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Over the last two years our studies have focused on further studies of electrochemical reactions in liquid crystals as well as the use of x-rays as in-situ probes of electrochemical interfaces.

In the area of liquid crystals, we have studied the electrochemical response of electrodes modified with cholesteryl oleyl carbonate (COC; a cholestric phase with optical activity) and on the differences in the electrochemical responses of the optically resolved forms of $[\text{Ru}(\text{bpy})_3]^{+2}$ at such electrode surfaces.

We have investigated a wide range of preparations including the modification of electrode surfaces with polymer films containing COC as a dopant and have found these to exhibit a high degree of enantioselective discrimination (ca.20%) in the oxidation of (+) and (-) $[\text{Ru}(\text{bpy})_3]^{+2}$.

We have also investigated the effect of adding chiral supporting electrolytes such as 2,3 dimethoxy bis 1,4 dimethylamino butane and again, significant chiral discrimination was observed. ←

Most recently, we have begun a series of studies employing rotated disk techniques in order to assess the propagation distance of orientational effects in electrochemical processes in liquid crystal solvents by monitoring differences in behavior as a function of rate of rotation.

Concerning the use of x-rays as probes of electrochemical interfaces, we have shown that electrochemical techniques can be employed in the deposition of molecularly ordered films. The specific material employed was $[\text{Ru}(\text{v-bpy})_3]^{+2}$ which was electrochemically polymerized and the resulting film was characterized via the x-ray standing wave technique. A well developed angular modulation in the $\text{RuK}\alpha$ fluorescence intensity was indicative of an ordered layer.

We have also demonstrated the applicability of surface EXAFS (extended x-ray absorption fine structure) for the in-situ structural study of chemically modified electrodes. We were able to show that for electropolymerized films of $[\text{Ru}(\text{v-bpy})_3]^{+2}$ good quality spectra could be obtained for coverages as low as five monolayers and that the metal-ligand bond distances and coordination numbers were in excellent agreement with known values. Redox transformations could also be followed in-situ as ascertained from the shift in the Ru K edge position towards higher energy (ca. 2eV) upon oxidation from

Ru^{2+} to Ru^{3+} . We have performed similar experiments with osmium complexes where in addition we were able to follow changes in the near edge features with changes in the coordination environment, pointing to the feasibility of determining the coordination environment of electrocatalytic intermediates.

Most recently we have investigated the underpotential deposition of copper on a Pt(111) surface. Experiments were performed at half-monolayer coverage and the plane of polarization of the x-ray beam was parallel to the electrode surface so that the experiment was most sensitive to in-plane scattering of copper by other copper neighbors. From analysis of the data we determined a Cu-Cu distance of 2.91\AA which is very close to the Pt-Pt distance in the (111) direction and suggests that the copper atoms are present at three-fold hollow sites and that they form a commensurate layer with the platinum substrate. More important, however, was the finding that the average number of Cu near neighbors was six. This strongly suggests that at half-monolayer coverage the surface is better represented by nucleated sites than by a surface that is randomly decorated with copper atoms. This is significant since it is a direct experimental documentation of the assumption that in forming a monolayer, the mechanism typically involves nucleation and growth rather than random deposition with subsequent coalescence.

We have also been able to follow the potential dependence of the adsorption of iodide on a platinum surface as well as the distance of the adsorbed iodide layer from the platinum surface by employing the x-ray standing wave technique.



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Technical Reports:

1. Transport Properties of Liquid Crystal Doped Films of Polyvinylferrocene
2. Enantioselective redox transformations at electrodes modified with cholesteric liquid crystals
3. Molecularly ordered electropolymerized films of $[\text{Ru}(\nu\text{-bpy})_3]^{+2}$: An x-ray standing wave study
4. In-situ surface EXAFS at chemically modified electrodes
5. X-rays as probes of electrochemical interfaces

Publications:

1. R.D. Mariani, H.D. Abruña; "Transport Properties of Liquid Crystal Doped Films of Polyvinylferrocene" *Electrochim. Acta* **32**, 319 (1987)
2. R. D. Mariani, H. D. Abruña; "Enantioselective Redox Transformations at Electrodes Modified with Cholesteric Liquid Crystals" *J. Electrochemical Soc.* (submitted)
3. H. Abruña; "X-rays as Probes of Electrochemical Systems;" *Modern Aspects of Electrochemistry* J.O'M. Bockris, ed. (invited and submitted)
4. M.J. Albarelli, J. H. White, G. M. Bommarito, M. McMillan and H.D. Abruña; "In-Situ Surface EXAFS at Chemically Modified Electrodes" *J. Electroanal. Chem.* (submitted)
5. J. H. White, M. J. Albarelli, G. M. Bommarito, M. McMillan and H. D. Abruña; "Onset of Nucleation of Underpotentially Deposited Copper on Pt(111)" (manuscript in preparation)
6. J. H. White, M. J. Albarelli, G. M. Bommarito, M. McMillan and H. D. Abruña; "In-situ Measurement of I/Pt Adsorption Isotherm" (manuscript in preparation)
7. M.J. Albarelli, J. H. White, G. M. Bommarito, M. McMillan and H.D. Abruña; "Surface EXAFS and X-ray Standing Wave Studies of Polymer Modified Electrodes" in *Molecular Phenomena at Electrode Surfaces; ACS Symposium Series*, (manuscript in preparation)

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