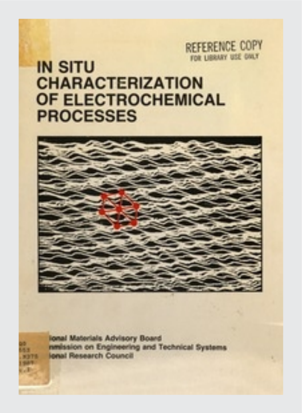

In Situ Characterization of Electrochemical Processes

DETAILS

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IN SITU CHARACTERIZATION OF ELECTROCHEMICAL PROCESSES

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Panel on In Situ Characterization of Electrochemical Processes

of the Committee on
Electrochemical Aspects of Energy Conservation and Production

National Materials Advisory Board
Commission on Engineering and Technical Systems
National Research Council (U.S.)

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On the Cover: A scanning tunneling microscope (STM) image of a graphite surface immersed in water. The lattice visible in this image has hexagonal symmetry, which can be seen by noting that the features line up in rows along three axes separated by about 120°. The imaging process emphasized the rows at a slight angle to horizontal and the rows falling at about 45° from upper left to lower right. A third set of rows may be seen that is nearly vertical but slopes to the right from bottom to top. The distance between the atom positions at the nodal points of the hexagon superimposed on the image is approximately 2 Å. (R. Sonnenfeld and P. Hansma. Atomic-resolution microscopy in water. *Science*, 232:211-213, April 11, 1986.)

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ABSTRACT

This report identifies outstanding needs and opportunities for in situ characterization of electrochemical processes. It has been prepared by a panel that obtained input principally through a workshop on this topic held in October 1985. The report provides an overview of in situ characterization in electrochemical systems, followed by chapters on specific topics: interfacial chemical composition, interfacial structure, ex situ methods for characterization of interfaces, interfacial dynamics, and processes in the boundary layer.

This study has found that advances in in situ characterization can be achieved most effectively by focusing attention on twelve issues, and conclusions and recommendations are made for each of these: identification of participants in electrode reactions with high chemical specificity; observation of dynamics on short time scales and over wide ranges of time scale; fine spatial characterization of interfacial structures; correlations of in situ and ex situ observations; utilization and evaluation of clean, smooth, well-defined surfaces; exploration of electrochemistry in unconventional media; improved characterization of boundary layers; advancement and standardization of simulation methods; development of standard reference materials for electrochemistry; provision of a reliable thermodynamic data base for surface chemistry and electrochemistry; balance between effective individual and collaborative research; and access to central facilities.

PANEL ON IN SITU CHARACTERIZATION OF ELECTROCHEMICAL PROCESSES

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PREFACE

The Panel on In Situ Characterization of Electrochemical Processes was constituted in May 1985 as a subgroup of the National Materials Advisory Board's Committee on Electrochemical Aspects of Energy Conservation and Production. The committee was convened in response to a request from the Department of Energy for a critical evaluation of issues and opportunities in two particular areas of electrochemical science and technology—electrochemical corrosion and in situ characterization of electrochemical processes.

Techniques capable of probing the liquid-solid interface to aid in elucidating electrochemical phenomena are emerging rapidly at this time. Therefore it is appropriate to examine the present status and future potential of these techniques and the opportunities for advancing the science and technology of electrochemistry. The panel was formed to carry out this evaluation. One of the panel's principal tasks was to organize a workshop on in situ characterization of electrochemical processes. This report summarizes both the panel's activities and recommendations and the proceedings of the workshop.

The intended audience for this document is the community of people primarily responsible for the evolution of electrochemical research. They include program managers in government, research directors and bench scientists in industry, and academic principal investigators together with their students and postdoctoral associates. The panel has presumed that this audience has a working knowledge of electrochemical issues; hence no attempt has been made to provide introductory or background material for a casual audience. Readers who are concerned with the subject at an introductory level, or who are interested in justifications for electrochemical research based on economic impact, should consult the report of the Committee on Electrochemical Aspects of Energy Conservation and Production, *New Horizons in Electrochemical Science and Technology* (NMAB 438-1).

The panel comprised eight members, all of whom are currently active in electrochemical research at industrial or academic laboratories. Biographical sketches of the panel members are provided in Appendix E.

The workshop that provided the primary resource for the panel was held in Denver, Colorado, on October 18-20, 1985. The panel then met to discuss the results of the workshop and draft this report.

ACKNOWLEDGMENTS

A great many people have assisted the panel in preparing this report. We wish to express our genuine appreciation for their efforts.

The primary forum for considering the matters of concern here was the workshop. Each participant had an influence on this report and deserves thanks. It is impractical to mention all by name here, so we ask that the workshop program in Appendix A and the roster in Appendix B be accepted as our acknowledgment of the participants' contributions. The scribes of the workshop summarized key issues raised during discussion and thus provided important draft documents for chapters in this report; we note with gratitude the contributions of H. D. Abruña, J. L. Anderson, D. A. Buttry, M. Majda, O. R. Melroy, J. D. Porter, D. A. Scherson, M. Soriaga, H. White, and A. Wieckowski.

An important feature of this report is the inclusion of tutorial appendixes describing experimental techniques having special promise for the future. Appendix D was prepared by S. Chiang and R. J. Wilson at the request of the panel. We especially appreciate their willingness to provide this material on short notice.

We could not have produced a timely report without several excellent efforts. In Urbana, Jane L. Daehler coordinated communication among panel members and attended to many details in editing of this report. Glenna Wilsky managed with care the preparation of the final manuscript and its predecessors. Stanley M. Wolf worked resourcefully with the panel as the NMAB technical staff representative throughout the study and report preparation and publication. Jennifer Tilles assisted especially efficiently with the arrangements for our meetings in Washington and for the workshop.

Finally, we wish to express our appreciation to A. R. Landgrebe for helping us define the scope of the workshop. The comments and critiques of the Committee on Electrochemical Aspects of Energy Conservation and Production at various points during our work is appreciated.

Larry R. Faulkner
Chairman

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EXECUTIVE SUMMARY

All branches of science have a growing interest in the nature of interfaces, because many molecular events are influenced by the presence of a nearby interface. Electrochemistry, historically the senior surface science, retains a central importance in understanding interfacial phenomena, and its contributions will be essential in resolving the intellectual challenges in the characterization and deliberate design of surfaces. These issues in turn will fundamentally influence the evolution of the molecular sciences as a whole, which will be increasingly concerned with tailored supermolecular systems.

Electrochemical processes are also of general importance to the energy and the materials technologies of all developed countries, including the United States. An advanced position in electrochemical science will benefit industrial efficiency and competitiveness by leading to the development of new processes, new products, new materials, and new sensors for the control of quality in industrial processing. For example, the advent of rechargeable lithium cells would open up a multibillion-dollar industry and would introduce vastly improved portability into intelligent, automatic equipment of all kinds. A second prospect is the advent of tailored electrochemical sensors for clinically important species such as glucose or individual pharmaceuticals; these could offer sizable improvements in the cost and quality of health care. The impact of electrochemical technology is widespread, especially in industries of high dollar and energy volume.

Superior technology in electrochemistry arises from superior science, and both rest in large part on experimental tools for observing electrochemical processes directly at the interfaces where they occur. Experimental insight into electrochemical processes is largely limited now to information obtained within a framework of macroscopic thermodynamic and kinetic concepts. This limitation retards development and validation both of microscopic and molecular theories and of detailed interfacial models. It also constrains design of commercial electrochemical systems to empirical methods, resulting in loss of process efficiency, product yield, and flexibility of product design.

An opportunity exists now to utilize advanced instrumentation to define detailed features of electrochemical reaction dynamics, participating chemical species, and interfacial structure with a precision heretofore not possible. This information is essential to an improved scientific and technological basis for electrochemical phenomena. Techniques capable of probing interfaces to aid in elucidating these phenomena are emerging rapidly.

Therefore, a panel was formed to evaluate opportunities and needs concerning capabilities for in situ characterization. This evaluation is reported herein. It concludes that advances in the in situ characterization of electrochemical processes can be achieved most effectively by focusing attention on twelve issues:

- Identification of participants in electrode reactions with high chemical specificity
- Observation of dynamics on short time scales and over wide ranges of time scale
- Fine spatial characterization of interfacial structures
- Correlations of in situ and ex situ observations
- Utilization and evaluation of clean, smooth, well-defined surfaces
- Exploration of electrochemistry in unconventional media
- Improved characterization of boundary layers
- Advancement and standardization of simulation methods
- Development of standard reference materials for electrochemistry
- Provision of a reliable thermodynamic data base for surface chemistry and electrochemistry
- Balance between effective individual and collaborative research
- Access to central facilities

These issues provide the framework for the key conclusions and recommendations, which are detailed in Chapter 1. The recommendations address needs and directions for improved in situ techniques, important experimental and modeling concerns, and matters of general research policy. Overall, the study proposes that special emphasis in the near term should be placed on developing general capabilities: (a) methods that can characterize interfacial structure with greater chemical detail and with spatial resolution approaching the atomic scale and (b) methods that can characterize dynamics more effectively, for example, in ways that will provide views of faster reactions.

In Chapter 3, this report provides a technical overview of in situ characterization of electrochemical processes and the electrode-solution interface. In subsequent chapters, it discusses the state of the art and opportunities in five domains: interfacial chemical composition, interfacial structure, ex situ methods for characterization of interfaces, interfacial dynamics, and processes in the boundary layer.

Chapter 1

CONCLUSIONS AND RECOMMENDATIONS

Advances of real significance in in situ characterization of electrochemical processes are possible in the near term. A favorable scientific climate has arisen from several factors: First, there has been an advent of new tools for characterization of materials in a variety of contexts, including electrochemical ones. Second, powerful established tools for characterization in other contexts (such as nuclear magnetic resonance and infrared spectroscopy) have now gained the sensitivity and experimental sophistication required for application to electrochemical surface science. Finally, advances in electrochemical science itself have opened up certain exciting opportunities.

In brief, the field is ready for significant progress toward microscopic delineation of the chemical species, the extended chemical structures, and the elementary chemical events that determine the rates and products of electrode processes. Electrochemical science is prepared to develop insights into its domain at an unprecedented level of structural and mechanistic detail, comparable to that now available for homogeneous chemical reactions in solutions. As electrode processes are examined in more fundamental terms because shorter time scales, greater molecular specificity, and finer spatial resolution are available, the design of electrochemical surfaces and processes to achieve specific objectives will be possible.

The conclusions and recommendations given here are derived largely from results of the Workshop on In Situ Characterization of Electrochemical Processes, which was held in October 1985. The bulk of the text in the following chapters summarizes conclusions from the technical sessions of the workshop. Of the twelve issues of emphasis (discussed below), ten represent opportunities that emerged as having special promise for research:

- **Identification of participants in electrode reactions with high chemical specificity.** A knowledge of chemical participants is indispensable to achieving an understanding of electrode processes that will permit manipulation and improvement of important processes, such as the electro-oxidation of methanol or the adsorption of olefins on platinum. Among established techniques for chemical identification, vibrational spectroscopy offers the best opportunities for improvement.

The current high level of effort in vibrational spectroscopy should be sustained. In addition, new opportunities of importance should be pursued with two other techniques, mass spectrometry and magnetic resonance. Mass spectrometry has a demonstrated but largely undeveloped general applicability to the characterization of intermediates and products in electrochemical processes. Magnetic resonance techniques apart from electron spin resonance (ESR) have not yet been applied in electrochemical situations, but recent dramatic improvements in sensitivity and in applicability to surfaces and solid samples suggest that it is time to examine the possibilities for using this powerful family of characterization tools in electrochemistry.

- **Observation of dynamics on short time scales and over wide ranges of time scale.** Faster experiments will permit the observation of mechanistic steps and intermediates that are now obscured. Current knowledge of homogeneous chemistry suggests that important elementary reactions in complex electrode processes, including electrocatalysis, occur on submicrosecond time scales.

It is important to produce new capabilities for dynamic characterization in this (submicrosecond) time regime. Opportune means to achieve faster responses lie with ultramicroelectrodes and spectroelectrochemical experiments involving pulsed lasers. Observations of electrochemical dynamics over wide ranges of time scales allow the assignment of mechanistic models with greater confidence. Extended time scale ranges will automatically come to many techniques as they are applied at greater speeds. Certain impedance techniques that have benefited from improved commercial instrumentation are already available for service over a wide bandwidth. They can gain broader and more effective use if straightforward means can be found for linking features in impedance spectra to steps in electrochemical mechanisms.

- **Fine spatial characterization of interfacial structures.** Electrode reactions often involve kinetic steps that occur in three-dimensional structures, such as active catalytic sites, nucleation centers, and adsorbed layers. Their structures are rarely known; in fact, their existence is often inferred from indirect evidence. Recent years have seen the deliberate construction of microstructures on electrode surfaces, in the interest of manipulating kinetics or developing specificity of response. Lack of knowledge of structural relationships at sites of electrochemical activity strongly inhibits understanding of the fundamental steps in reaction mechanisms. In situ techniques that are now available for characterization of structures are based on interferometry with visible light, and hence they have resolutions limited normally to hundreds or thousands of angstroms.

Parallel avenues should be explored in an effort to achieve a markedly improved capability for spatial characterization of interfaces. Excellent opportunities exist for new initiatives in the application of x-ray methods, particularly diffraction and extended x-ray absorption fine structure (EXAFS), which probe the sample with photons having wavelengths ideally suited to the atomic and molecular spatial regime. Newer methods that might produce striking results in electrochemical situations include scanning tunneling microscopy and nonlinear optical processes at surfaces. These should be explored. The ex situ methods of surface science must continue to play an important role in providing fine spatial characterization of interfacial structure.

- **Correlations of in situ and ex situ observations.** The characterization methods of surface science have already been established within an electrochemical context, because they can provide structural definition on fine distance scales, atomic composition of a surface, and sometimes vibrational spectroscopy of adsorbates. These ex situ methods normally involve transfer of an electrode from the electrochemical environment to ultrahigh vacuum, and the degree to which they provide accurate information about structure and composition in situ is continuously debated.

Resources should be provided for additional efforts to clarify the effect of emersion of samples and their transfer to ex situ measurement environments. The most appropriate experimental course requires observations by techniques that can be employed in both environments. Vibrational spectroscopy, ellipsometry, radiochemical measurements, and x-ray methods seem appropriate to the task. Once techniques suited to this problem are established, emphasis should be placed on the refinement of transfer methods so that the possibilities for surface reconstruction and other alterations in interfacial character are minimized.

- **Utilization and evaluation of clean, smooth, well-defined surfaces.** Information about fundamental relationships between interfacial structure and reaction dynamics (e.g., in electrocatalysis) requires studies on surfaces free of impurities and with well-defined structures and dimensions.

It is recommended that procedures for preparing such surfaces, including but not limited to single-crystal metals and semiconductors, continue to be investigated. The general ex situ characterization methods of surface science will continue to be important in this work. Certain new electrochemical experiments will require electrodes that are atomically smooth over an appreciable area. Methods of producing and evaluating such electrodes are needed. The rates of reorganization and contamination of well-defined surfaces within the electrochemical environment are also important questions.

- **Exploration of electrochemistry in unconventional media.** Electrochemical research has traditionally focused on measurements at electrodes fabricated from conductors immersed in solutions containing electrolytes.

Interfacial processes between other phases need to receive further attention, and they can be probed effectively with electrochemical techniques. Electrochemistry offers unique experimental power in exploring chemistry under extreme conditions. The movement of charges in frozen electrolytes, poorly conducting liquids, and supercritical fluids can be measured readily with ultramicroelectrodes. Opportunities exist to study previously inaccessible redox processes in these media. Electrochemistry in environments of restricted diffusion, such as polymers and biological tissue, requires appropriately modified theories of mass transport. New research should be undertaken to provide unique insights into microscopic environments in such media. The use of ordered structures, conducting polymers, and semiconductor electrodes may also require new considerations of transport processes in the bulk of a material, as well as of dynamics directly at an interface.

- **Improved characterization of boundary layers.** The boundary layer adjacent to an electrochemical interface is the extended zone through which species must be transported to a site of electron transfer. This layer often involves complex situations. Intercalation electrodes and separators that have fixed-geometry channels for transport or mediated reaction and motion through natural or synthetic surface-attached networks of charged polymers are prominent examples in which dynamics in a boundary layer may control an overall rate. As electrochemical science becomes more concerned with the deliberate manipulation of interfacial structure, it will be necessary to learn more about boundary layers in complex structures like these.

Support is warranted for new research aimed at understanding the behavior and enhancing the performance of such systems. They will require applying structure-sensitive techniques in both in situ and ex situ circumstances. Surface spectroscopies, x-ray methods, and microbalance techniques must become important adjuncts to electrochemical studies for molecular and structural interpretation.

- **Advancement and standardization of simulation methods.** Electrochemistry is now addressing problems for which the mathematical analysis of material transport and reaction rates can rarely be expressed in analytic equations. Most new important problems require simulation or some other numeric approach. The geometric configurations of electrodes (e.g., arrays of microelectrodes), the complexity of the mechanisms of interest, or the inclusion of mass transfer effects beyond simple diffusion (e.g., migration of ions in electric fields or diffusion in porous media) can render the treatment otherwise intractable. Digital simulation methods have already been developed extensively in the electrochemical context, but there is a need now for algorithms that can conveniently handle a wider range of phenomena, and there is always a place for more efficient algorithms.

Encouragement should be given to the creation of transportable, documented simulation packages that can be used easily by experimental and theoretical electrochemists. Efforts ought to be initiated to standardize and permit better cross-checking of simulation software used in the field. As greater reliance is placed on simulations to guide experiments designed to characterize electrode processes, there will be a concomitant need for more general confidence in the software.

- **Development of standard reference materials for electrochemistry.** Effective allocation of limited resources probably requires a research strategy based on a balance between the pursuit of fine chemical detail and the development of more generalized knowledge. Real understanding of any particular chemical system requires concentrated studies involving many techniques. Such detailed work can be done for only a few systems. On the other hand, the power and utility of chemistry comes from the discovery and application of general principles that can be gleaned only from a systematic study of many different systems by relatively few techniques. Both approaches need to be pursued. The detailed investigations will require cooperation between different laboratories.

To facilitate these investigations and to maximize the effectiveness of expensive or inconvenient experiments (e.g., those requiring central facilities such as synchrotrons or nuclear reactors), standard reference materials are needed and the development of the requisite capabilities should be supported. Particular difficulties exist in the reproducibility of semiconductors (SnO_2, GaAs, InP) and samples of carbon, so these are materials for which standard reference sources would be especially valuable.

- **Provision of a reliable thermodynamic data base for surface chemistry and electrochemistry.** Thermodynamic data are used routinely to interpret kinetics and predict patterns of reactivity in homogeneous chemical systems. Surface scientists, including electrochemists, are usually unable to analyze their experimental results in the same way because of the lack of any comprehensive collection of critically evaluated thermodynamic data for surface chemistry (e.g., free energies of formation or of adsorption on surfaces, phase and stability diagrams for surface species, and entropies of reactants confined to surfaces). Both in situ and ex situ characterization of electrochemical processes at interfaces could benefit greatly from access to such a compilation of thermodynamic data.

It is recommended that encouragement and support be offered to qualified scientists who could help to meet this increasingly critical need.

In addition to the above target areas for research, the panel recommends that attention be paid to two matters of general research policy:

- **Balance between effective individual and collaborative research.** In applying elaborate nonelectrochemical characterization tools to electrochemical problems, there can be difficulty in establishing adequate specialized knowledge about both the electrochemistry and the characterization methodology. Collaborative research between investigators can be helpful in such circumstances, and it ought to be encouraged when it can be beneficial. Collaboration may be timely now in projects involving applications of x-ray methods, ultrahigh-vacuum surface science techniques, and pulsed laser spectroscopy to electrochemical problems. However, the panel strongly disagrees with a view that important future research cannot proceed without collaboration. *It is important to maintain a flexibility in funding structures so that they remain responsive to proposals of high quality from individual investigators while being receptive to genuinely promising collaborative ventures.*

- **Access to central facilities.** National laboratories now provide important new tools for in situ electrochemical characterization. These include facilities for synchrotron radiation, soft neutrons, high-power pulsed laser light, and supercomputing. They provide investigators with new capabilities but demand a new mode of operation. Experiments must be prepared and rehearsed and then transported to the central facility for an intensive, scheduled experimental run. The complexity of the apparatus may require collaboration with others more familiar with the equipment.

The central laboratories are essential for many of the research opportunities identified herein and should be funded at levels appropriate to the anticipated new users.

Chapter 2

ORGANIZATION OF THE WORKSHOP ON IN SITU CHARACTERIZATION OF ELECTROCHEMICAL PROCESSES

From the outset it was understood that the workshop was to focus on the outstanding problems of in situ characterization and to define the best opportunities for significant advances in the near and intermediate terms. Progress in electrochemical science has always been limited by the capabilities of its tools for in situ characterization. Now there are prospects for significant improvements in capability, and the panel hoped that it would be possible to use the workshop to develop a technical agenda together with a commentary illuminating both the obstacles to serious progress and the new capabilities that might be achieved if the obstacles could be overcome.

The program of the workshop is given in Appendix A. A keynote address at the beginning of the meeting provided a broad view of opportunities throughout the domain of concern. Five focused sessions dealing with particular aspects followed:

I. *Interfacial Chemical Composition.* The primary emphasis here was on tools and procedures for identification of chemical species that participate in electrochemical processes. Characterization of the composition of an interfacial region in molecular, not simply atomic, terms was stressed.

II. *Interfacial Structure.* Of particular concern here were experimental tools and procedures for characterization of the three-dimensional spatial arrangement of the components of an interfacial system. Information about spatial organization is needed on distance scales as large as micrometers and as small as fractions of angstroms.

III. *Ex Situ Methods for Characterization of Interfaces.* The primary focus here was the validity with which the ultrahigh vacuum methods of surface chemistry and surface physics can be applied to the characterization of electrochemical interfaces. There is widespread use of these methods, but questions remain about the extent to which one can regard the characterization of an electrode surface in ultrahigh vacuum, after its removal from an electrochemical cell, as accurately reflecting its character in situ.

IV. *Interfacial Dynamics*. The major issue here was to examine experimental means by which kinetic processes at electrochemical interfaces might be more effectively examined in situ. Stress was placed on means by which faster dynamic processes might be examined and on methods by which wider time scale ranges might be attained.

V. *Processes in the Boundary Layer*. This session addressed the spatial structure of the layer of altered composition extending away from an electrochemical interface and the dynamic processes that occur within that region. These factors often exert a substantial and sometimes controlling influence on an overall electrode reaction.

Each of these sessions opened with a speaker who defined issues and opportunities in the specific area of concern. This was followed by other speakers who presented separate, more detailed discussions of specific aspects. Approximately one-third of the time was allotted for discussion. Scribes assigned to each session took notes of the major points and prepared oral and written reports. A final session of the meeting was devoted to the oral reports of the scribes and to a discussion of their perceptions of the major conclusions. Short presentations were made by persons other than invited speakers; these were distributed among the five focused technical sessions and the concluding sessions.

A substantial body of written material was collected. Speakers were asked to provide, in advance, a "white paper" describing their views of the current status of their topic and of outstanding opportunities. There were also written reports from the scribes serving the five main technical sessions. This material was organized as a primary record of the workshop and was used extensively by the panel in its preparation of this report.

The names, affiliations, and addresses of persons who participated in the workshop are provided in Appendix B.

The remainder of this document comprises (a) a summary of the main points arising from the workshop and (b) a description of the panel's recommendations for a research agenda. Chapters 3 through 8 are essentially reports from the workshop. Chapter 3 provides an overview of issues and opportunities, while the remaining five chapters are devoted to the individual technical spheres described earlier. The detailed recommendations of the panel are given in Chapter 1.

The panel discerned several families of powerful materials characterization methods that are ready for important new applications in electrochemistry. To facilitate a consideration of these methods by the audience of this report, the panel sought expert commentaries on capabilities and constraints of a few experimental techniques, with particular reference to the electrochemical environment in situ. Commentaries were obtained on two important subjects—x-ray scattering and scanning tunneling microscopy. They are included here as Appendixes C and D. Commentaries on other important areas, such as magnetic resonance, were sought but could not be obtained in the time available for preparation of this report.

Chapter 3

IN SITU CHARACTERIZATION OF ELECTROCHEMICAL PROCESSES AND THE ELECTRODE-SOLUTION INTERFACE: AN OVERVIEW

Recent advances in instrumentation have made possible new methods of looking at surfaces (e.g., by ultrahigh vacuum spectroscopy and laser techniques), and new electrode structures (e.g., ultramicroelectrodes and polymer-modified electrodes) have emerged. As a consequence, this is an especially opportune time to consider the state of the art for characterizing electrochemical processes. This introductory chapter is meant (a) to define the terms and scope of this study, (b) to raise questions (but not provide answers), (c) to assess in a general way the state of the art in this field, and (d) to set the tone for the following chapters.

During the past 30 years a number of electrochemical and spectroscopic techniques have been introduced for the study of electrochemical processes and the interface between the electrode and solution. Many of these date from the post-dc-polarography period of the 1950s, when instrumentation based on operational amplifiers was introduced and techniques such as chronopotentiometry and cyclic voltammetry were developed. In the middle of this period, ESR spectroscopy was introduced as a means of studying species produced at electrode surfaces in an electrochemical cell within the cavity of an ESR spectrometer. This represented one of the earliest spectroelectrochemical techniques. The rise of instrumentation based on transistors and integrated circuits, the widespread use of general-purpose digital computers for both computation and instrument control, and the application of more sophisticated spectroscopic techniques led to important advances in understanding electrochemical processes and the species produced at electrodes. However, this report only briefly considers existing techniques, methodologies, and obvious extrapolations of these. Rather, the primary intention is to consider what future techniques will arise and what special opportunities now exist to characterize electrode surfaces and study electrode reactions. Some questions we might attempt to answer are these:

- What are the questions that need to be addressed to make an impact in the understanding of electrode surface reactions?

- What are the "cutting edge" problems that, if solved, would lead to new or improved electrochemical systems?

- If we had unlimited resources (and ability), what methods would we introduce and what techniques would we use? In considering these, we should think big and be daring.

DEFINITIONS

In situ is defined as "in the natural or original position." This term therefore implies that the electrode is examined while it is in the cell and immersed in the solution. A synonymous term sometimes used is *intra muros*, "within the walls" of the cell. The requirement that an electrode be examined while immersed in solution can severely limit the range of available experimental techniques. Thus there are numerous studies, termed here *ex situ* (or sometimes "quasi in situ"), in which (a) the electrode is withdrawn from the solution with some of the solvent still adhering in a thin layer on the surface (i.e., the electrode is "emersed") or (b) the electrode is transferred as quickly as possible via an inert atmosphere to an ultrahigh-vacuum environment. These techniques are examined in this report.

ASPECTS OF CHARACTERIZATION

In seeking to "characterize" an electrochemical process, one may need quite a variety of information. Some, for example, relate to chemical identity, some to spatial arrangement, and some to sequences of events in time. Needed information may concern structures and events on a molecular scale, or it may concern bulk phases. It is useful to point out seven distinct aspects of characterization:

1. *Molecular identification of the species at electrode-solution interfaces.* The species of concern would include stable stoichiometric species, which may survive transfer out of the original solution, stable nonstoichiometric species (e.g., hydrated molecules), nonstoichiometric surface films (e.g., WO_{3-x}), and unstable intermediates (e.g., free radicals or radical ions). Studies of unstable intermediates, which are often crucial in working out a mechanism for an electrode reaction, require direct in situ observation.

2. *Elemental analysis in the interfacial region.* It is often useful to know whether a particular element is present, as can sometimes be ascertained by x-ray photoelectron spectrometry. Examples of the many topics that need to be addressed are the following: Can one identify a peak attributable to sulfur on the surface? Can one estimate the ratio of cadmium to zinc?

3. *Spatial characterization in two and three dimensions.* Questions concerning spatial arrangements of adsorbates on surfaces, electro-

catalytic reaction sites, and microstructures built deliberately on electrodes require resolution if a sophisticated understanding of advanced electrochemical systems is to come about.

4. *Orientation characterization of the substrate.* Answers are sought for several types of issues: What crystal faces are exposed to the solution? How are surface species oriented with respect to the electrode surface?

5. *Energetic and dynamic characterization.* New knowledge could help resolve these kinds of questions: Can one obtain information about the quantum state of a reacting molecule, as can be done in molecular beam techniques? What are the lifetimes of intermediates?

6. *Bulk properties of phases on the electrode surface.* Properties of thin films need to be determined: If a film is formed, what are its electronic properties, its refractive index, its thickness, etc.? Do bulk properties vary with spatial position in a boundary layer?

7. *Quantitative characterization of concentrations.* Information is needed on topics such as the following: What are the surface concentrations or coverages of molecules on an electrode? What are the concentrations of the different species in the vicinity of the electrode?

PROVOCATIVE QUESTIONS

In thinking about new opportunities for in situ characterization, one ought to think imaginatively. One must ask questions about the ultimate limits of one's ability to characterize in time and space and chemical nature. One also ought to raise some challenges in fundamental terms, so that they can be examined outside the context of a particular experimental approach. Thinking in this way is the surest way to revolutionary changes in experimental capability and fundamental understanding. The following questions are meant to stimulate a focus on such matters:

1. *What spatial resolution is attainable in situ?* Resolution in an optical experiment is generally related to $\lambda/(\sin \underline{a})$ where λ is the wavelength of light and $\underline{a}$ is the angular aperture. Generally, this feature implies that spatial resolution is limited by the wavelength of the radiation that can be used for the observation. In the visible region, spatial resolution is usually restricted to 1 μm, although more advanced microscopic techniques, such as near-field scanning microscopy, methods involving luminescent tags, and techniques involving digital image intensification and manipulation, can give much better resolutions with visible light, reportedly down to 0.05 μm. By proper design of the electrochemical cell (e.g., the choice of window material, or control of the thickness of the solvent layer between window and electrode), it may

be possible to use much more energetic radiation and obtain spatial resolutions of angstroms. Thus studies are now emerging that involve the use of x-rays (e.g., EXAFS) with cells having Mylar windows and containing thin aqueous layers. Resolution in the angstrom region is sometimes possible by interferometric and ellipsometric techniques. Field gradient imaging, such as that used in magnetic resonance imaging methods, has not yet been applied to electrochemical systems. High spatial resolution, at the atomic level if possible, is important in the characterization of designed electrode interfaces (e.g., for application as sensors) and of corrosion products on surfaces.

2. *What time resolution is attainable in electrochemistry to observe unstable species or surfaces*? Most electrochemical experiments involve time windows longer than 0.1 to 1 millisecond, although experiments a little below the 1-microsecond region have been reported. However, the time scale in many spectroscopic experiments in homogeneous solution extends to the picosecond region, with femtosecond studies a real possibility. Extension of short time scale techniques to electrochemical interfaces would provide a new view of fundamental processes occurring at electrode surfaces, since it is well known that a great many homogeneous chemical events occur on timescales below 1 microsecond.

3. *Can one prepare atomically smooth or atomically clean surfaces*? If these are prepared, how does one gauge their smoothness or cleanliness, and how stable will they be as electrodes immersed in solution? These questions matter to a host of experimental methods and fundamental questions, as discussed in more detail below.

4. *How far can charge "jump" (or electrons tunnel?) from the electrode surface or between redox sites*? What factors are important in measuring experimentally and describing theoretically the rates of heterogeneous electron transfer reactions?

5. *What do we really know about the structure of the Helmholtz and diffuse layers*? Most of the information we have about the structure near an electrode surface has been obtained from macroscopic measurements (e.g., of the double layer capacitance or surface tension) that are interpreted indirectly via detailed models. Can we obtain a better picture from more direct methods?

6. *Can one meaningfully describe surface species in conventional chemical terms*? Generally, electrochemists have been unable to agree on the nature of even important species such as hydrogen and oxygen on platinum electrode surfaces, not only because it is difficult to study monolayers of these, but also because their description in conventional chemical terms (e.g., "adsorbed oxygen," "hydroxyl radicals," or "oxide") may not be appropriate. Perhaps new ways of thinking about chemical nature and reactivity are needed.

7. *Can one establish a "surface thermodynamics"*? Because of the unique nature of the energetics of species at electrode surfaces, conventional free energies do not apply. It would be useful to have standard thermodynamic tables, such as those available for bulk species, to describe species and reactions at surfaces.

CHARACTERIZATION STRATEGIES

To a large extent, our concepts about the nature of electrode surfaces and electrochemical reactions are based on electrochemical measurements and interpretations of these from models that have been developed over the years. While these approaches have proved useful, they often seem less "direct" than methods available for characterization or analysis of reactions in homogeneous media or on surfaces in high vacuum (e.g., by nuclear magnetic resonance, photoelectron spectroscopy, electron microscopy, laser flash methods, or molecular beam techniques). The result has been that electrochemistry has been somewhat less molecularly oriented than other areas of chemistry.

So far, the methods that have been applied can be classified according to the nature of the excitation or probe and the type of detection employed. Both can involve electrical, optical, chemical, mechanical, and thermal signals (Figure 3-1). Many new techniques involve electrical-electrical (electroanalytical techniques) and optical-optical (spectroelectrochemical methods) signals. Other combinations have been used less frequently.

What imaginative approaches (perhaps with piezoelectric devices, thermistors, tunneling probes, or other unconventional devices) are possible for studying electrode reactions? We should be aware that a number of very powerful tools used in mainstream chemistry, such as nuclear magnetic resonance (NMR), x-ray scattering, electron microscopy, mass spectroscopy, and ultrahigh-vacuum techniques, have been applied only to a very limited extent in electrochemical systems. Nuclear magnetic resonance and x-ray techniques are appearing on the horizon as realistic new prospects for use in this field. Electron spin resonance methods involving spin labels are just appearing in electrochemistry. These can provide information about the spatial arrangement of species on surfaces and about their freedom of motion. A great deal of effort is now being expended on the design of electrode surface layers (e.g., in surface-modified electrodes and in organized assemblies on electrode surfaces), and it is important to have techniques that can provide the information about the extent of orientation and organization. Indeed, even the definition of "surface" depends on both the method used to probe the interface and particular properties or applications that are of immediate concern (Figure 3-2).

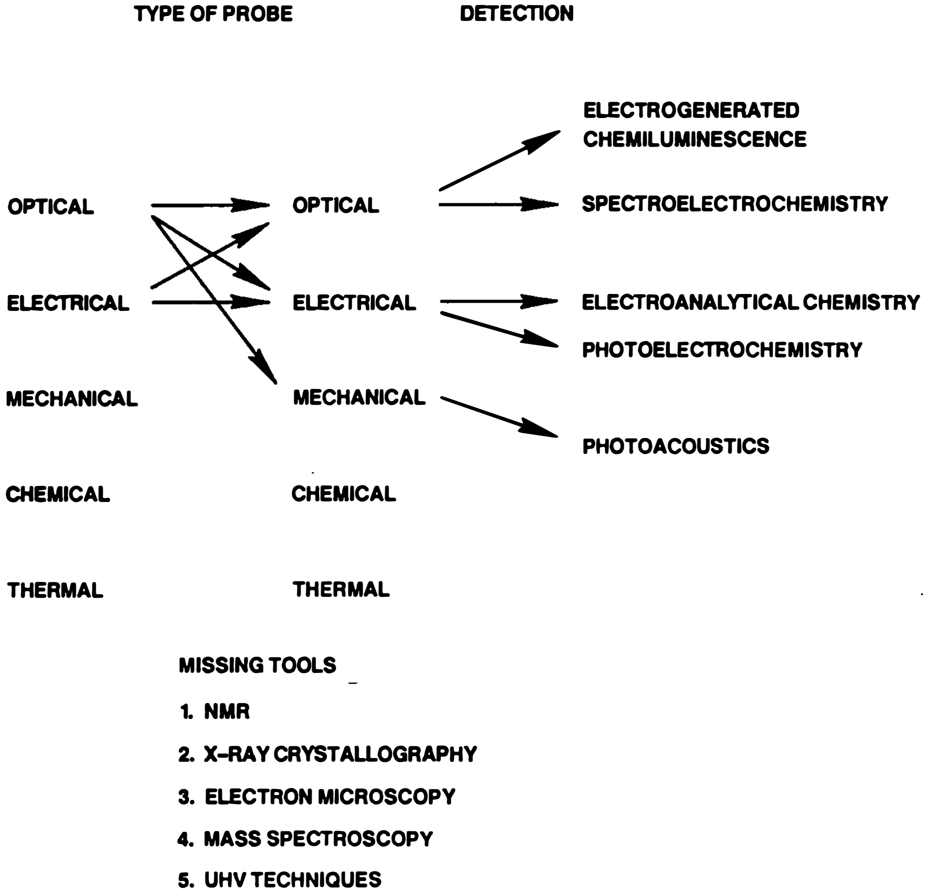

FIGURE 3-1 Classes of experimental methods for investigating electrochemical systems, organized by the nature of the probe and the nature of the detection.

Finally, a number of nonspectroscopic techniques are emerging that have not yet been applied in electrochemistry but might provide unique information about electrode surfaces. For example, the mica balance technique, which involves measuring the forces between two atomically smooth mica surfaces as they are moved together, has been developed to the point that resolution on the angstrom level is possible, and information about solvent and polymer layers near a mica surface can be obtained. Similarly, scanning tunneling microscopy, which involves movement of a scanning needle tip positioned above a sample surface, can give information about surface structure with atomic resolution.

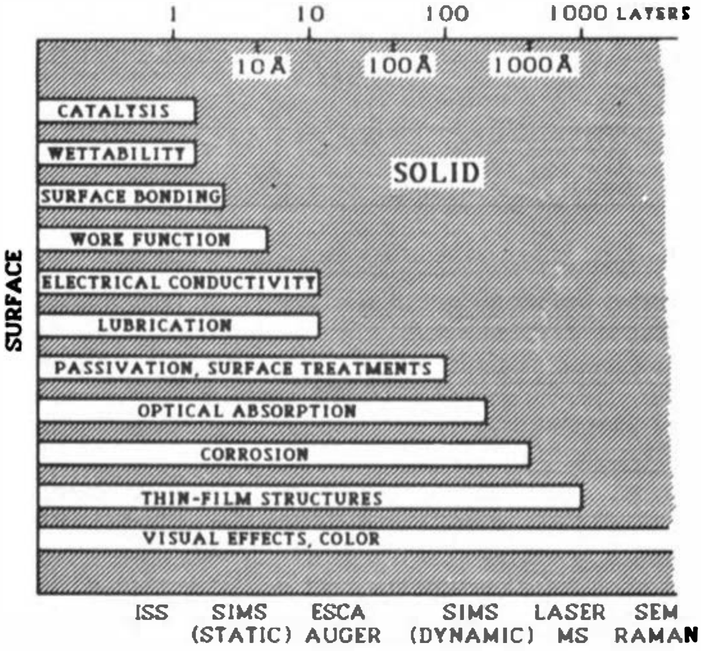

FIGURE 3-2 Effective depth of a "surface" in relation to particular properties of interest. The lower axis shows some experimental techniques that can probe the corresponding depths. (From *Opportunities in Chemistry*, Board on Chemical Science and Technology, National Academy Press, Washington, 1985, p. 270.)

Thus it seems to be an especially exciting time in electrochemistry. There are new tools to probe complicated systems, and there is a growing realization of the importance of electrochemistry, both for practical applications and also as a way of obtaining fundamental information about surfaces and charged interfaces. However, the instrumentation involved in many of these techniques is expensive and sophisticated, and the theory may be complex. It may be difficult for electrochemists to utilize these techniques effectively and simultaneously to maintain their expertise in electrochemistry. We probably will see more collaborative efforts between electrochemists and experts in other areas. In some cases, the useful facilities will be so large and expensive (e.g., synchrotron light sources) that electrochemists will have to join their colleagues in other branches of chemistry in traveling to central facilities to carry out certain classes of important experiments.

Chapter 4

INTERFACIAL CHEMICAL COMPOSITION

An important part of "characterizing" an interface includes the elemental and molecular identification of species at or near the electrode surface and the determination of information about orientation of crystal faces or surface species. The first session of the workshop dealt with these matters.

Electrochemistry's historical reliance, by necessity, on indirect experimental approaches and model-based interpretive schemes has produced a perception that the field is less molecularly oriented than other areas of chemistry, which have effectively used more direct characterization methods such as NMR, photon or particle spectroscopies, and electron- and atom-scattering techniques. While indirect electrochemical approaches will remain extremely useful, indeed indispensible, for the foreseeable future, recent advances in instrumentation make this an especially appropriate time to foster the exploitation of state-of-the-art methods for in situ determination of interfacial composition.

Spectroscopic methods suitable for in situ characterization of electrochemical interfaces are restricted to the absorption, emission, and scattering of photons and a few other fundamental particles. A partial list of current techniques and their key characteristics are given in Table 4-1.

The vibrational spectroscopies, especially Raman and reflection IR, are destined to become the most widely used and powerful of the in situ tools for chemical identification. Vibrational spectroscopy is usually considered a structural probe because the spectra contain information about molecular structure and orientation. It is also especially suited for molecular-level analysis because the spectra "fingerprint" the species present. No real alternatives to vibrational spectroscopy are available for providing molecularly specific information about an interface.

Extensive investigations have been reported using these techniques. The reports have described the identification of ions, solvents, neutral molecules, reactants, and products at electrode surfaces. Some studies have probed the interactions between adsorbates and the electrode, while

TABLE 4-1 Summary of In Situ Spectroscopic Techniques

Technique	Characteristics
Raman spectroscopy	High sensitivity on special surfaces Wide vibrational frequency range Species- and environment-specific New nonlinear and multiphoton processes promise improved time response and sensitivity
Infrared spectroscopy	Family of techniques Species- and environment-specific Orientation information Monolayer sensitivity Thin layer cell required
Photoacoustic spectroscopy	Weak effect, but monolayer sensitivity achievable Powders and nonreflective surfaces Quantitative interpretation difficult
Inelastic electron tunneling spectroscopy	Atomic-scale resolution Topographic, electronic, (elemental?) mapping Vibrational spectroscopy requires low temperature
Mössbauer spectroscopy	Many scatterers required Fe, Sn easy; others more difficult Symmetry- and oxidation state-sensitive
X-ray fluorescence	Elemental analysis Surface sensitive with synchrotron sources
Nuclear magnetic resonance spectrometry	Extreme molecular specificity Large surface area samples Low conductivity Small metal particles
Mass spectrometry	Dynamic Low molecular weights monitored Requires porous electrode

TABLE 4-1 Summary of In Situ Spectroscopic Techniques (continued)

Technique	Characteristics
Visible-ultraviolet spectroscopy	Sensitive Low molecular specificity Fast response
Electron spin resonance spectroscopy	Requires free spins Moderate molecular specificity Moderate sensitivity
(Chemical derivatization)	High sensitivity Functional group specific Surface modification Used with spectroscopic techniques

others have followed the kinetics of surface reactions. Several of the more important or interesting spectroscopic methods are discussed in more detail in the following sections.

RAMAN SPECTROSCOPY

Raman spectroscopy has the important advantages of being able to access the entire vibrational frequency range and, since visible light is usually used, having an excitation beam that easily penetrates most electrolyte solutions. Its major disadvantage is that normal Raman scattering is a weak effect. Consequently, there was substantial enthusiasm over the discovery of surface-enhanced Raman scattering (SERS), which not only provides a strong, easily detected signal but also is inherently surface-sensitive. Unfortunately, the effect seems to be restricted to a few electrode materials (usually Ag, Au, Cu), although there is some evidence that (weaker) enhancements occur on other metals. More general advantage may be available from the SERS effect by including enhancing metals in otherwise nonenhancing materials. Improvements in premonochromator optics, signal processing, and detector design seem likely to permit extension of normal Raman scattering (no enhancement) or resonance Raman scattering to smooth surfaces and may lead to two-dimensional Raman imaging of surfaces. In addition, other techniques utilizing nonlinear optical effects are on the horizon, for example, hyper-Raman spectroscopy, Raman gain spectroscopy, and second harmonic generation. These promise, in special situations, inherent surface selectivity along with increased sensitivity (gain) or extremely short time response.

INFRARED SPECTROSCOPY

IR techniques are not restricted to a particular electrode surface, but these are difficult to apply in the far infrared. Improvements in instrumentation (and the availability of commercial Fourier-transform spectrometers) have caused a surge in activity for in situ infrared absorption spectroscopy. The technology has developed largely along two different branches: multiple-reflection ATR (attenuated total reflection) and specular external reflection.

External reflection from immersed electrodes is a recent development, but it has rapidly grown into a powerful general approach to in situ vibrational spectroscopy of electrochemical systems. Spectra are readily obtained down to 500 cm^{-1} from submonolayer amounts of adsorbate (simple ions, organic adsorbates, and reaction intermediates) on smooth (including single crystal) electrodes, and the feasibility of extending the range to 100 cm^{-1} has been demonstrated. Currently, absorbance changes as small as 10^{-5} to 10^{-6} are detectable. At this level, background effects (e.g., electroreflectance) become appreciable, and future enhancements will be in the direction of extending the range of systems for which this sensitivity is achievable rather than measuring even weaker bands in currently accessible systems.

External reflection infrared spectroscopy actually is a family of related techniques, each of which has advantages in particular situations. Taken together, they permit infrared spectra to be obtained from a wide range of substrates and solvents. They also exhibit high sensitivity to nonadsorbed species or reaction intermediates in the diffusion layer. This can be an advantage or disadvantage, depending on the situation. A challenge for the future is the development of methods for quantitative measurement of band intensity and coverage. All current approaches employ thin layer cells, which limit the response time and require that careful attention be paid to current distribution and resistance effects in interpreting dynamic measurements. Spectrometer technology is not a limitation. Fourier transform instruments already record spectra in tens of milliseconds, and gated repetitive scanning techniques may effectively shorten this to microseconds. With tunable infrared lasers and state-of-the-art detectors, optical systems with subnanosecond response times can probably be designed. Actual improvements in dynamic measurements require advances in cell design.

The ATR technique is infrequently used in electrochemistry but has benefited from recent advances in new materials for ATR plates and from the availability and rapid development of FTIR (Fourier transform IR) techniques. High sensitivity toward adsorbed species or deposited films has been achieved. For example, multiple-reflection ATR has been used to identify intermediates in the anodic oxidation of thin films of iron. Nevertheless, applications are necessarily limited by restrictions on the nature of the electrode—either the ATR material itself or a very thin layer of metal deposited on it.

PHOTOACOUSTIC SPECTROSCOPY

Photoacoustic spectroscopy has seen increasing nonelectrochemical application but has been little used in solution. The effect is rather weak, and although photoacoustic detection has been used with FTIR spectrometers, it really needs IR laser sources and piezoelectric detectors to be effective in solution. These are now becoming available, but problems in interpreting the amplitude of the photoacoustic signal limit its utility for quantitative measurements. Although there are some promising developments in direct photothermal detection, that approach and the related method of photothermal deflection share most of the advantages and disadvantages of photoacoustic detection. In principle, photoacoustic and photothermal techniques should be particularly useful for rough surfaces that are not suitable for specular reflectance, but at their present stage of development they are less generally useful than IR reflection or Raman spectroscopy.

INELASTIC ELECTRON TUNNELING SPECTROSCOPY

Another surface-sensitive vibrational spectroscopy, inelastic electron tunneling spectroscopy (IETS), has so far not proved particularly useful for electrochemistry because a metal:metal-oxide:metal structure is required. The recently developed scanning tunneling microscope (STM) may alter this situation (see also Appendix D). The STM has been used primarily as a topographical mapping tool. In the STM, tunneling occurs across a vacuum gap a few angstroms wide between a planar sample and a sharp tip, rather than across the oxide gap used in conventional IETS. No one has yet reported a vibrational spectrum obtained by IETS using the STM, but there is no fundamental reason why one should not be able to do so. It is already clear that the STM response is sensitive to the composition and electronic structure of the surface as well as to its topology. With it, an electronic excitation has been observed in NiO, and the phonon spectrum and the superconducting energy gap (a few millivolts wide) have been observed in a superconductor. Calculations suggest that a tunneling spectrometer with a vacuum gap should be several times more sensitive than one with an oxide gap. The main experimental hurdle for vibrational spectroscopy is the necessity of maintaining very tight control of the gap thickness, ideally within less than 0.02 Å. The current state of the art is ±0.1 Å. Also, reduction of thermal noise probably requires operation at low temperature, which precludes IETS as an in situ electrochemical tool, at least for vibrations, although it may work at room temperature for electronic transitions.

MÖSSBAUER SPECTROSCOPY

Another technique that is sensitive to the chemical environment is Mössbauer spectroscopy. It is easily applicable only to a few elements, but for those it can be a very sensitive probe of local symmetry and oxidation state. For example, Mössbauer spectroscopy has been used to monitor the transformation of ferric oxyhydroxide to ferrous hydroxide after precipitation of the ferric species onto a high-surface-area carbon electrode.

X-RAY FLUORESCENCE

X-ray techniques have so far been largely neglected by electrochemists, but the neglect is not justified. X-ray fluorescence is widely used for elemental analysis, and even with laboratory sources, monolayer sensitivities can be obtained in solution for elements heavier than fluorine. With a synchrotron source and excitation at grazing incidence, true surface selectivity and even depth profiling are possible. X-ray diffraction has already been valuable in identifying thin surface films on electrodes and warrants consideration for more frequent use by electrochemists. The availability of synchrotron sources will also make this technique surface-selective. The discussion here pertains to using x-ray techniques to identify interfacial species. Other applications, particularly structural characterization, are discussed in Chapter 5.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

NMR has not yet been applied to electrode surfaces, but recent developments suggest that this may soon be possible. The traditional problems have been low sensitivity and quenching by metal surfaces. But, by using magic-angle spinning and cross-polarization techniques, spectra of adsorbates at submonolayer coverages on high-surface-area nonconducting substrates have been obtained. Even more important for opening up new research opportunities is the observation that relaxation effects in small metal particles are sufficiently different from the bulk metal that NMR spectra of the metal and adsorbed species could be obtained from highly dispersed metal catalysts. There is some reason to believe that polarization transfer techniques (combined ESR/NMR) may provide an additional increase in surface sensitivity. One disappointing note is that at present there seems to be no hope of obtaining spectra from smooth metal electrodes. Nevertheless, supported, dispersed metals and high-area carbon particles are important practical electrodes. They might be examined effectively by NMR. While the experimental problems of doing electrochemistry in an NMR tube are not trivial, the possibility of applying such a powerful analytical technique should be a strong incentive, particularly for organic electrocatalysis.

MASS SPECTROMETRY

Mass spectrometry is another technique that has been little used by electrochemists, yet it has considerable promise. Reports by a few pioneering scientists have demonstrated that it can be applied in electrochemical cells, where it is a powerful product analysis tool. Electrochemical mass spectrometry relies on the injection of the volatile products of an electrochemical reaction directly into a mass spectrometer. A porous hydrophobic membrane (usually Teflon covered on one side with a porous electrode material) separates the aqueous electrolyte from the spectrometer. The key characteristics of the technique are that sampling can be made fairly near the electrode surface, the response time is fairly rapid, and the mass intensities are quantitatively related to the concentrations of the species in the sampling zone. By scanning the electrode potential and monitoring a specific mass peak, one can correlate product appearance potentials with the current-potential curves. With proper calibration, the number of electrons needed to produce a given product can be determined. Mass spectrometry is a powerful adjunct to electrochemical product analysis, since it can detect electroinactive species and distinguish between isotopes.

So far, only small diatomic and triatomic molecules have been detected, but practical limits have probably not been reached. Coupling of the sampler to a rapid scanning mass spectrometer would permit the simultaneous detection of multiple products (and product distributions) in transient electrochemical experiments. The advent of Fourier transform mass spectrometers may improve considerably the experimental ease of such experiments. With continued development, mass spectroscopy can become a very powerful tool for investigating electrode reaction mechanisms and inferring the identities of intermediates.

CHEMICAL DERIVATIZATION

"Chemical" analysis techniques should not be neglected. One can exploit derivatization to tag a surface if appropriate functional groups are present. Location and quantification can then be accomplished by ex situ or in situ spectroscopic analysis or by traditional electrochemical techniques. These techniques can be very valuable in following the course of a surface reaction or modification and in correlating surface composition with reactivity. They are likely to be particularly powerful for carbon electrodes or polymer-modified electrodes. The biological sciences, for instance, have developed highly selective, site-specific tags that permit quantification at femtomole levels. This is orders of magnitude less material than is contained in 1 cm^2 of a monolayer. Electrochemists must develop and use tags in a similar fashion for probing the molecular composition of electrodes. They should be particularly useful for identifying defects or reaction sites present at the surface in low concentrations.

VISIBLE-ULTRAVIOLET SPECTROSCOPY

Visible-ultraviolet optical techniques should also not be neglected. Although they have a long history and are well developed, new approaches such as the long-optical-path thin-layer cell continue to appear. While they lack the functional specificity of vibrational spectroscopy, they are frequently more easily implemented and can be both quantitative and selective in properly chosen cases.

ELECTRON SPIN RESONANCE SPECTROSCOPY

For more than 25 years, ESR methods have been used to observe electrochemical processes in the homogeneous solution adjacent to an electrode. The methods have some of the power for detailed molecular characterization possessed by NMR techniques, but ESR offers generally superior sensitivity and might prove attractive as a probe of interfacial structure and composition. Clever spin-labeling or spin-trapping techniques will probably be needed to realize this prospect, but with the recent progress in synthetic manipulation of interfaces, a good foundation for such work now exists.

Chapter 5

INTERFACIAL STRUCTURE

The second session of the workshop was devoted to an analysis of two related questions:

- What kinds of more detailed information about molecules near electrode surfaces are needed to sustain progress in electrochemical science?

- What instrumental techniques are best suited for obtaining the desired information and how can they be utilized most effectively?

More quantitative information on the atomic and molecular scale is needed about the fine structure existing at and near interfaces that divide electrodes from the electrolyte solutions in which they are emloyed. Examples include the effect of the underlying electrode structure on ions and molecules that approach it. Structural effects are to be expected, not only on reactants but also on solvent and supporting electrolyte components, and all can be important in controlling the rates and courses of electrochemical processes. The electric field present in the interfacial region can affect the orientations, dielectric properties, and adsorptive bonding of molecules at surfaces, as well as the rate of electron transfer across the surface.

Reactant adsorption at electrode interfaces is one of the most important characteristics distinguishing heterogeneous from homogeneous electron transfer reactions, and it is of crucial importance in most catalyzed electrode processes. Despite these well-known facts, reliable data on the thermodynamics, not to mention the kinetics, that govern adsorption at electrodes are available for very few systems. Almost all knowledge concerns mercury or (to a lesser extent) platinum. Questions about the nature of the adsorptive bond, the free energies of adsorption, the orientation of adsorbed species, the rate of exchange between dissolved and adsorbed molecules, and the role of adsorbed states in overall electrode processes remain largely unanswerable in a definitive way because data of sufficient quality are lacking.

There is considerable current research on the preparation and study of electrodes with surfaces that have been modified by the permanent attachment of a wide variety of chemical structures. Although the results reported so far with such modified electrodes are impressive and promising, they suffer from the same lack of detailed structural information that impedes more rapid progress in understanding the behavior of unmodified electrodes. For example, as elementary yet important a parameter as the in situ thickness of a modifying film on an electrode surface can rarely be specified with high certainty.

EXPERIMENTAL STRATEGY

In choosing techniques to attack the many difficult problems associated with in situ structural characterization of interfaces, some general guidelines can be provided:

1. Techniques that yield more direct information (e.g., x-ray crystallography), as distinguished from those dependent on models (e.g., ellipsometry), are usually more attractive, but may entail additional computational effort.

2. Applying a combination of techniques, both electrochemical and spectroscopic, to study a single system of interest is a strategy that has much to recommend it. However, the advantages to be gained will be fully realized only if there is no compromise made with the rigor and care required to conduct and interpret the electrochemical measurements.

A variety of nonelectrochemical techniques await more widespread adoption for characterization of electrochemical interfaces: The in situ spectroscopy of electrode-solution interfaces now includes some powerful tools, including ellipsometry (wavelength scanned or conventional); Fourier transform infrared reflectance spectroscopy; ordinary, resonance enhanced, and surface-enhanced Raman vibrational spectroscopies; visible-ultraviolet reflectance, internal reflectance, and transmission spectroscopies; and EXAFS. For semiconductor electrodes and for chromophorically modified electrodes, luminescence and photocurrent action spectra are also useful tools. The newer vibrational and EXAFS spectroscopies promise exciting fresh information about static arrangements of surface molecular functionalities with respect to the electrode; but these experiments remain in a formative stage, and progress will require considerable surface modeling, including, for semiconductors, the development of chemical models for surface states.

The understanding of the manner in which the dynamics of interfacial events are influenced by structure is in a primitive state. There are no satisfactory molecularly sensitive probes of dynamics within the electrical double layer or of the motions of interfacial molecules, either attached or adsorbed. Clearly, there are opportunities for new ultrafast spectroscopic experiments and for NMR spectroscopy using magic-angle spinning (perhaps of model systems fashioned from high-surface-area diamagnetic materials) in fundamental interfacial investigations. Further discussion of dynamic processes at interfaces is given in Chapter 7.

Modified electrodes invite a variety of additional in situ probes. Electrodes modified with electrocatalytically active films are an important topic in analysis and in energy conversion. The catalysts may furthermore be embedded in an electron-conducting inorganic or polymeric matrix. The corresponding needs to detect electron, substrate, and ionic transport events are being addressed largely with electrochemical methods. Defining the details of substrate-catalyst adducts, reaction intermediates, and catalyst degradation is important in seeking more efficient and stable molecularly designed catalyst sites and modification layers, but there has been little progress on in situ spectroscopy or separations-oriented sampling of such surfaces. In situ weighing of both modified and unmodified electrode surfaces by means of piezoelectric balances is potentially an important tool for both static and dynamic compositional information. The physical location of the "electron transfer interface" becomes ambiguous for electrodes modified with conducting, electroactive polymers. Unsolved problems include the electrolytic compositional changes that accompany the flow of current through cells with desirable energy storage or discharge properties.

The development of electrochemical sensors based on modified electrode surfaces requires better microstructural information about surfaces than is available at present. In situ analogs of transmission and scanning electron microscopies are called for.

OPPORTUNITIES INVOLVING X-RAY METHODS

A considerable portion of the second session of the workshop was devoted to exploration and discussion of the power and potential utility of techniques based on x-rays for in situ characterization of electrode interfaces. A tutorial description of advanced x-ray methods is given in Appendix C. A key point is the ability of x-rays to penetrate to interfaces that are "buried" within condensed phases. Most of the new opportunities in this area are consequences of the ideal match of x-ray wavelengths to the dimensional information that is needed, the development of synchrotron light sources, and the extremely high fluxes of x-rays that are available from such sources. These high fluxes decrease the time required for a typical experiment by several orders of magnitude below that required for an x-ray experiment using a laboratory source, such as a rotating anode.

Two types of x-ray experiments offer unrealized prospects for in situ atomic-level characterization of chemical processes at electrodes. X-ray absorption near edge structure (XANES) has capabilities for spectroscopic characterization of spin state, valence, and local symmetry. EXAFS concerns the region above the absorption edge and is a modulation of the absorption coefficient extending 100 to 2000 eV above the edge. The structural information obtainable from EXAFS includes local bond distances, coordination number, chemical identity of coordinating atoms, and a measure of structural disorder. Long-range order in the sample is not required for these measurements, a highly desirable attribute for electrochemical applications.

Also of potential value in electrochemical applications is x-ray diffraction. As typically carried out, the method is not element-selective, and it requires (and gives information on) long-range order in the sample.

X-ray beams emanating from synchrotron sources are trains of pulses picoseconds wide and nanoseconds apart; hence x-ray experiments designed to probe changes in the interfacial structure on very short time scales become possible. However, high-flux x-ray beams can lead to extensive radiation damage in experimental systems of interest, and it will be necessary to take appropriate steps to minimize such damage for full exploitation of the methods.

SCANNING TUNNELING MICROSCOPY

A very promising new tool for surface structural characterization is the scanning tunneling microscope (STM). This device has excited the surface science community because of the detailed, atomic-scale topographic pictures it produces. A tutorial discussion of this fresh experimental approach is given in Appendix D.

In the STM, tunneling occurs across a vacuum gap only a few angstroms wide between a planar sample and a sharp tip. Because the tunneling current varies strongly with the gap thickness (as much as a decade per angstrom), it is restricted to that part of the tip closest to the surface. When the end of the tip consists of a single atom, the STM has atomic lateral resolution. By keeping the tunneling current constant and scanning the tip in a raster fashion, one can generate a relief map of the surface. Currently one can achieve spatial resolutions as high as 0.1 Å vertically and 2 Å horizontally. Although most experiments to date have been done in vacuo, the STM does not require ultrahigh vacuum. It has been operated successfully at atmospheric pressure in air and under immersion in liquid nitrogen, liquid helium, oil, and water. Therefore, it is probably usable in an electrochemically interesting environment. Furthermore, it is now evident that the STM response is a function of the chemical composition and electronic structure of the surface, as well as the surface relief. For instance, differences are observed between clean and oxide-covered nickel. Although a quantitative interpretation of the voltage-dependence of the STM traces is not yet available, it seems certain that distinguishing one adsorbate from another will eventually be possible.

OTHER NEW METHODS

Recently developed nonlinear optical techniques based on the use of pulsed lasers also offer promise for in situ characterization in some circumstances. The time resolution inherent in such experiments allows fast surface processes to be monitored (e.g., adsorption-desorption kinetics). However, these techniques seem less suitable for determining structure at electrode surfaces. The vibrational spectroscopies discussed in Chapter 4 seem likely to be more potent than the nonlinear optical methods for assessing molecular structures on surfaces.

Conventional electron microscopy, well established as a useful technique in determining the structure of microbiological samples, also seems likely to have a role in the characterization of the types of structures being generated or applied to electrochemical interfaces. Recent advances in technology may allow microscopic observations of electrode surfaces under conditions close to those that apply in situ.

Recent experiments with the quartz crystal microbalance have shown it to be capable of extreme mass sensitivity for detecting adsorbed species at the interface as well as for measuring physical parameters (viscoelastic properties) of microstructures on electrodes. While obviously giving no direct information on interfacial structure, it provides an additional parameter to which any model of the interface must answer.

Chapter 6

EX SITU ANALYSIS OF INTERFACIAL STRUCTURE AND ITS RELEVANCE TO IN SITU CHARACTERIZATION

Great strides have been made in the understanding of solid-vacuum interfaces over the past decade as a result of the development and application of surface spectroscopic and diffraction techniques. In most instances, electron, ion, atom, or molecular beams are involved, and this aspect has restricted the use of these methods to the vacuum environment. Electrochemists are attempting to take advantage of these powerful surface tools. The third session of the workshop addressed the extent to which ex situ surface physics techniques involving ultrahigh vacuum can be used to gain insight concerning the conditions prevailing at an electrode-electrolyte interface.

Two approaches have been used. One involves the transfer of samples between electrochemical cells and ultrahigh-vacuum (UHV) environments and vice versa. The second involves studies of adsorption at the solid-vacuum interface in a manner that is complementary to corresponding electrochemical adsorption studies. These studies may involve a solvent, and observations are usually made on well-defined crystallographic planes. Electrochemical interfaces, however, cannot be fully simulated in this manner, because the three-dimensional structures and the potential distributions across electrochemical interfaces cannot in general be duplicated in UHV. Nonetheless, insight can be obtained about chemical interactions and structural features that may influence the adsorption of various species at the corresponding electrochemical interface. The best opportunities for valid correlation between ex situ characterizations and actual in situ structure probably lie with systems involving very strong adsorption, because in such systems adsorbate-substrate interactions may overshadow other interactions, such as those between adsorbate and solvent or between solvent and substrate. In other instances, these latter factors could lead to differences between ex situ and in situ interfacial structures.

TRANSFER EXPERIMENTS

The electrochemical properties of solid-metal and semiconductor electrodes are strongly dependent on the crystal plane that is used as the electrode surface. In approaching an understanding of electrocatalysis, it is often instructive to carry out electrochemical studies on a single-crystal surface, either free of impurities or bearing intentionally adsorbed impurities.

In situ techniques for examining the surface structures of single-crystal electrodes are now lacking. The electrochemist needs methods such as low-energy electron diffraction (LEED) for single-crystal electrode studies in order to establish conditions under which surface reconstruction occurs and to examine ordering phenomena in adsorbed layers. Other surface physics techniques such as Auger electron spectrometry (AES) and x-ray and ultraviolet photoelectron spectrometries (XPS, UPS) are needed to provide information concerning elemental analysis and the chemical environment in the interfacial region. These methods can be used with polycrystalline and amorphous electrodes as well as with single-crystal electrodes. All of these techniques are restricted to the vacuum environment.

Still another basis for interest among electrochemists in ex situ methods is that procedures for preparing well-defined low- and high-index single-crystal surfaces are well worked out for UHV environments but often not for electrochemical environments. These factors have prompted several research groups to prepare and characterize single-crystal electrode surfaces, free of impurities, in vacuo using LEED, AES, XPS, and other techniques and then to transfer these surfaces into an electrochemical environment using techniques designed to minimize the possibility of restructuring and contamination of surfaces during the transfer. Following electrochemical characterization, the electrode surfaces are then returned to the ultrahigh vacuum environment for reexamination with various surface physics methods.

With metal electrode surfaces on which the solution exhibits a high contact angle, it is possible to emerse the surface from the solution in a manner that will retain only strongly adsorbed species. Such transfer experiments are elegant but are vulnerable to criticism because the surface analyses are performed in the absence of the extended interfacial structure that is found in solution. Even so, electrochemistry at present has access to no other experimental methods that can provide a view of interfacial structure in such fine, atomic-level detail. It is therefore important that these powerful surface physics techniques continue to be applied in electrochemical contexts. In the near term, there is no realistic basis for replacing such ex situ methods with new in situ approaches capable of providing the equivalent structural information. Therefore, a great emphasis must be placed on establishing confidence in the ability of the ex situ methods to reflect accurately the circumstances at electrochemical interfaces. It is very important now to gain a greater understanding of the changes that accompany the process of emersion. This problem is best approached by methods for interfacial characterization that can be used both in situ and ex situ. Among these are infrared, visible-ultraviolet, and Raman spectroscopy, ellipsometry, and radiochemical methods.

COMPLEMENTARY UHV/ELECTROCHEMICAL STUDIES

Metal-adsorbate systems formed at solid-vacuum interfaces may be very useful as models for electrochemical (electrode-electrolyte) systems. Single-crystal studies in UHV have been helpful in the understanding of heterogeneous catalysis; hence, advances in electrochemical science through the use of well-defined electrode surfaces can be expected. Studies of water multilayers, with and without ions present, using vacuum spectroscopic techniques may help clarify questions on the nature of water layers at electrode surfaces.

FUTURE PRIORITIES

For fundamental, quantitative, and molecular-level studies of electrode surface phenomena, surface physics techniques are extremely powerful and valuable. A proper combination of these methods with in situ spectroscopic and electrochemical techniques can provide information unsurpassed in microscopic detail. Ex situ UHV techniques should therefore continue to be actively pursued.

The highest priority should be given to the development of in situ techniques for establishing crystal surface structure and changes in that structure for both metals and semiconductors in electrolytic solutions. Even following the development of such, it will continue to be necessary to carry out ex situ measurements before and after electrochemical measurements with single-crystal electrodes, because ex situ methods provide information (e.g., interfacial elemental compositions) that largely complements the findings from in situ techniques. The following are specific recommendations for ex situ studies of electrode surfaces:

1. The development of more refined techniques for the transfer of single-crystal electrode surfaces of well-defined structure between the ultrahigh vacuum and electrochemical environments, and vice versa, with the possibility of restructuring and other changes kept at an absolute minimum. Further investigation of emersion techniques is warranted with gold and other hydrophobic electrode surfaces, which appear to retain only the compact double layer upon emersion and even seem to retain the same surface charge before and after emersion.

2. The development of correlation techniques to give some indication of any possible surface structural changes during the transfers. For example, infrared and/or Raman techniques might be used to monitor the vibrational properties of adsorbed species, or ellipsometry could be employed to monitor the optical constants of interfaces and films.

3. Studies to establish under what conditions restructuring occurs in the electrochemical environment, particularly with the more noble metals (e.g., Pt, Pd, Au, Ag), and the nature of this restructuring.

These studies should determine whether single-crystal electrode surfaces may be electrochemically annealed.

4. Comparative studies of adsorbed species at electrochemical and solid-vacuum interfaces. Current studies should be continued and extended to include other adsorbates as well as solvent multilayers, and high-index as well as low-index single-crystal surfaces.

Chapter 7

INTERFACIAL DYNAMICS

One basis of interest in interfaces is the desire to understand and control the dynamic processes that occur in the interfacial region. Of special interest are the factors that affect these processes at liquid-conductor and liquid-semiconductor interfaces. For example, in the case of corrosion, inhibition of dynamic processes is of prime concern. In contrast, battery and fuel-cell applications require exceptionally facile interfacial dynamics. Other applications of electrochemistry, such as synthesis and the development of analytical sensors, require activation of selected interfacial processes.

The fourth session of the workshop dealt with means for characterizing the kinetics and mechanisms of transfer of electrons, ions, neutral species, and energy across the electrode-electrolyte interface. Several fundamental questions were stressed during this session:

- What species are transported across the interface?
- What are the rates of interfacial processes and how can the measurement process be improved?
- What is the effect of the structure of the interface on the processes being measured?

The common theme was that improved experimental techniques and reliable theoretical models are required to provide fresh insights into interfacial dynamics.

Rate processes at solid-liquid interfaces have been previously studied by standard electrochemical techniques, such as cyclic voltammetry, potential- and current-pulse techniques, ac methods, and rotating electrodes. However, these methods are often limited to time scales longer than 0.1 millisecond and do not provide spatial resolution. Information obtained at clean metal surfaces from these techniques has been used to demonstrate the correlations of homogeneous and heterogeneous mechanisms of electron transfer. These data form much of the basis for the current understanding of interfacial dynamics.

THEORIES OF ELECTRON TRANSFER

Existing models of electron transfer allow predictions of changes in rate for the simplest case, where there are weak interactions between the reactant and the electrode surface. Inner- and outer-sphere contributions can be accounted for via their separate contributions to the energy of activation. However, calculated absolute rate constants for simple electrode processes still show discrepancies with experimental results.

This situation suggests that the theoretical description of heterogeneous electron transfer needs refinement, perhaps by the use of a non-transition-state approach. The question of whether contemporary electron-transfer theories can be applied to the interface needs consideration. If not, what information needs to be developed for new predictive capabilities? One aspect that is certainly important is to gain insight into tunneling distances. Scanning tunneling microscopy and kinetic measurements with surface-attached species may lead directly to new insights into this question.

ULTRAMICROELECTRODES

Ultramicroelectrodes offer new capabilities for measuring the dynamics of interfacial electron transfer. Electrodes of micrometer dimensions or smaller have reduced capacitance and potential (iR) drop and can be used to make measurements in the time domain from steady-state to nanoseconds. Thus, they offer access to extremely fast interfacial events, including heterogeneous charge transfer reactions for species with nanosecond lifetimes. This new capability raises several practical and theoretical questions concerning the design of new experiments that might take advantage of these capabilities. For example, voltammetry under steady-state conditions is a powerful technique to measure fast heterogeneous charge transfer, but the theory of these charge-transfer diffusive processes needs considerable refinement. There is also a need for describing the basic factors influencing current-voltage curves at frequencies exceeding 1 MHz. Eventually, the measurement of rapid interfacial events will lead to the measurement of rates that approach the limits predicted by existing theories and thus will represent a significant advance in experimental capabilities. Certain completely new measurement strategies are on the horizon. The reduced dimensions of the electrodes make single-electron counting conceivable. The measurement of currents on short time scales via electron-to-photon conversion, with subsequent correlated detection, shows considerable promise for the measurement of rapid events such as electron transfer and follow-up chemical reactions. The new domains that have already been opened to electrochemistry by ultramicroelectrodes dictate that continued developments occur in this area.

A key question to be addressed at electrodes of all sizes is the relationship of surface structure to rate. Until a fuller description of the surface structure of an electrode exists, it will be difficult to develop specific theories that will predict details of experimental behavior. For example, it is possible that measured rate constants sometimes reflect events at relatively few active sites on an electrode or at surface imperfections. Thus, the concept of the interface as an ensemble of dispersed reactive zones must be considered.

IMPEDANCE METHODS

Impedance spectrometry offers considerable advantages for understanding dynamic processes at electrode surfaces. Advances in data processing and electronics have made impedance measurements much less difficult in recent years. For simple electrochemical systems, interpretation of impedance measurements can be straightforward, operationally simple, and no more model-dependent that other conventional electrochemical experiments such as cyclic voltammetry. Furthermore, the information content of a single impedance spectrum is extremely high, and the effects of mass transport, heterogeneous kinetics, adsorption, film growth, etc., are all manifested in the data. Frequencies from 50 KHz to 0.01 Hz can be probed in a short measurement time, so that a wide spectrum of events can be quantified. This is not possible with most electrochemical techniques, which operate in a narrower band of frequencies. Therefore, the approach should have considerable utility in kinetic studies of short-lived species (at high frequencies) or for chemically unstable systems where repetitive voltammetric runs are not feasible.

SPECTROELECTROCHEMICAL METHODS

Combinations of spectroscopic tools with electrochemistry can be used to gain new insights into interfacial dynamics. Ellipsometry is useful to study film growth when reliable optical constants are known. Considerable promise for new insights exists with the use of laser spectroscopic techniques to probe electrode surfaces, since these techniques permit in situ characterization of dynamics. Measurements in the millisecond and microsecond domains are now possible and can be used to probe heterogeneous electron transfer, photon-induced electron transfer, surface chemical reactions, adsorption and desorption, surface diffusion, and microstructure growth. These measurements have primarily been made via Raman scattering. However, two-photon processes (such as Raman mixing and second harmonic techniques), luminescence, photoionization, and photoelectron emission can also be studied with laser sources.

Pulsed lasers with femtosecond and picosecond pulses may become useful for fundamental studies of interfacial dynamics. For example, photo-induced electron transfer, vibrational energy transfer, and electronic energy transfer can be probed on these short time scales. In addition, advances in spatial resolution allow surface-enhanced laser spectroscopy to be used for in situ molecular spectroscopic microscopy. This family of spectroscopic tools holds a good deal of promise for studying processes in composite materials, at microelectrodes, and in local zones on semiconductor surfaces. The principal advantages of all of these techniques are molecular specificity, sensitivity, and time resolution, and these advantages should be fully exploited. However, the techniques still require better theory for interpretation of results. Efforts are especially needed in the theory of interactions of electromagnetic waves with electrified interfaces. They clearly will require collaboration between electrochemists and physicists.

OVERALL PERSPECTIVES

In the future, new electrochemical as well as spectroscopic methods will become important for the investigation of interfacial electron transfer. Microelectrodes and impedance techniques diminish considerably the temporal limitations of electrochemical measurements. The prospect of observing single-electron transfer events at microelectrodes is becoming a possibility and could greatly influence new electrochemical measurement strategies. Vibrational, structural, and electronic information from picosecond experiments with lasers will improve understanding of very rapid processes at solution-electrode interfaces. However, the relation between interfacial structure and experimental measurements of dynamics needs to be carefully addressed. In addition, more sophisticated theories that are relevant to experimental measurements need to be developed to provide a clearer understanding of the events occurring at electrode surfaces.

Chapter 8

PROCESSES IN THE BOUNDARY LAYER

This chapter refers to the boundary layer adjacent to an electrochemical interface, where mass transport and homogeneous chemical reactions are coupled to double-layer phenomena and heterogeneous electron transfer at the electrode itself. The fifth session at the workshop focused on a variety of phenomena in boundary layers. The range of electrode processes under present study and in prospect includes not only the traditional convection-diffusion systems involving macroscopic electrodes, but also a host of important and more complex combinations of media and electrodes. For many of these latter examples, the transport of charge, electroactive species, and counterions depends on factors often not understood in detail. Some of these systems have practical possibilities in areas such as energy conversion, while others represent important natural processes. Further understanding of the boundary layer transport and kinetics could have a significant impact on research directions.

For the hydrodynamic layer, whose mathematics and experimental engineering are already a part of the electrochemical canon, characterization at a more molecular level is needed, in parallel with the same spectroscopic advances that have been discussed in previous chapters devoted to the interface. When the system gets more complicated, as in many cases cited below, the usual pathway of phenomenological to molecular knowledge may be reversed. A higher degree of molecular-level information may be necessary before mathematical description is feasible and modeling can be done.

NEW MEDIA AND NEW PHENOMENA

Electrode processes can now be studied in unusual media and under conditions that are extreme relative to those normally compatible with liquid electrolyte solutions and the classical simplifications for transport. There is now much interest in solid phases in which ionic charge must move, including intercalation electrodes, "frozen" electrolytes, membranes, ionic surface compounds, separators, electrocatalysts, a variety of polymeric substrates modified and chemically tailored to a particular purpose, surface redox mediators, and ionic-electronic mixed conductors. Other hitherto uncommon examples are nonpolar or low-dielectric media, including gases, supercritical fluids, and liquids without electrolyte. Biological systems and in vivo probes for the study of such systems introduce further multiphase and rheological complications to redox and transport-dependent processes—intercellular fluids, for example.

Electron transfer over extended distances is now being explored very seriously. This phenomenon may be significant in electrochemical processes, particularly in biological or ordered systems. Constraints here are limited reactant mobility in extended structures, as in solids or polymers, and the limits on tunneling of charges. In the active field of semiconductor electrodes, transport of holes and electrons in the solid phase and the recombination of these carriers must be considered. The solid phase is no longer (as with metals) a simple sink for charge. Thus, the two systems of transport must be coupled and must maintain continuity across the phase boundary. Modification of an interface can alter the kinetics on both sides (e.g., with respect to both recombination and electrocatalysis).

CHARACTERIZATION METHODS

The variety of electrochemical systems in which understanding related to a boundary layer is sought makes it unlikely that given in situ experimental techniques would have universal applicability. A number are mentioned as offering particular promise in this area.

Of wide interest is the use of ultramicroelectrodes, singly or in arrays and specially organized assemblies. Ultramicroelectrodes promise significant advancement in the measurement of fast kinetics and in the development of electrochemical sensors because they combine both enhanced transport at electrodes that are virtually all "edge" and reduced capacitance and potential (iR) drop (because of the inverse relation of resistance to an electrode linear dimension and the direct dependence of current on area). They make low-conductivity media accessible to measurement and thereby provide electrode potential windows that allow a view of electrode reactions unattainable in the presence of normal electrolytes. With their reduced dimensions, they can be used to probe selected phases or regions in inhomogeneous media. Properly spaced arrays allow the advantageous properties of single electrodes to be realized while passing enough current to make measurements easier and product detection possible.

With organized assemblies of microelectrodes or structurally ordered media containing lattices, pores, and multilayers, it becomes feasible to carry out new experiments in which electrochemistry proceeds in designed environments. The detection of products generated at selected areas by means of dual electrode pairs (ring-disk electrode analogs) having no moving parts is a direct capitalization on geometry and transport interactions in micro-scale structures. Applications to catalysis, selective sensors, and kinetics are in prospect.

Probing the concentration profiles in boundary layers at electrodes by optical techniques based on lasers is reaching micrometer-level resolution. Greater spectroscopic detail for monitoring the reaction layer is being made available. Schemes of external and internal reflection and transmission through the boundary layer parallel to the electrode are being examined. Temporal resolution is also enhanced, and such techniques with spectroscopic discrimination are a promising adjunct to simultaneous electrochemical data acquisition. Spatial resolution of concentration profiles by techniques sensitive to refractive index (e.g., light deflection or interferometry) has considerable value in this respect.

Further development of more structurally specific probes of the hydrodynamic layer would provide more molecular-level identification of electrochemical reaction processes. Some promising possibilities for examination of "fast" kinetics are resonance Raman or normal Raman spectroscopies and gated Fourier transform infrared spectroscopy, which have microsecond resolution capabilities. Less structurally specific, but even faster, is visible-ultraviolet spectrometry. Fluorescence spectrometry can be applied most usefully for the detection of fluorescent species generated from non-fluorescent reactants. For "slow" kinetics, electron spin resonance and nuclear magnetic resonance have application; both would benefit from improved hydrodynamic flow configurations. These techniques should be able to detect species with lifetimes on the order of seconds. Slower, or steady-state, processes may be amenable to mass spectrometric analysis or EXAFS.

Modulation techniques have considerable value for differentiating between solution and surface reactions and should be more widely used. These include thermal modulation, which may be especially valuable for fast kinetics using laser-based temperature jump methods to heat an electrode surface, and hydrodynamic modulation, which significantly enhances sensitivity and selectivity toward convectively transported species versus surface-bound species. The latter technique has the particular advantage of separating transport-dependent processes from others such as supporting electrolyte reactions, many film-forming reactions, and electrode charging. It also provides unique diagnostic criteria for electrode processes complicated by various kinds of kinetics.

THEORY

Mathematical modeling and simulation are vital to advances in the understanding of processes in boundary layers. Many improvements in the modeling of transport and current distribution problems have been made.

Schemes for simulation of many complex situations now exist. Faster algorithms for more efficient computation would be valuable. Further developments in finite difference and orthogonal collocation techniques and in vector processing would be especially advantageous here.

The newer geometries engendered by organized assemblies require new theoretical treatments. More complicated media may need simultaneous consideration of transfer by diffusion, migration, and convection. Local turbulence and non-Newtonian fluid dynamics may be additional complications. It is obvious that various modes of mass transfer can no longer be as readily decoupled as with standard macroelectrodes in aqueous electrolytes. The influence of phase charge may enter in new ways. Statistical calculations for smaller ensembles and time-dependent transport are further complications to be addressed in this area.

A traditional function of hydrodynamic methodology in electrochemistry is providing the quantitative experiments by which kinetic parameters and new theories of electron transfer can be tested. This function is not likely to be reduced in the future. While voltammetric methods already exist for much of this effort, coupling to spectroscopic probes to achieve some of the purposes outlined here will require new infusions of instrumentation.

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Appendix A

PROGRAM OF THE WORKSHOP ON IN SITU CHARACTERIZATION OF ELECTROCHEMICAL PROCESSES

October 18-20, 1985
Denver, Colorado

FRIDAY, OCTOBER 18

Keynote	A. J. Bard	In Situ Characterization of Electrochemical Processes and the Electrode-Solution Interface: An Overview
Session I	**Interfacial Chemical Composition**	
Chairman	J. G. Gordon, II	
Scribes	H. D. Abruña D. A. Scherson	
Main Speakers	M. Fleischmann	Putting Interfacial Electrochemistry on a Molecular Basis
	J. G. Gordon, II	Interfacial Composition: A Review of Experimental Approaches
	A. Bewick	In Situ IR Spectroscopy at Electrode Surfaces
	T. Kuwana	Interfacial Molecular Composition
Contributor	D. A. Scherson	Mössbauer Spectrometry
Session II	**Interfacial Structure**	
Chairman	F. C. Anson	
Scribes	D. A. Buttry O. R. Melroy	
Main Speakers	R. W. Murray	In Situ Characterization of Interfacial Structure in Electrochemical Processes: Current Status, Needs, and Opportunities
	G. Richmond	Nonlinear Optical Probes of the Electrochemical Interface
	F. W. Lytle	In Situ Characterization with X-ray Techniques
	W. O'Grady	X-ray Studies of the Solid-Electrolyte Interface

Session II (continued)

Contributors	O. R. Melroy	Weighing the Electrode Surface In Situ: The Quartz Microbalance
	D. A. Buttry	Applications of Quartz Microbalance Techniques to In Situ Electrode Characterization

Session III Ex Situ Methods for Characterization of Interfaces

Chairman	E. B. Yeager	
Scribes	M. Soriaga A. Wieckowski	
Main Speakers	E. B. Yeager	Ex Situ Spectroscopic and Diffraction Techniques: Needs, Problems, and Challenges
	A. T. Hubbard	Electrochemistry at Well-Defined Surfaces
	P. N. Ross	Ex Situ Surface Analysis of Emersed Electrodes: Positive Results, Problems, and Promise
	W. N. Hansen	The Emersion of Electrode Surfaces
	J. K. Sass	Complementary Studies at Solid-Vacuum Interfaces
Contributor	A. Wieckowski	In Situ, Radiochemical Charactization of Well-Defined Single Crystal Electrode Surfaces

SATURDAY, OCTOBER 19

Session IV Interfacial Dynamics

Chairman	R. M. Wightman	
Scribes	J. D. Porter H. White	
Main Speakers	R. M. Wightman	Interfacial Dynamics: A Survey of Problems and Methods
	M. J. Weaver	Future Directions in Electrochemical Dynamics: A Brief Overview
	R. P. VanDuyne	Surface Laser Spectroscopy as a Probe of Electrode/Solution Interfacial Dynamics
	D. D. Macdonald	Impedance Spectrometry
Contributor	H. D. Abruña	Electrochemical Application of EXAFS

Session V Processes in the Boundary Layer

Chairman	B. Miller	
Scribes	J. L. Anderson M. Majda	
Main Speakers	B. Miller	Characterization in the Boundary Layer: An Overview
	S. W. Feldberg	Processes in the Region Outside the Outer Helmholtz Plane
	R. L. McCreery	Spectroscopic Probes of the Electrochemical Boundary Layer
	S. Pons	The Use of New Electrode Geometries for the Investigation of Processes in the Hydrodynamic Layer
Contributors	M. Majda	Vectorial Electron Transport in Self-Assembled Monolayers
	J. L. Anderson	Microelectrode Arrays as Analytical Sensors in Hydrodynamic Regimes

SUNDAY, OCTOBER 20

Buffer Session

Chairman	L. R. Faulkner	
Contributors	H. White	Measurements With a Quartz Crystal Microbalance
	M. Soriaga	Concepts of Coordination Chemistry as Applied to Electrochemical Interfaces
	J. D. Porter	Strategies for Interfacial Characterization
	B. A. Parkinson	New Semiconductor/Electrolyte Interfaces
	J. K. Sass	Surface Infrared Spectroscopy

Reports of Scribes

Chairman	L. R. Faulkner

Appendix B

LIST OF PARTICIPANTS AT THE WORKSHOP ON IN SITU CHACTERIZATION OF ELECTROCHEMICAL PROCESSES

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Appendix C

X-RAY TECHNIQUES FOR IN SITU CHARACTERIZATION OF ELECTROCHEMICAL PROCESSES

Farrel W. Lytle
The Boeing Company

> "*Electronic and molecular structure is basic to understanding reactivity....*" Henry Taube

Understanding of the structure of chemical systems at the atomic level must come from probes of structure having wavelengths of atomic dimensions. X-ray, electron, and neutron diffraction techniques are well known for this purpose. In addition, certain indirect information at the atomic or molecular level may be obtained by various spectroscopies spanning the electromagnetic spectrum. This discussion concentrates on x-ray techniques, including variants of x-ray absorption spectroscopy (XAS), that have unrealized potential for in situ, atomic-level characterization of chemical processes at electrodes.

X-ray absorption near edge structure (XANES) from the region near the onset of the absorption edge has the usual capabilities for spectroscopic characterization—i.e., spin state, valence, and local symmetry. Extended x-ray absorption fine structure (EXAFS), which occurs in the region extending 1000 to 2000 eV above the absorption edge, is a modulation of the absorption coefficient caused by elastic scattering of ejected photoelectrons from neighboring atoms. The structural information obtainable from EXAFS consists of local bond distances, coordination number, chemical identity of coordinating atoms, and a measure of structural disorder. This is in addition to the local chemical information obtainable from XANES. Thus XAS involves the absorption of x-rays, but the actual structure probe is the photoelectron, where the source of electrons is the atom involved in the x-ray absorption event. This imparts element specificity, because the x-ray absorption edges of different elements are separated in energy. Simply by choosing the energy range of measurement, the various elements present in a material may be characterized in turn.

As an example, the L-absorption edges of platinum metal are shown in Figure C-1. The EXAFS wiggles are apparent on each edge. In the inset is shown the Fourier transform of the EXAFS from the L_{III} edge. The coordination shells out to number 5 are clearly visible, and their radii can be accurately measured; however, it is apparent that EXAFS is a near-neighbor phenomenon. Also note that the structure at the edge itself—i.e., the

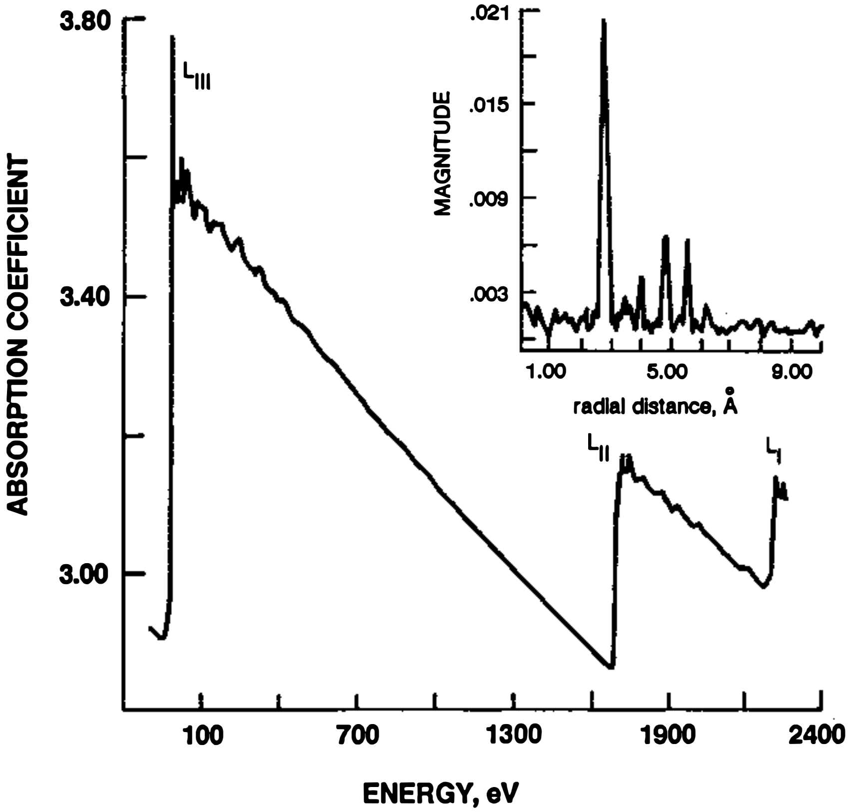

FIGURE C-1 The L-absorption edges of platinum metal. Zero of energy is Pt L_{III} at 11563.7 eV. The inset is the Fourier transform (including phase shift) of the Pt L_{III} EXAFS. Bond distances are accurate for the first five coordination shells to ±0.005 Å.

XANES—is different for each edge. This is because the transitions arise from different core electrons; therefore, the favored dipole transition involves appropriate Franck-Condon states above the Fermi level, which are different in platinum for the electrons of different symmetries.

The fact that x-rays are penetrating is germane to the task of devising useful experimental techniques for in situ characterization. The calculated mean free path for x-ray absorption in water as a function of x-ray energy is shown in Figure C-2. Also indicated are the K-absorption energies of selected elements (to place the graph in perspective with the periodic table). Since it is often possible to

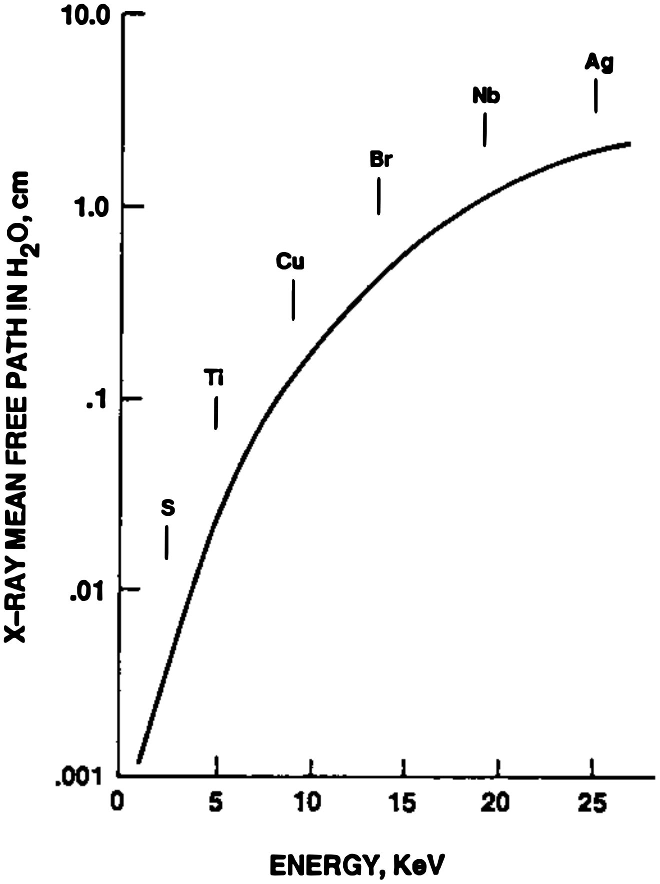

FIGURE C-2 Calculated mean free path of x-rays in water. The energy position of the K-edges of various elements is indicated.

work through two to four mean free paths of extraneous absorbing media, considerable experimental flexibility is possible. Thus, XAS offers a number of unique advantages for in situ electrochemical characterization:

- The penetrating x-ray beam is capable of getting inside a material or experimental apparatus.

- XAS can be combined with reflection or diffraction.

- Once the x-ray beam is at the desired interface, the x-ray absorption event converts the structure probe to electrons, which have a high cross section for interaction with nearby atoms.

- The technique is element-specific.

Considerable experimental flexibility is inherent with XAS techniques. It derives from combining XAS with x-ray diffraction or reflection, or from detecting various products of the x-ray absorption event. The possibilities include fluorescent x-ray photons, optical photons, electrons, ions, and photon desorbed atoms. All of these have different escape depths, and hence they can be used to isolate the region of the sample characterized.

The following list gives x-ray techniques now in use and their most appropriate applications. The first 6 items involve XAS with various geometries and detectors, items 7 and 8 combine XAS with x-ray diffraction, and item 9 is pure x-ray diffraction.

1. Normal x-ray absorption, EXAFS: bulk characterization
2. Fluorescent x-ray EXAFS: trace quantities, bulk
3. Optical EXAFS: near surface, optical depth
4. Electron yield EXAFS: surface to near-surface
5. Photon-stimulated desorption EXAFS: surface species
6. Reflection EXAFS: grazing incidence, surface 10 to 100 Å
7. X-ray scattering with anomalous dispersion: atom-specific, bulk
8. Coupled-beam x-ray diffraction: single-crystal, surface species
9. Reflection x-ray diffraction: top layer

The previous discussion suggests that with carefully conceived experiments it is now possible to measure in situ structural parameters for an electrode surface and, for the double layer in the contacting solution, to measure the concentration of each atomic species at the interface and to monitor changes in species concentrations. All of this could be done in real time and with full reversibility. In the future, it should be possible to obtain atom-specific images at atomic-level resolution of selected surfaces by using x-ray holographic techniques followed by reconstruction with optical lasers. X-ray holography has already been demonstrated with conventional sources. X-rays with a high degree of coherence will be available at very high intensity from undulators. The problems of producing beam splitters, mirrors, etc., for x-ray wavelengths will be difficult but not insurmountable. Wavelength tunability for atomic specificity, penetration to the desired region of the experiment, and high, pulsed intensity for snapshots in time would make this the ultimate atomic-level structure probe. None of these techniques were even imagined 10 years ago. What will we find 10 years in the future?

All of the x-ray techniques mentioned are possible only because of the availability of x-ray beams of unprecedented flux, stability, and collimation from synchrotron sources. The progress in the science of electron storage rings and insertion devices has resulted in a new era, a renaissance in x-ray physics. The flux available is shown in perspective with other light sources in Figure C-3. For comparison, rotating anode x-ray sources are 5 orders of magnitude below the bottom of the graph. The synchrotron x-radiation has the following properties: high and stable intensity, broad spectral range, smooth and predictable shape, narrow vertical collimation, high degree of polarization, and pulsed time structure. Sources are now available in the United States at Stanford University, Cornell University, University of Wisconsin, and Brookhaven National Laboratory. Experimental time is awarded to qualified investigators without cost by reason of the scientific merit of their proposed research.

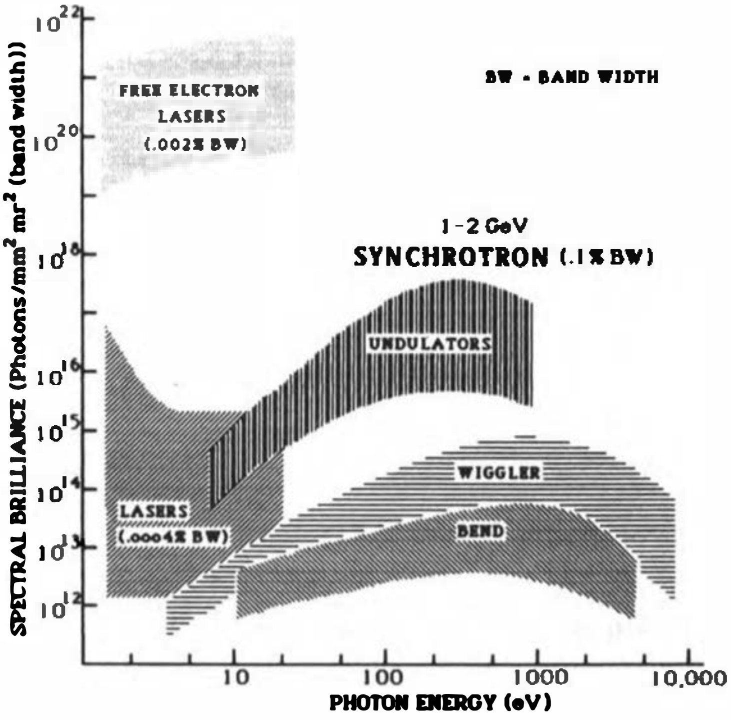

FIGURE C-3 Spectral brilliance compared for various photon sources. Note that the graphs for the various synchrotron radiation sources all may be extrapolated to the right by 10,000 eV for the projected 6 GeV ring. (From *Opportunities in Chemistry*, Board on Chemical Science and Technology, National Academy Press, Washington, 1985, p. 102.)

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Appendix D

SCANNING TUNNELING MICROSCOPY

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The scanning tunneling microscope (STM) is a tool for characterizing surface topography on an atomic scale. It was recently developed by Binnig et al. (*1-5*) at the IBM Zurich Research Laboratory. The best vertical resolution attained with the technique to date is 0.1 Å, with a lateral resolution of 2 to 5 Å. The technique is based on the quantum mechanical tunneling of electrons between two electrodes through an insulating space, typically a vacuum. The electrodes consist of the sample under study and a sharp tip. As the tip is scanned over the surface, the measurement of the tunneling current allows the plotting of a "topographic" map of the surface in real space in all three dimensions. The technique can be used to measure both periodic and nonperiodic surface features on metals and semiconductors.

Because the tunneling current depends on the overlap between the electronic wavefunctions of the sample and the tip, the STM images also depend on the chemical properties of the sample and tip. Therefore, the STM has the potential for studying these chemical properties. In addition, with sufficient stability against mechanical vibrations, inelastic tunneling spectroscopy (*6*), to give information on the vibrational modes of molecules on the surface, may be added in the future to the more basic capabilities of such apparatus.

DESCRIPTION OF TUNNELING AND THE PRINCIPLE OF THE STM

The tunneling of electrons from one conductor to another through an insulator is a purely quantum mechanical phenomenon known for over 50 years (*7*). Although the electrons involved do not have enough energy to surmount the potential energy barrier of the insulator in a classical fashion, they have a small quantum-mechanical probability of reaching the other side of the barrier if the height and width of the barrier are sufficiently small. If two conductors are placed within a few angstroms of each other, the exponentially decaying electronic wavefunctions of the two conductors can overlap enough so that the electrons then have a probability of "tunneling" from one conductor to the other. If a potential is applied between the two conductors, a tunneling current will flow. For two flat, parallel electrodes, this tunneling current, I_T, has an exponential dependence on the distance s between the two conductors (*7*):

$$I_T \propto \left(\frac{V_T}{s}\right) \exp\left(-A\,\phi^{\frac{1}{2}} s\right)$$

Here $A \approx 1.025(\mathrm{eV})^{-\frac{1}{2}}$ Å^{-1} for a vacuum gap, ϕ is the average of the two electrode work functions, s is the distance between the electrodes, and V_T is the applied voltage. With work functions of a few eV, I_T changes by an order of magnitude for every angstrom change of s.

A schematic diagram of the STM is shown in Figure D-1. The tunneling tip is mounted on three orthogonal piezodrives, P_X, P_Y, and P_Z. An electronic feedback circuit keeps I_T constant by applying a voltage V_Z to piezodrive P_Z. For a constant work function, this circuit thus keeps the tip a constant distance s from the surface as it is scanned along

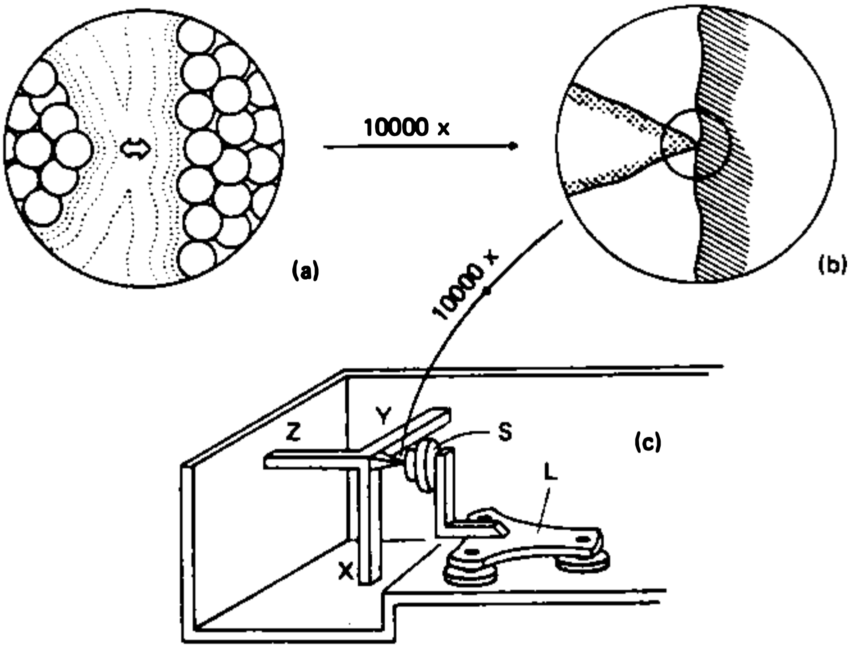

FIGURE D-1 Schematic of the physical principle and technical realization of STM: (a) Apex of the tip (left) and surface (right) at a magnification of about 10^8. The solid circles indicate atoms, the dotted lines electron density contours. The path of the tunnel current is given by the arrow. (b) At a magnification of about 10^4, the tip (left) appears touching the surface (right). (c) STM with rectangular piezodrive X, Y, Z of the tunnel tip at left and "louse" L (piezoelectric "walker" with electrostatic clamping) for rough positioning (μm to cm range) of sample S. After Binnig et al. (*5*).

the x and y directions. A plot of the voltages on the three piezodrives, V_Z versus (V_X,V_Y) thus gives directly the surface topography z(x,y). At constant tunneling current, a change in the work function will also appear in the tunneling scan as a change in the distance s of the tip from the surface. For the case of flat, parallel electrodes, the work function can be separately measured by modulating s while scanning, since the logarithmic derivative of the tunneling current with respect to the electrode separation is

$$\frac{\Delta(\ln I_T)}{\Delta s} \approx \phi^{\frac{1}{2}} + \frac{s(\delta\phi)}{(2\phi^{\frac{1}{2}})\,\delta s}$$

From this equation, one can estimate ϕ far away from the surface, as well as the potential barrier change as the tip approaches the sample. Recent experiments show that $\Delta(\ln I_T)/\Delta s$ is nearly constant and approximately equal to the square root of the average work function ϕ_0, despite the lowering of the actual tunneling barrier by the image potential (*8*). Since the average work function is equal to the barrier height at large distances, the logarithmic derivative directly measures the work function independently of the tip-to-surface distance.

This simple interpretation of STM measurements of surface topography is based on a local approximation that is valid only when the radii of curvature of the sample and the tip are large compared to other relevant distances (*9*); i.e.,

$$r_s, r_t \gg s, (A\phi^{\frac{1}{2}})^{-1}$$

Since the sample and tip are not parallel on an atomic scale, the interpretation of high-resolution STM scans requires more complicated theoretical analysis.

The STM scans actually give the shape of the electronic wavefunctions near the Fermi level, roughly in the middle of the vacuum gap, rather than the positions of the atomic cores (*3*). To make the quantitative correspondence between the electron wavefunctions and the atomic cores requires a tunneling theory on an atomic scale. This is a complex problem requiring, in principle, the solution of the Schroedinger equation for the many-body charged-particle Hamiltonian. In practice, approximations are required, and in the past year several model calculations for the three-dimensional tunneling problem have been performed (*10-14*).

INSTRUMENTATION OF THE SCANNING TUNNELING MICROSCOPE

Since the vertical resolution of the instrument depends on the stability of the tip-to-sample distance, suppression of vibrations is extremely important. To obtain high resolution, this distance must remain stable within 0.1 Å. In the early models in Zurich (*3*), the vibrations were successfully suppressed by supporting the microscope from two sets of spring stages, reducing most of the vibrations to frequencies below 1 Hz. Viton spacers were used to dampen the high-frequency vibrations propagating along the springs. Additional damping of low-frequency vibrations was provided by magnetic eddy currents induced in pieces of copper on the support and on the inner stage by $SmCo_5$ permanent magnets mounted on the intermediate stage. Simpler arrangements have been used in more recent instruments, such as IBM Zurich's "pocket-size" STM, which consists of a stack of stainless steel plates separated by Viton spacers (*15*), or the University of Virginia model, which uses latex tubing and a single spring for vibration isolation (*16*).

The tip of the STM is scanned by three orthogonal piezoelectric devices having a maximum range of a few thousand angstroms to a few micrometers, depending on the instrument. To obtain tunneling current, the sample must be within a few angstroms of the tip, and hence a large motion positioner is needed to bring the sample within the range of the piezodrive. Various devices are used, ranging from a piezoelectric walker (*3*) to mechanical levers or screws (*16,17*).

Relatively simple feedback circuitry is required to control the tip motion so as to keep the current constant as the tip is scanned laterally across the surface. This typically consists of a low-noise preamplifier followed by a logarithmic amplifier (since the tunneling current is an exponential function of the distance between the tip and sample), the output of which is filtered and amplified further to generate the high voltage needed for the Z piezodrive. The scanning electronics in their simple form can be just two ramp generators, one about an order of magnitude faster than the other, which control the motion of the X and Y piezodrives.

Since scanning tunneling microscopy is still a relatively young technique, some difficulties with reliability and reproducibility of high-resolution operation remain.

Thermal drift is an important problem. A small temperature change in the apparatus can cause a relatively large change in the observed scans. In fact, in Zurich a common mode of operation is to use the scanning electronics only to scan the tip along the x-direction while the slower thermal drift, caused by the sample's cooling after cleaning, is used to scan the tip along the y-direction (*18*).

Another still developing area is the fabrication of suitable tips. To obtain subatomic resolution, the end of the tip closest to the surface must consist essentially of a single atom. Some workers (*3,4*) have successfully used mechanically ground tips that have a radius of less than 1 μm. These tips have many small minitips. Since the tunneling current depends so strongly on the distance between the tip and sample, the current density will be concentrated at the minitip closest to the sample surface.

It is also possible to use sharp field emission tips (*19*) prepared by electrochemically etching tungsten wire in NaOH solution. Using this method, tips with a radius of approximately 1000 Å, as observed by scanning electron microscopy (SEM), can be reproducibly fabricated and give atomic resolution in an STM.

The lateral resolution of the STM depends not only on the radius of curvature and the included angle of the end of the tip but also on the size of the structures on the surface (*20*). If the surface is flat on an atomic scale, the lateral resolution of the instrument will depend on the size of the single atom or cluster of atoms at the end of the tip. If the surface is very rough, the tip dimensions must be small compared to the surface structure in order to follow the contours of the surface reliably. Sharp tips are important, even for scanning relatively rough surfaces with features on the scale of thousands of angstroms.

To date, much of the reported work has been on surfaces in ultrahigh vacuum. These reports have demonstrated that atomic-scale information on surface topography can be obtained for reconstructed metal surfaces (*18,21*), semiconductor surfaces (*22*), and adsorbates on metal surfaces (*23*). Recently, results have also been obtained for layered compounds in liquid nitrogen (*24*), graphite in water (*25*), and biological samples in air (*26*).

An example is the famous 7 x 7 reconstruction of Si(111), which has been an intriguing surface problem for 20 years. Figure D-2 shows a STM scan of a reconstructed Si(111) surface. The 7 x 7 unit cell is bounded by lines of minima with deep corners and 12 maxima in each cell. These maxima are interpreted as 12 Si adatoms sitting on top of the Si(111) surface in distinct sites. The different depths of the minima are attributed to nonuniform relaxation of the top layer.

The scanning tunneling microscope is capable of measuring surface topography on an atomic scale on both periodic and nonperiodic structures. It is also able to observe rough surfaces fairly easily and with better resolution than most other types of microscopes. Experiments with oxygen chemisorbed on nickel show that the technique also gives useful information on adsorbed molecules. Other types of chemical analysis of surfaces on an atomic scale, such as tunneling spectrometry, may also follow from the improvements in the technique.

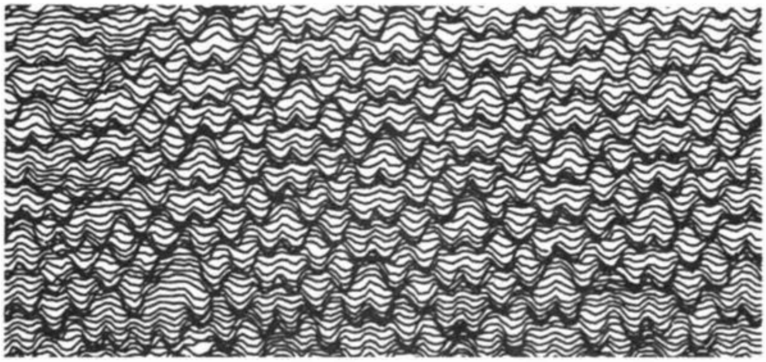

FIGURE D-2 Topographical scan of a 190 x 65 Å region of Si(111) 7 x 7 surface. The data points here were taken at 1.25 Å intervals in this line scan and are linearly connected (not curve fit) (*22*).

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Appendix E

BIOGRAPHICAL SKETCHES OF PANEL MEMBERS

FRED C. ANSON received his B.S. degree in chemistry from the California Institute of Technology in 1954 and his M.S. degree in 1955 and Ph.D. degree in chemistry in 1957, both from Harvard University. He joined the faculty at the California Institute of Technology in 1957, and at present is serving as chairman of the Division of Chemistry and Chemical Engineering. He directs an active research group that has concentrated on the chemistry that accompanies electron transfer across charged interfaces. Understanding the chemical basis of adsorption on electrodes and determining electron transfer rates to molecules attached to surfaces are topics to which his group has contributed. He recently co-discovered one of the most potent electrocatalysts ever tested for the four-electron reduction of dioxygen.

ALLEN J. BARD received a B.S. degree, summa cum laude, in 1955 from City College of New York and A.M. and Ph.D. degrees from Harvard University in 1956 and 1958, respectively. In 1958 he joined the faculty of the University of Texas at Austin, where he now holds the Norman Hackerman/ Welch chair in chemistry. He is editor-in-chief of the Journal of the American Chemical Society and is a member of the National Academy of Sciences. His research interests have included investigations in electroorganic chemistry, photoelectrochemistry, electrogenerated chemiluminescence, and electroanalytical chemistry, and he has published about 400 papers and several books and holds six patents in these areas.

LARRY R. FAULKNER is professor of chemistry and head of the department at the University of Illinois at Urbana-Champaign. He received his B.S. degree from Southern Methodist University in 1966 and his Ph.D. degree in chemistry from the University of Texas at Austin in 1969. He has served since that time as a member of the chemistry faculty at Harvard University, at the University of Texas at Austin, and at the University of Illinois at Urbana-Champaign. He has been a member of the Materials Research Laboratory of the University of Illinois since 1978. He served as U.S. Regional Editor of the Journal of Electroanalytical Chemistry from 1980 to 1985. His research activities focus on electron, energy, and mass transfer processes in systems of controlled chemical architecture.

JOSEPH G. GORDON, II is a Manager of Interfacial Sciences at IBM's Almaden Research Center in San Jose, California. He received an A.B. degree in physics and chemistry from Harvard College in 1966 and a Ph.D. degree in chemistry from the Massachusetts Institute of Technology in 1970. After graduating, he was assistant professor of chemistry at the California Institute of Technology in Pasadena until 1975, when he joined the staff of the San Jose Research Laboratory. His scientific interests are reaction mechanisms and the structure and composition of the electrode-solution interface.

FARREL W. LYTLE received B.S. and M.S. degrees from the University of Nevada and did additional graduate work at the University of Washington. He has worked for the U.S. Bureau of Mines and since 1960 for the Boeing Company. He is at present a principal research scientist for Boeing Aerospace. His research interests include x-ray physics, catalysis, and materials science. He also owns and manages the EXAFS Company, a consulting and instrumentation firm.

BARRY MILLER received an A.B. degree in chemistry from Princeton University and a Ph.D. degree from Massachusetts Institute of Technology. After graduating, he spent 3 years at Harvard University as instructor in chemistry, then became a member of the technical staff at AT&T Bell Laboratories. His research interests include photoelectrochemistry, electroanalytical chemistry, electrosynthesis, and corrosion.

R. MARK WIGHTMAN received his B.A. degree (honors in chemistry) from Erskine College, Due West, South Carolina, in 1968. Following 2 years in the U.S. Army, he attended graduate school at the University of North Carolina and received his Ph.D. degree in 1974. From 1974 to 1976, he was a postdoctoral research associate at the University of Kansas. He joined Indiana University in 1976 as assistant professor of chemistry, and now has the rank of professor. His research interests are electroanalytical chemistry, ultramicroelectrodes, and bioanalytical chemistry.

ERNEST B. YEAGER received a B.A. degree in 1945 from Montclair State College and M.S. and Ph.D. degrees from Case Western Reserve University in 1946 and 1948, respectively. He is Hovorka Professor of Chemistry and Professor of Chemical Engineering at Case Western Reserve University and he is director of the Case Center for Electrochemical Sciences. His research interests are in the field of physical electrochemistry and particularly electrocatalysis, electrode kinetics, and electrolytes. He is a past president of the Electrochemical Society and the International Society of Electrochemistry.