTROCATALYSIS OF OXYGEN
USING WATER SOLUBLE METAL PORPHYRINS
AND CHEMICALLY MODIFIED PORPHYRIN ELECTRODES

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Research Foundation
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ELECTROCATALYSIS OF OXYGEN USING WATER SOLUBLE METAL PORPHYRINS AND CHEMICALLY MODIFIED PORPHYRIN ELECTRODES

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iron porphyrin, oxygen, oxygen reduction, carbon, carbon surfaces, platinum, platinum particles, spectroelectrochemistry

Abstract
Primary effort was devoted to the study of oxygen reduction using water-soluble iron and cobalt porphyrins, namely, iron and cobalt tetrakis[N-methyl-4-pyridyl]porphyrin. These porphyrins with the metal in the +3 oxidation state can be electrochemically reduced to the divalent state which then reacted with oxygen. In the case of the iron containing porphyrin, oxygen was reduced at a bimolecular rate of ca. $1 \times 10^7$ 1/m/s to hydrogen peroxide which was then rapidly reduced to water. A mechanistic scheme was postulated for the reduction (continued)
and using experimentally determined parameters, current-potential curves were simulated. Good agreement between the experimental and computer calculated current-potential curves supported the proposed scheme. Cross-correlation between optical, electrochemical and magnetic circular dichroism results have provided axial ligation, dimerization and spin state information of the ferric and ferrous tetrakis[N-methyl-4-pyridyl]porphyrins. Glassy or graphitic carbon electrodes were rendered catalytic by the incorporation of iron porphyrin derivatives e.g., iron tetra-(o-amino-phenyl)porphyrin and iron tetra-[N-(2-hydroxyethyl)pyridyl]porphyrin in thin polymeric films adhering to the carbon. The extent of oxygen reduction to hydrogen peroxide and water depended on the amount of iron porphyrin.

In the case of the water-soluble cobalt tetrakis[N-methyl-4-pyridyl]porphyrin, it irreversibly adsorbed onto the glassy carbon surface and produced hydrogen peroxide as the main product with nearly a 100% current efficiency. It was found that the electron transfer rate between the adsorbed cobalt porphyrin and that in solution could be accelerated by the presence of thiocyanoate ion.

It was also deemed important to prepare in a predictable manner the surface of carbon electrodes and to be able to determine the physical and chemical nature of the surface. Radio frequency plasma was one method of introducing surface functional groups with the functionality dependent on the nature of the reactive gas. Surface topography of the carbon electrodes was determined by scanning electron microscopy and surface elemental and functional group analysis was by x-ray photoelectron and auger spectroscopy. Optical methods (FTIR reflectance, uv-vis spectroelectrochemistry) were also explored as part of our effort to analyze functional and molecular species on carbon surfaces.

Finally, it was discovered that metals could be electrodeposited as dispersed microparticles into a thin polymeric matrix of polyvinylacetic acid adhering on a glassy carbon surface. These microparticles were randomly dispersed through the polymer with a gaussian size distribution. Large surface areas of the metal could be achieved with low loading levels. The electrocatalytic generation of hydrogen and reduction of oxygen were studied.
AFOSR FINAL REPORT

November 1, 1983

The contents of this report contains the following:
a) 1978:1983 AFOSR supported personnel; b) list of publication resulting from
AFOSR sponsored research; and c) summary of research accomplishments.

a) PERSONNEL:

Senior Research Personnel:

Dr. Armand Bettelheim  Dr. Shu-Huan Weng
Dr. Dennis DiMarco  Dr. Jerzy Zak
Dr. Dale Karweik

Junior Research Personnel:

Graduate Students

Jui-Hsiang Ray Chan  Charles W. Miller
Paul Forshey  Marc D. Porter
Wen-Hong Kao  Lorraine Siperko

Undergraduate Students

Terry Harbaugh  Lorraine Jean Marshall
Kenneth Lyons  Robert Trask

b) LIST OF PUBLICATIONS:

"Rotating-Ring-Disc Analysis of Iron Tetra-(N-methylpyridyl)porphyrin in

"Electrocatalysis of Oxygen Reduction. Part III. Selective Reduction to
Hydrogen Peroxide Reduction or Water Using Polymeric Attachment of

"Electrochemical and Spectral Speciation at Iron

"Scanning Electron Microscopic and X-Ray Photoelectron Spectroscopic
Examination of Tokai Glassy Carbon Surfaces Subjected to Radio Frequency


C) SUMMARY OF RESEARCH ACCOMPLISHMENTS:

BACKGROUND In the mid-1970's it was proposed that the physical and chemical nature of electrode surfaces could be manipulated to "tailor" make
active sites for electrocatalysis. Early work were directed mainly to the immobilization of redox species (mediators) that accelerated electron transfer from the electrode to the solution species being catalyzed. The modes of immobilization were a) strong adsorption; b) covalent bonding; and c) incorporation into polymeric films. All of these modes have been demonstrated in our laboratory. To probe the physical and chemical nature of electrode surfaces, prior to, during and after various modifications, several optical and ultra-high vacuum spectroscopies were applied.

The research undertaken under AFOSR support was directed to the development of a catalyst for the electroreduction of dioxygen to water. We chose to work with metal porphyrins since they were known to catalyze oxygen. However, most investigators immobilized metal porphyrins to electrode surface via strong adsorption because of the limited water solubility of porphyrins. The mechanism of the electrocatalysis was difficult to determined as is the case with most heterogeneous reactions. Thus, we proposed to work with the water soluble, iron and cobalt porphyrins...soluble because of methylated or protonated pyridyls placed in the meso- positions of the porphyrin periphery. It was therefore possible to study the mechanism of oxygen reduction with these porphyrins homogeneously in aqueous solutions. The idea was to correlate the chemical and electrochemical behavior of these porphyrins in the homogeneous phase with their corresponding behavior as heterogeneous catalysts...made heterogeneous through appropriate immobilizations onto carbon electrode surfaces. It was also deemed important to prepare in a predictable manner the surface of the carbon electrode and to be able to determine physical and chemical nature of the surface. The carbon of choice was glassy carbon made by Tokai Co. (Tokyo) and radio frequency plasma was one method of treating the carbon surface. Surface topography was determined by scanning electron microscopy and surface elemental and functional group analysis was by x-ray electron and Auger spectroscopy. Optical methods (FTIR reflectance, uv-vis spectroelectrochemistry) were also explored as part of our effort to analyze functional and molecular species on carbon surfaces. Finally, it was important to model the proposed mechanism for oxygen electrocatalysis and to computer simulate the electrochemical response characteristics and compare them to actual experimental results.

RESULTS

1. ELECTROCATALYTIC REDUCTION OF MOLECULAR OXYGEN USING WATER-SOLUBLE AND IMMobilIZED IRON AND COBALT PORPHYRINS

Our work has centered around the water-soluble iron and cobalt tetrakis(N-methyl-4-pyridyl)porphyrins [abbr: Fe or CoTMPyP] and the structure of FeTMPyP is shown:
These metal macrocycles are rendered water-soluble via the cationic methylpyridyl groups on each of the meso-positions of the porphyrin ring.

In 0.1N H$_2$SO$_4$, Fe$^{III}$TMPyP undergoes a fast, one electron reduction to form Fe$^{II}$TMPyP at a highly polished glassy carbon electrode. The one electron stoichiometry was also verified by exhaustive electrolysis of a known amount of the compound in a thin-layer cell. There was no evidence of Fe$^{III}$/IIITMPyP adsorbing on the electrode surface. The formal potential, $E^0'$, for the reaction

$$\text{Fe}^{III}\text{TMPyP} + e^- = \text{Fe}^{II}\text{TMPyP} \quad (1)$$

was +0.18 V vs. NHE. From analysis of the current-time function for chronoamperometric experiments, a diffusion coefficient for Fe$^{III}$TMPyP of 2.0 (+0.4) x 10$^{-6}$ cm$^2$/s was determined. The rate constant for the electron transfer step of reaction 1 was evaluated to be 5.8 (+0.9) x 10$^{-3}$ cm/s by cyclic voltammetry. Optical spectroscopic (uv-vis) and electrochemical studies of Fe$^{III}$/IIITMPyP as a function of pH have indicated that in the acidic region below pH 4, the ferric species is a 5 coordinate, high spin iron. Similarly, the reduced ferrous porphyrin, as examined by magnetic circular dichroism, appeared to be in the high spin form. Thus, one can write the electrode reaction as involving the species

$$[\text{Fe}^{III}\text{TMPyP(H}_2\text{O})]^+ + e^- = [\text{Fe}^{II}\text{TMPyP(H}_2\text{O})]^+ \quad (1')$$

with the additional equilibrium reaction of

$$[\text{Fe}^{II}\text{TMPyP(H}_2\text{O})] + \text{H}_2\text{O} = [\text{Fe}^{II}\text{TMPyP(H}_2\text{O})_2]^+ \quad (2)$$

At pH > 4.5, a pH dependent electrode reaction occurs:

$$[\text{Fe}^{III}\text{TMPyP(OH)(H}_2\text{O})]^+ + e^- + \text{H}^+ = [\text{Fe}^{II}\text{TMPyP(H}_2\text{O})_2]^+ \quad (3)$$

which predominates at pH values above $pK_{a2}$ of Fe$^{III}$TMPyP and $pK_{a1}$ of Fe$^{II}$TMPyP. Another reaction with similar pH dependence would be

$$[\text{Fe}^{III}\text{TMPyP(OH)}_2]^+ + e^- + \text{H}^+ = [\text{Fe}^{II}\text{TMPyP(OH)(H}_2\text{O})]^+ \quad (4)$$
The monohydroxy species is present in varying concentrations over the pH range of 4-7. An additional complication is a monomer-dimer equilibrium

\[
2[\text{Fe}^{III}\text{TMPyP(OH)(H}_2\text{O})]^4 + 4 \xrightleftharpoons{K_F} [\text{Fe}^{III}\text{TMPyP(H}_2\text{O})]^8
\]  

(5)
in agreement with earlier reports. The dimer is reduced at a potential of -0.31 V and is independent of pH in the range of pH 7-12. The electrode reaction proposed is

\[
\text{dimer} + 2e^- + H_2O = 2[\text{Fe}^{II}\text{TMPyP(OH)(H}_2\text{O})]^3
\]  

(6)
where the dimer readily dissociates to the monomer ferrous porphyrin upon reduction.

In the presence of oxygen, the electrogenerated ferrous porphyrin produces an enhancement in the current function due to the catalytic reduction of oxygen. From an analysis of the cyclic voltammetric current-potential response curves as a function of pH and concentration ratios of iron porphyrin to oxygen, the following reaction sequence was proposed:

\[
\text{Fe}^{III}\text{TMPyP} + e^- \xrightarrow{k_5} \text{Fe}^{II}\text{TMPy}
\]  

(1)
\[
2\text{Fe}^{II}\text{TMPyP} + O_2 + 2H^+ \xrightleftharpoons{k_{f1}} 2\text{Fe}^{II}\text{TMPyP} + H_2O_2
\]  

(7)
\[
2\text{Fe}^{II}\text{TMPyP} + H_2O_2 + 2H^+ \xrightleftharpoons{k_{f2}} 2\text{Fe}^{III}\text{TMPyP} + 2H_2O
\]  

(8)
where reactions (7) and (8) reflected the reactant stoichiometry of the homogeneous steps. Hydrogen peroxide is an intermediate product in this mechanism. The above mechanism does not preclude the possibility of the 2nd electron in reactions (7) and (8) transferring from the electrode rather from another ferrous porphyrin. The reaction of the ferrous porphyrin to reduce hydrogen peroxide was experimentally verified.

Using stopped-flow kinetics and rotating ring disk electrode experiments,
the values of $k_f_1$ and $k_f_2$ were determined to be $1.5 \times 10^7$ and $2.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for 0.1 N H$_2$SO$_4$ solutions.

The cyclic voltammetric i-E profiles for the oxygen catalysis by iron porphyrin were simulated with use of the finite difference method. The computer programs were designed to account for the kinetic rates of both the heterogeneous electron-transfer rate, $k_s$, of reaction 1 and the homogeneous reactions, $k_f$, the differences in the diffusion coefficients of the reactants, the concentrations of the electroactive and other species in the reaction sequence (reactions 1, 7 and 8), and the stoichiometry of any homogeneous reactions. The results of this simulation are summarized in Table I, and the i-E profiles are shown in Fig. 1.

As may be seen in this figure, the shapes of the experimental and simulated i-E profiles are nearly identical over a wide range of scan rates for the concentration ratio used. The data in Table I indicate that the peak potentials agree within 4 mV and the peak currents within 4% between the simulated and experimental results...and give credence to the values of the kinetic rates within an estimated error of $\pm 10\%$. An iron porphyrin-oxygen complex was suggested as an intermediate in the mechanistic pathway. This intermediate could be reduced by another ferrous porphyrin or an electron from the electrode. Similarly, an iron porphyrin-hydrogen peroxide intermediate may also be formed and reduced in a similar pathway. Nonetheless, the results verified that an one electron reductant, the ferrous porphyrin, could rapidly
reduce oxygen to water, an overall 4-electron process, via an intermediate produce of hydrogen peroxide. This "2+2" electron stoichiometry for oxygen reduction is probably common to many of the iron macrocyclic compounds.

The computer simulation programs developed in our laboratory possess considerable flexibility to simulate the cyclic voltammetric response curves for a wide variety of different electrochemical mechanisms. They are available on request.

Immobilization of iron porphyrins onto glassy carbon electrodes were accomplished with the compounds of FeIII tetra-(o-aminophenyl)porphyrin and FeIII tetra-(N-(2-hydroxyethyl)pyridyl) porphyrin through amidization or esterification of the methylvinylchloride polymer. The extent of oxygen reduction to \( H_2O_2 \) and \( H_2O \) was dependent on the amount of iron porphyrin immobilized in the thin polymer film adhering on the glassy carbon surface. The above results demonstrated the catalysis of oxygen with a polymerically modified electrode.

The electrochemical properties of the corresponding water-soluble cobalt tetramethylpyridylporphyrin was quite different from that of the iron porphyrin. The cobalt porphyrin irreversibly adsorbed onto the glassy carbon surface and produced hydrogen peroxide with nearly 100% current efficiency. An interesting observation was that the electron transfer to the dissolved, solution CoIII/IITMPyP, presumably through an adsorbed layer of the cobalt porphyrin, was relatively slow resulting in a separation of the cathodic and anodic peak potentials by cyclic voltammetry of 100-150 mV's in 0.1N \( H_2SO_4 \). However, the rate of this electron transfer step can be accelerated by the addition of thiocyanate ion. The formation of the monothiocyanato complex of the cobalt(III)porphyrin corelated well with the observed rate enhancement.

2. RADIO FREQUENCY PLASMA INTRODUCTION OF SURFACE FUNCTIONALITIES ONTO CARBON AND SURFACE CHARACTERIZATION BY X-RAY PHOTOELECTRON SPECTROSCOPY
Radio frequency plasma (RFP) treatments have been used in our laboratory to produce physical and chemical modifications of glassy carbon surfaces. When RFP treatments are used to prepare surfaces to perform specific electrocatalysis, it would be desirable to limit the physical erosion of the carbon surface to the smallest amount necessary to remove surface impurities while still producing an optimal surface coverage of desired functionalities. Glassy carbon samples with heat-proof limits between 1000°C and 1500°C have shown the least susceptibility to surface damage. These samples also possess surfaces that are the most physically uncomplicated and therefore, electrochemical most desirable. The more reactive plasmas such as oxygen RFP produce more surface damage than the milder RFP's (water, carbon dioxide, ammonia or ethylenediamine).

In general the chemical changes induced in the surface by reactive gas RFP consist of incorporation of the desired functionalities and the removal of surface impurities. Although RFP's of gases containing oxygen-, nitrogen- and halogen-sources have been used, this report will be restricted to discussing results from the oxygen-sources on glassy carbon.

The oxygen-containing gases used were O₂ (USP grade), O₂ (99.6% pure), H₂O, CO and CO₂. The oxygen/carbon (O/C) ratio and the changes in the shape of the high resolution carbon peak of the x-ray photoelectron spectra provided evidence of surface functionalities and removal of deliterious surface impurities. Considerable effort was devoted to the development of a sample introduction system to maintain sample integrity during transfers, of hardware for computer data acquisition and manipulation, and software for curve smoothing, baseline correction and deconvolution of XPS spectra. Examples of XPS spectra for carbon-oxygen containing functionalities via RFP treated glassy carbon (Tokai GC-20 grade) are shown in Figure 2.
Fig. 2. High resolution carbon, C_{1s}, spectra following smoothing and baseline subtraction for various treatments. The treatments include: (a) O_{2}(Linde, 99.6%) RFP, (b) O_{2} (Liquid Carbonic, USP grade) RFP, (c) sample (a) following 90 min exposure to water vapor (double distilled, degassed), (d) water vapor (double distilled degassed) RFP, (e) sample (d) following post plasma treatment with a reducing agent, NaAlH_{2}(OCH_{2}CH_{2}OCH_{3})_{2} (Vitride, Hexcell Corp., Zeeland, Mich.) at 50°C for 4 hrs., and (f) sample (c) treated using the same conditions as in (e). The RFP treatments were performed with a gas pressure of 100 ± 20 mtorr and an applied RF power of 35 W.

The vertical lines drawn correspond to the binding energies associated with single bonded (+1.5 eV) and double bonded (+2.5 eV) functionalities found on homo-polymer samples. It is reasonable that an O_{2} RFP treated glassy carbon surface might contain ketone (or quinone)-like and hydroxyl (or phenol)-like surface functionalities as indicated by spectrum a of Fig. 2. The surfaces treated with USP grade (slightly wet) oxygen show a less well defined valley at ca. 1.5 eV higher BE, Fig. 2b, indicative of a slightly larger surface concentration of the hydroxy-like species. The changes produced by the plasma are graphically shown in the corresponding difference spectra, Fig. 2a' and 2b', respectively. Subtraction of the as-polished spectrum scaled to equal peak height, from each of the XPS spectra yields difference spectra which show a maximum at +2.5 eV and a shoulder at +1.5 eV. Water vapor RFP's introduced a lower concentration of oxygen functionalities onto the glassy carbon surface. However, it was possible to produce predominately hydroxylic surface with a mild post plasma chemical reduction using NaAlH_{2}(OCH_{2}CH_{2}OCH_{3})_{2} [called
Vitride, Hexcell Corp.], as shown by the carbon, C$_{1s}$, spectra of Fig. 2e and 2e'. The enhancement in the high BE shoulder at +1.5 eV indicates an increase of the hydroxyl-like species resulting from the Vitride reduction of higher oxidation state functionalities. The identity of the surface functionalities was confirmed by comparing the spectrum of the modified surface to a spectrum of poly-vinyl alcohol homo-polymer reference sample (Polysciences Inc., Warrington, PA). Coincidence of the spectra was confirmed by the matching of overlayed, deconvoluted spectra.

The above example, is to our knowledge, the first time that an oxygen functionality was introduced directly on carbon surface and identity proven by comparison with a known standard. Correlation of surface functionalities with the electrochemical response characteristics on carbon is an important area of research that needs to be continued. RFP treatments also appear to be a versatile method for the introduction of surface functionalities.

3. ELECTRODEPOSITION OF METAL MICROPARTICLES IN THIN POLYMERIC ADHERING ON CARBON ELECTRODE

During the study of immobilizing iron or cobalt porphyrins onto polymer/GC electrodes, it was discovered that metal could be electrodeposited into the polymeric matrix as dispersed microparticles. These particles were randomly dispersed throughout the polymer with a gaussian size distribution. Preliminary results indicated that the quantity and the particle size of the metal in the polymer could be controlled by the electrochemical method of deposition. Thus, large surface areas of the metal could be achieved with low loading levels. For example, H$_2$ could be electrogenerated at or near reversible potentials with as little as 10 ug/cm$^2$ (geometric area of electrode) of Pt. The polymer used was polyvinylacetic acid with an estimated
thickness of 100 nm or less. Oxygen reduction was also catalyzed by the Pt particles and the pH dependence of the potential and the exchange current density ($I_0$) were similar to those determined at smooth Pt. The $I_0$ calculation assumed that the total surface area, assuming spherically shaped particles, was electroactive.

The Pt particles dispersed in PVAA/GC were not removed by ultrasonic cleaning for periods up to 15 minutes. However, Pt particles deposited directly on the GC surface without polymer, the particles were readily removed by the ultrasonic treatment. The entrainment of the particles in the polymer apparently prevented particle aggregation.

Preliminary experiments have indicated that other metals such as Pd, Ni, Cd, and Ag could be similarly deposited into PVAA/GC. It should also be possible to disperse multilayer metals or alloys as particles into a variety of polymers on conducting and semiconducting substrates. Dispersed micro-particles in polymeric films coated on electrodes will be attractive for a variety of redox applications including photocatalysis.

4. FURTHER DEVELOPMENT IN OPTICAL ANALYSIS OF CARBON SURFACES AND SOLUTION-ELECTRODE INTERFACES

Our laboratory has continued the pioneering of methods for optically probing electrode surfaces and monitoring of species at or near the electrode-solution interface. For example, two new spectroelectrochemical thin-layer cells have been developed specifically for optical monitoring species using carbon electrodes. Because carbon electrodes are opaque, a very thin cylindrical "hole" was drilled through a glassy carbon electrode thereby creating an optically transparent, thin layer cell. The advantages of such a cell were that 1) the optical pathlength was much longer than conventional
optically transparent thin-layer cells (OTTLE); 2) OTTLE's could be readily fabricated with opaque conducting materials; and 3) small volumes and short electrolysis times could be achieved. The diffusional mass transport of electroactive species within the cyclindrical shaped hole was modelled by assuming that the finite volume elements consisted of a series of concentric cylinders. Excellent agreement was obtained between experimental and computer simulated results for the current-time or absorbance-time responses of the "holey" electrode cell. This cell will be useful for equilibrium and kinetic studies of redox reactions at carbon surfaces.

The second thin-layer cell was designed so that the electrode area to confined solution volume ratio was much larger than conventional thin-layer cell configurations. The light beam traversed the thin-layer solution parallel to the electrode surface. A typical cell had a solution volume of 12-14 uL, an electrode area of 1.5 cm², and an optically path length of 1.5 cm. Similar to the previously described cell, the measured optical absorbance is increased by virtue of the larger optical pathlength by ca. 100 times over a conventional thin-layer cell.

An interesting application of this cell will be to optically monitor the rate and quantity of solution species adsorbing onto an electrode surface. For example, a change in the optical absorbance, ΔA, of 0.002 A.U. can be determined by most high quality spectrophotometers. A change in concentration, ΔC, is given by

$$\Delta C = \Delta A / \varepsilon_{\lambda}$$

where $\varepsilon_{\lambda}$ is assumed to be 1,000 M⁻¹cm⁻¹ for the sake of the calculation, and the pathlength is 1.5 cm. The ΔC will be 1.33 x 10⁻⁶ M. For a thin-layer solution volume of 12 uL, a ΔC of 1.33 x 10⁻⁶ M corresponds to 1.6 x 10⁻¹¹ moles of electroactive chromophore. If a molecule has a size of 60 Å²/molecule, than a monolayer coverage in the closest packing arrangement
would be $5 \times 10^{-11}$ mole/cm$^2$. Thus, it becomes possible to quantitate the absorption of electroactive chromophores on an electrode surface with a sensitivity of ca. 3 times that required to give a monolayer coverage. The cross-correlation of electrochemical and spectral data for adsorption processes is predicted to provide heretofore unattainable information regarding quantitation of amount and rate of adsorption/desorption of reactants, intermediates and products involved in electrode reactions.

An objective of our laboratory in cooperation with funding support from other sources has been the development of optical methods to determine quantity and orientation of carbon functionalities and/or molecular species on carbon electrode surfaces. As part of this development, Fourier transform infrared external reflection and photoacoustic spectroscopies have been used to vibrationally characterize a thin film deposited on Pt and glassy carbon surfaces. It was experimentally observed, however, that the optical responses were substrate dependent (Pt vs. GC) and consequently, the mean-square electric fields as a function of the optical constants of the substrates and the films were calculated. It was found that the electric field intensity near the GC interface was much greater than that near the Pt interface. Therefore, it was concluded and experimentally verified, that greater sensitivity could be achieved to detect a thin film at the GC than the Pt surface, assuming that all other factors were constant. Such calculations will be important for the quantitation and understanding of infrared responses for thin films on a variety of electrode surfaces.