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TECHNICAL PROGRESS REPORT

entitled

PHOTON SCATTERING AND INTERACTION ANALYSIS
OF INTERFACIAL CORROSION AND CATALYSIS

MASTER

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TECHNICAL PROGRESS REPORT

Objectives The goal of this research program is to establish new, photon spectroscopic techniques as reliable tools with which to study fundamental and applied problems associated with the composition, structure, and evolution of the metal-electrolyte interface. In doing so we identify important prototypical systems as examples of the application of the new techniques. We have built our plan around surface enhanced Raman scattering with differential reflectance and photovoltage spectroscopy as supplementary techniques. Each of these experiments provides information of a different type. Raman is capable of revealing the molecular identity, orientation, and coordination of adsorbed material. Differential reflectance measures the electronic energy level changes as the interfacial region undergoes a spontaneous or externally induced change. And photovoltage spectroscopy yields information about the structure of semiconducting oxide overlayers. All of these techniques are used in situ, while the sample is exposed to the electrochemical environment of interest. Whenever possible we correlate our new information with the results of more traditional electrochemical experiments such as cyclic voltammetry, differential capacitance, and rotating ring-disc analysis.

Our program is divided into two major parts on the basis of the sample type. One component is concerned with the surface modification of metal electrodes through the controlled deposition of foreign metals. The optical, electronic, and chemical characteristics of the sample can be changed in this way. We hope to observe preferential chemical activity which is the key to specifically tailored electrodes. We will concentrate on the overlayers themselves--their vibrational and electronic properties--and on the interaction of the modified surfaces with probe molecule adsorbates. The second component of our program

deals with corrosion and corrosion protection. Because of its simplicity from an electronic and electrochemical perspective, copper has been chosen as the primary metal for study in this part of our plan. We will investigate molecular corrosion inhibitor adsorption using Raman and reflectance spectroscopies. Our aim is to understand the primary features of the action of inhibitors with the hope of being able to specify general trends which more effective inhibitors must conform to. Electrochemically grown copper oxides will also be investigated using Raman and photovoltage spectroscopies. We seek to understand the mechanism of oxidation through a better understanding of the corrosion product film. When these phenomena are understood on the pure metal we will expand the study to include copper alloys so as to gain an appreciation of the influence of multi-component substrate effects. By the time these studies have been completed we should be in a position to tackle the more technologically important alloys of iron, aluminum, and titanium.

Overview During the reporting period we have concentrated on understanding some of the fundamental characteristics of surface enhanced Raman scattering which is the primary technique in this project. We have established that the signal intensity alone cannot be used as a measure of the surface coverage of a surface Raman active molecule. We have added to the growing evidence in favor of metal adatoms as the active sites through which the most effective communication between the adsorbate demonstrating enhancement and the metal surface can take place. In application of the technique, we have characterized adsorbed water at the electrochemical interface, and have observed dramatic, applied voltage induced changes in the structure of the first layer of water. We have made significant progress on nearly all aspects of our underpotentially deposited metal monolayer program. This includes experiments in which the enhancement of a probe molecule was modified

by the presence of foreign metals both in the double layer and on the surface. We have evidence that, in some cases, the enhancement is communicated through a monolayer of Pb from to Ag pyridine. We have started investigations of corrosion inhibitors on Cu and have been able to identify the vibrational signature of the bond between the inhibitor and the metal surface.

Thiourea Characterization For a number of reasons having to do with other aspects of our program we have chosen thiourea as the ideal probe molecule with which to study the influence of surface modification by UPD on the nature of surface enhanced Raman scattering. In characterizing the state of adsorption of this molecule on Ag we discovered a number of interesting things. (a) The intensity of the scattering per molecule increases with decreasing applied voltage. This makes it difficult to use the scattered intensity as a measure of the surface coverage. It is a reflection of the chemical component of the enhancement. (b) The applied voltage induced changes in the vibrational frequencies indicate that the thiourea is bound to the surface through the sulfur end of the molecule, most probably in the perpendicular orientation. (c) Modes which, although Raman allowed for free thiourea, are very weak in a normal spectrum, become intense when the molecule is on the surface. This is a direct consequence of the adsorption perturbation of the molecule polarizability. (d) Thiourea is stable on the surface at very negative applied voltages, in contrast to pyridine at the same concentration. Thiourea also behaves very predictably in acid solutions. Together, these observations confirm our prediction that thiourea would be a very good probe molecule which is complementary to pyridine.

Adsorbed Water Characterization We have been able to identify the first layer of water at the interface between an aqueous electrolyte and Ag by using enhanced

Raman spectroscopy. We have shown that this water is most likely a monomer which is only weakly hydrogen bonded to its neighbors. However, the hydrogen bonding is strong enough so that the surface Raman active water is strongly influenced by its environment. We identify two major forms of surface water, both with their oxygen ends facing the metal under conditions where the metal is positively charged. The two forms differ in their degree of association with their neighboring water molecules. We see one form or the other dominate depending on the pH of the solution and on the cation in the solution. It is most probable that the surface Raman active water is preferentially associated with a Ag adatom which, in turn, is stabilized by adsorbed halide ions. It is not known as of yet, to what degree this association represents the majority of material at the interface. We have also shown that the applied voltage produces dramatic vibrational frequency shifts in the observed water. These data are being compared to X-alpha scattered wave LCAO calculations, including an applied field, for the vibrational frequencies of water. The calculations are being performed by Dick Messmer at the Corporate R & D Center at General Electric. Preliminary results for the scissors vibration show the correct trends.

Temperature Dependent Adatom Coverage One of the most highly quoted mechanisms for surface enhanced Raman scattering is an increased effective polarizability due to the participation of metal electrons in the scattering process. This may take place through the creation of electron-hole pairs in the metal which then interact with the adsorbate. An increased excitation probability of electron-hole pairs would result in more intense scattering. An atomic singularity would act as a site at which electron-hole pairs could be preferentially created in an interaction with the incident photon. Conditions which promote a high-concentration of surface adatoms of Ag should be good for the enhancement. We have

shown that the thermally induced migration of adatoms to kink sites on the surface leads to an irreversible loss of the enhancement. This result is similar to the results of experiments in vacuum at very low temperature. In our experiment, the adatoms are initially stabilized by adsorbed chloride ions. This makes it possible to perform enhanced Raman studies at room temperature in the electrochemical environment. However, upon increasing the temperature, we observed that the adatom stabilization was lost. We also demonstrated that the signals could be regenerated under conditions where a constant "rain" of adatoms was coming down onto the Ag by deposition from solution.

Metal Layer Modified Surfaces We have used thiourea and pyridine as probes of the surface enhancing ability of Ag which has been covered by sub-monolayers and multilayers of a foreign metal. To our surprise we observed irreversible partial intensity losses of previously established surface Raman signals merely upon exposure to metal cation containing solutions. This means that the cations are present in the double layer even before undergoing reduction, and that their influence on the enhancement is most likely through a disruption of the Helmholtz layer. When Pb is deposited in underpotential fashion a further significant loss in pyridine Raman intensity is observed. This loss can be recovered when the Pb is stripped away. At more negative applied voltages bulk Pb is deposited upon the UPD Pb but the Raman intensity is still observed. Finally, at a still more negative applied voltage the Raman intensity drops to very low levels as a current peak is registered in the electrochemical monitor. This is associated with the breakdown of active sites and the subsequent coverage of the exposed surface with metallic Pb. It is significant to note that, even under these circumstances a measurable, voltage dependent, surface enhanced pyridine signal is seen. It is also important to note that the vibrational frequency of the pyridine is

slightly shifted from its value in the absence of the Pb. This might be interpreted as evidence that the residual enhanced signal, when the Ag is entirely covered with Pb, is due to pyridine on the Pb which is on top of the Ag. If this is the case, it would be direct evidence that the long-range electromagnetic component of the enhancement reaches through at least one layer of Pb. More work is in progress on this point. We can say, however, that the majority of the observable enhancement is quenched by one layer of Pb--a direct confirmation of the importance of the short-range chemical component of the enhancement.

Metal Layer Stabilized Structures In contrast to the quenching observed when Pb is deposited onto Ag, Cu stabilizes the active site against irreversible destruction with negative voltage application. This is an indication that the halide induced stability of the active site, the adatom, is replaced by a cation stabilization. When Pb is additionally deposited upon the Cu stabilized surface it does not lead to irreversible decay as previously described. This again is evidence of the power of Cu to fix a particular configuration of Ag atoms on the surface so as to preserve the enhancement. This is important from the perspective of being able to create active surfaces which demonstrate enhancement under conditions which have previously led to loss of the surface signal.

Bulk Phonon Observation We have used underpotentially deposited layers to separate surface from bulk processes in the low energy vibrational spectra of noble metals. We have shown that, in contrast to most surface enhanced Raman spectra, features which are due to bulk defects also appear. When a monolayer of a foreign metal is deposited upon a substrate which demonstrates these features, the surface related spectra disappear while the vibrations due to bulk phonons are preserved. It is possible to detect the bulk phonons because momentum conservation is relaxed in a defect laden substrate. Further work is in progress

with regard to the correlation between bulk and surface scattering and, in particular, to the role played by surface adatoms in this correlation.

Corrosion Inhibitors on Copper We are studying mercaptobenzothiazole (MBTA) on Cu as an extension of earlier studies of the adsorption of benzotriazole in corrosive environments. MBTA is more interesting in that there are two dominant forms, the thione form, and the ionized thiol form, which possess very different Raman signatures. Depending on the pH and the applied voltage either form may be present at the surface of Cu. We see primarily the ionized thiol species in acid media. We expect that the most effective corrosion inhibition occurs through a polymerized network. It is most likely that the coordination of MBTA to the surface is through the nitrogen. This is based on the observation of a low energy feature around 280 cm^{-1} . Sulfur coordination would be expected to display vibrations at lower frequencies. In addition, the sulfur atom of the thiazole ring is expected to have weak coordinating ability because the orbitals of sulfur are already committed to the resonant structure of the molecule. When chloride ions are present in the solution we increase in the surface concentration of the thione species without losing the ionized thiol coverage. This is in contrast with what is observed from MBTA on Ag, where exclusive switchover takes place. This may be due to the multiple oxidation states which are possible with copper, or to a fundamental difference in the surface structure. These preliminary results are currently being expanded upon with more detailed studies of the Cu system.

Metal Surface Phonons in the Adsorbate Lattice Extensive efforts to detect the optical surface phonon due to an underpotentially deposited layer have thus far proven unsuccessful. There are numerous low energy features which were considered, however, most of these have been identified with bulk phenomena or with solution

species. There have been unpublished reports from other laboratories that these vibrations have been seen. The Northwestern group claims to have observed Pb on Au at 90 cm^{-1} and the Southampton group claims to have observed Pb on Ag at 300 cm^{-1} . We are extremely conservative when it comes to the publication of a discovery of this importance. We have identified a feature with Cu on Au which may be a surface phonon, however we are performing further tests to verify this conclusion. The rumored reports previously mentioned have not been duplicated. We feel that the Cu on Au system is the most favorable since the lighter metal overlayer will lead to higher energy vibrations which should be easier to detect. We also expect that the adsorbate lattice will be well behaved, in contrast to adsorbates whose ionic radius is larger than the inter-atomic spacing of the substrate.

Surface Topography Control In all of the surface enhanced Raman studies we would like to exploit the electromagnetic field enhancement which is associated with relatively large scale surface roughness. Since rough surfaces are poorly defined it is desirable to create controlled surfaces upon which the field enhancement is predictable. We have assembled a diffusion pumped evaporation system which is currently equipped with a quartz crystal thickness monitor and resistance heating of the evaporation charge. We have installed and are now repairing an old electron beam evaporation source as well. This system was resurrected from storage at RPI. We are using this system to grow Ag films on diffraction grating replicas so as to produce a substrate upon which surface plasmon coupling can be stimulated. Preliminary reflection monitoring of these gratings shows that they should perform satisfactorily, however, there is still a component of small scale roughness induced by the Ag evaporation process. We will try to perform Raman studies of these substrates, however we expect that we will have to make

our own gratings sooner or later. With that in mind we have initiated optical lithographic processing of photoresist layers on glass with the eventual goal of creating gratings with smooth sinusoidal profiles.

Solution Modulation Sample Chamber We have constructed and have tested the operation of the solution modulation chamber. It is capable of rapid, reversible exchange of the working solution in the electrochemical control of a sample while it is being studied with the Raman probe. This occurs while the sample and the two solutions are excluded from contacting oxygen. The chamber has not yet been tested in an experimental situation, however the first tests will involve preparation of the sample in a halide containing environment followed by exchange of the halide containing solution for the working solution. This will take place in an experiment designed to nail down the specific role of halide ions in stabilizing the Raman active sites.

Differential Reflectometer Using quartz fiber bundles, we have constructed a unique comparison reflectometer which is compatible with the Raman chamber currently in use. The incident and the detected beams are contained almost entirely in fiber bundles. This will allow us to measure the surface optical absorption induced by solution modification or by voltage changes. The incident light comes from an optical feedback stabilized Xenon lamp coupled through reflective components to a high throughput monochromator. We are interfacing this unit to our main micro-computer so that surface optical absorption can be measured while surface Raman data are being acquired on the same sample.

Contract Compliance The project as it has developed through the first seven months of work has complied with most of the contract stipulations. In particular,

the involvement of the Principal Investigator was 15% of his time during the academic year and 100% of his time during ten summer weeks. The only deviation from the original plan concerns the proposed post-doctoral associate position. Upon notification of the contract award recruiting efforts were immediately stepped up. This involved personal contact to numerous colleagues, the interview of one prospect in person, and a nationally publicized advertisement. After three months no suitable individual could be located. Those with the proper credentials were able to enter industrial jobs without post-doctoral training. We were unwilling to accept an individual who did not show reasonable promise from the start. The decision was made, at that point, to hire two extra graduate research associates instead of one post-doctoral fellow. This brought to four the total number of graduate assistants working on the project. It made it possible to start immediately on several fronts. Those who have started the work are unusually capable, requiring a minimum of instruction before being able to perform complex tasks for themselves. This scheme has worked out quite well. We will request that the project continue to support four graduate students in the future, as well as 15% of the Principal Investigator's time during the academic year and approximately one to two months of the Principal Investigator's time during the summer.

Bibliography

The following manuscripts have been submitted for publication under the sponsorship of this contract during the last six months.

"The Short Range Component of Surface Enhanced Raman Scattering: Thiourea Adsorbed on a Silver Electrode", accepted, Chemical Physics Letters, S. H. Macomber and T. E. Furtak.

"Enhanced Raman Characterization of Adsorbed Water at the Electrochemical Double Layer of Silver", submitted, Surface Science, S. H. Macomber, T. E. Furtak, and T. M. Devine.

"The Temperature Dependence of Surface Enhanced Raman Scattering: Evidence for Adatoms", submitted, Chemical Physics Letters, S. H. Macomber and T. E. Furtak.

"Current Understanding of the Mechanism of Surface Enhanced Raman Scattering" accepted, J. Electroanal. Chem., T. E. Furtak.