NBSIR 7~~5~~6-1049 (R)

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L. H. Bennett and A. D. Franklin

Institute for Materials Research
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Washington, D. C. 20234

May, 1976

Summary Report

Prepared for
Division of Materials Research
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U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, ***Secretary***

Dr. Betsy Ancker-Johnson, ***Assistant Secretary for Science and Technology***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Acting Director***

Energy Workshops:

The Electron Factor In Catalysis On Metals
Electrocatalysis On Non-Metallic Surfaces

(December 8-12, 1975, Gaithersburg, MD)

L. H. Bennett and A. D. Franklin

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1. THE ELECTRON FACTOR IN CATALYSIS ON METALS

1.1 Overview of the Workshop

Traditionally, the term electron factor in catalysis has denoted a relationship between catalytic activity and the bulk electronic structure of the catalyst. While there is abundant empirical evidence of the importance of the electron factor in heterogeneous catalysis, its precise definition and relation to other factors, particularly the geometric factor, have yet to be established. The interdependence of electronic and geometric factors in bulk bonding is well known: examples include the Hume-Rothery rules of alloy phase stability, relating valence, size, and electronegativity; and Pauling's famous equation relating bond length to bond strength. Chemical processes at a solid-fluid interface have not, thus far, been similarly systematized. However, many new and powerful techniques for the analysis and characterization of clean surfaces and small particles, and of chemical complexes on such surfaces have been developed in recent years. It was the aim of this workshop to move toward systematic understanding of this problem through interdisciplinary action. Specific panel topics were: Experimental Techniques, the Effects of Alloying, Geometrical Effects, and the Theory of Electronic Structure.

The workshop brought together workers in a range of fields including theoretical physicists engaged in band structure and surface calculations, theoretical chemists doing chemical bonding calculations, surface chemists working on clean surfaces and single crystals, practical catalytic chemists engaged in small particle and support effect studies, electrochemists concerned with activity in aqueous environments, etc. The names and affiliations of all participants are listed in the following section.

While progress toward quantitative expression of the Electron Factor in catalysis was limited, this aim served as a focus for the clarification of the capabilities and accomplishments of many experimental and computational techniques. The interdisciplinary emphasis of the conference was one of its most fortunate aspects; many of the distinguished experts present found clarification of the relation between their specialties and catalysis.

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1.3 Outline of Workshop

1.3.1 Format

The format of the workshop consisted of four working panel sessions, on the general topics of Experimental Techniques, Effects of Alloying, Geometrical Effects, and Electronic Structure. In each panel session, one panel member delivered a formal talk outlining the status of that area in his view; other panel members expressed their own views in shorter formal presentations; and the general audience participated most actively through questions and comments under the hand and spur of the moderator in all sessions.

Welcome and Indroductory Remarks: Dr. Ernest Ambler, Acting Director, NBS

Keynote Talk: M. Boudart, Stanford University, speaker

Prof. Boudart's talk will be published in full in the Proceedings.

Panel topics and panel members of the session are listed below.

1.3.2 Panel on Experimental Techniques

Discussion of those techniques providing information on the electron factor, with emphasis on the relation between surfaces in ultra-high vacuum and real catalytic situations.

G. L. Haller, Yale University, Moderator
J. T. Yates, N.B.S., Speaker
R. L. Park, University of Maryland
T. Rhodin, Cornell University
J. R. Katzer, University of Delaware

1.3.3 Panel on Effects of Alloying

Dealing with the effects of alloy composition, including the relation between surface and bulk composition, the nature of bimetallic clusters, and the role of hydrogen as bulk component.

H. Ehrenreich, Harvard University, Moderator

J. H. Sinfelt, Exxon Company, Speaker

V. Ponec, University of Leiden

C. D. Gellatt, Harvard University

1.3.4 Panel on Geometrical Effects

Differences in the electron factor on different crystal faces of the same material. The role of surface irregularities, such as edges, and dislocations on surfaces, and the possibility that such features serve as active sites on the surface.

R. S. Hansen, Ames Lab., Moderator

G. Ertl, University of Munich, Speaker

C. B. Duke, Xerox Corp

J. Turkevich, Princeton University

Prof. Ertl's talk will be published in full in the Proceedings.

1.3.5 Panel on Electronic Structure

The theory of electronic structure at surfaces, including clean surfaces, adsorbed atoms on clean surfaces, and the molecular cluster approach to adsorption. Theory of relationship of electronic structure to catalytic activity.

R. E. Watson, Brookhaven National Lab., Moderator

J. W. Gadzuk, NBS, Speaker

J. R. Smith, General Motors Corp.

A. B. Anderson, Yale University

D. R. Hamann, Bell Laboratories

1.3.6 Proceedings

An account of the formal and informal presentations, and discussions of the workshop is now being prepared. Assessments of the progress of the workshop towards clearer understanding of the electron factor in catalysis on metals, and recommendations for further critical research to that end will be summarized in the Proceedings. A copy of the Proceedings will be forwarded later as an appendix to this report.

1.4 Summary of the Discussions

In his keynote address, Prof. Boudart stressed that electronic effects, which he labelled "ligand effects", were orders of magnitude more effective than geometric factors in varying catalytic rates.

1.4.1 Experimental Techniques

The session began with a lecture by Dr. John T. Yates, Jr. concerned with experimental methods in catalysis. He emphasized the use of a variety of experimental techniques to address important conceptual problems in catalysis, such as the characterization of active sites and the identification of catalytic intermediates. Dr. Farrel Lytle presented a paper which discussed the utility of extended x-ray absorption fine structure (EXAFS) in studies of supported catalysts. Dr. Paul Citrin suggested that specific surface EXAFS (SEXAFS) may provide unique information about structural sensitivity of catalytic reactions.

The panel discussion following his presentation focussed on three general areas: a) The applicability of new experimental techniques to catalysis; b) The identification of concepts which can be examined experimentally; and c) The relevance of measurements on idealized systems to problems in practical catalysis.

Prof. Katzer noted that there is too frequently not much interaction between experiment and theory, and he called for stronger interactions. He also made a plea to bridge the gap between work on single crystals and real practical catalysts, and between low and high pressures. Prof. Rhodin stated that the study of the physics and chemistry of well defined systems can provide information on reaction rate mechanisms or the nature of chemical bonding and these serve as building blocks in the development of new concepts.

Prof. Boudart commented that many of the old conventional chemisorption methods and methods of chemical analysis can frequently be used to calibrate some new spectroscopies such as Auger spectroscopy.

Dr. Lawrence Bennett noted that there were some techniques that were not considered in any detail, including the Mössbauer effect and perturbed angular correlation.

1.4.2 Effects of Alloying

In the invited talk, Dr. J. H. Sinfelt emphasized the recent body of experimental data on transition-noble metal alloys which indicates that upon dilution with a noble metal, the transition metal retains its essential character of d-band vacancies. Also emphasized was the strong correlation between rates of methane hydrogenolysis over group VIII and noble metals and the metal's Pauling percent d-character. In the panel session, the transition metal-noble metal results were discussed at length; it was pointed out that such behavior is anticipated in the coherent potential model of alloying behavior; this topic served as a focal point for the discussion of many experimental techniques. Studies of bulk hydrides and the relation of their electronic structure to the host metal electronic structure were discussed as possible models of surface behavior. A strong need was pointed out for reliable characterization of very small pure metal and alloy supported particles; little is presently known with any certainty in this area.

1.4.3 Geometrical Effects

The discussion encompassed an assortment of geometrical considerations. Experimental methods for determining atomic surface geometry were briefly reviewed, and bonding properties of surface steps were theorized.

Geometric specificity in chemisorption was discussed at length, and questions about geometric specificity in some catalytic reactions were pondered. Prof. G. Ertl felt that some of the recent results on single crystals seem to indicate a considerable influence of surface geometry, in contrast to most investigations on particle size effects. An example is in the ammonia decomposition on tungsten, which is considerably higher on the (111) surface than on the (100) or (110) surfaces. Prof. R. Hansen further discussed this particular result. On the other hand Prof. Ertl reported that the catalytic oxidation of CO over Pd showed no noticeable influence of the surface crystallography on the reaction rate. As to the role of "steps" as active sites for catalysis, Prof. Ertl reported conflicting results from Somorjai and from his own laboratory.

Prof. Turkevich discussed the question of the shape and properties of small particles. He showed electron micrographs of 32Å platinum particles. A. B. Anderson asked whether a case can be made for electronic density of states calculations being relevant to chemisorption and catalysis. Prof. Ertl replied that it was not made in his research. Gail Painter discussed the bonding properties of stepped transition metal surfaces. Alldag noted pronounced differences in kinetics on (110) and (100) surfaces for the decomposition of formic acid on single crystal nickel.

The overall implication of the panel seemed to be an awareness of a great lack of knowledge about the geometrical details of real catalysts.

1.4.4 Electronic Structure

The chairman, Dr. R. E. Watson, charged the speakers with the responsibility for demonstrating to the listeners ways in which surface theory has provided useful insight for those people confronted with real catalytic problems.

The first speaker, Dr. J. W. Gadzuk (substituting for Prof. T. B. Grimley) spoke on the ways in which model Hamiltonian theories of chemisorption can be used in conjunction with *ab initio* calculations and/or experimental spectroscopic data to obtain potential energy surfaces and reaction coordinates for surface-catalyzed chemical processes. Both Gadzuk and Dr. R. P. Messmer stressed the inherent similarities between the solid state model Hamiltonian theories and chemical molecular orbital theories. Another approach for describing chemisorption events, and in particular H on simple metals, is the density functional method discussed by Dr. J. R. Smith. Messmer reviewed recent progress in cluster calculations using the X-α scattered wave technique and discussed how the electronic structure calculated in this way may be related to catalytic situations. Dr. A. B. Anderson presented some cluster calculations using extended Huckel methods, which related to localized chemisorptive bonding at surfaces. Dr. D. R. Hamann presented some of his theoretical calculations on the electronic structure of clean and hydrogen-covered Si surfaces to illustrate, via the case study method, the manner in which experimental and theoretical surface research are mutually reinforcing.

2. ELECTROCATALYSIS ON NON-METALLIC SURFACES

2.1 Overview of the Workshop

The workshop was conceived as a contribution to the science that underlies and supports the technology of fuel cells, which in turn appears to offer considerable hope for more efficient utilization of fuels in the generation of electricity.

Fuel cells hold considerable promise for improvement in the efficiency with which we convert liquid or gaseous fuels to electricity [1], and therefore, for stretching out what are now recognized as dwindling domestic, and world, supplies of natural gas and petroleum. In spite of this, fuel cell research directed toward large scale electricity generation until quite recently has been a relatively neglected area of R & D.

Fuel cells have figured importantly as power supplies for the space program, particularly Apollo, and later have been of interest to the military for remote-station and mobile equipment power supplies. These uses have, until recently, been the only ones contemplated in the Federal Government's R & D program, except for a relatively small project, terminated several years ago, on a high-temperature fuel cell for use with coal combustion gases.

The utility industry, on the other hand, has recently begun to take an active interest in the possibilities of fuel cells [2]. In 1967, Pratt and Whitney (a division of United Aircraft), supported by a number of gas utility companies, established the TARGET Program to prove the technical feasibility of small (12.5 kW) units for on-site generation of power in residences and small businesses. A number of such units have been undergoing field testing over the past several years. That an encouraging level of success has been achieved can be inferred from the fact that United Aircraft (now United Technologies) have recently established a new Power Utilities Division and have launched [2] a second stage program, supported by electric utilities, for the development of an intermediate-level (26 Mw) unit for generation of electric power at local points in the power grid, between the central station and the user.

At the same time, Jersey Enterprises, Inc. (Exxon), together with Alsthom of France, is engaged in a major effort to develop a methanolfueled cell aimed at power levels suitable for dispersed-site electricity generation.

In the latest moves, the Electric Power Research Institute (EPRI) has begun to support fuel cell research projects aimed at getting the first-generation fuel cells into industrial use in the 1975-1980 period, and The Energy Research and Development Administration is beginning a major program in this field. EPRI held a workshop during January 1975, in which the major limiting problems in the technology were thoroughly discussed.

The major potential immediate uses for fuel cells include the delivery of peak power in central station operation and the distributed generation of electricity on the neighborhood or local level [1,3]. These potentialities draw upon the considerably higher efficiency of even present fuel cells systems, as compared to conventional generators, when operating under partial load, their low environmental impact, and their modular construction. In addition, as liquid primary fuels become scarce, fuel cells, like batteries, may have potential for vehicular use and for energy storage.

The major present thrust in the electric utility field, thanks to the United Technologies effort, is the hot ($\sim$ 150-180°C) concentrated phosphoric acid fuel cell. This cell uses hydrogen and air, and with a reformer can burn hydrocarbon gases and liquids. It has the great advantage of lack of sensitivity to CO_2 in the fuel or the air. Alkaline fuel cells have also been highly developed, but, because of their sensitivity to CO_2, only for special applications, such as the Apollo Program.

The major limiting problems [4] in the acid cells are concerned in the first instance with cost, and therefore also lifetime, and secondarily with efficiency. In the acid cell the only electrocatalyst so far capable of achieving the needed performance is platinum. With Pt electrocatalysts of particle size large enough to be stable over the desired lifetime (5 years, or 4×10^4 hours) the loading is so high that the cost is prohibitive. If the particle size is made sufficiently small so that the cost is reduced enough to make first-generation (1975-80) cells commercially attractive, the lifetime cannot be achieved because of sintering of the Pt particles. Ultimately, also, the Pt will probably have to be replaced altogether to meet the cost requirements of the more general use contemplated beyond 1980. Other metals oxides or other compounds are possibilities.

Furthermore, at the air electrode in both acid and alkaline media, present catalysts (including Pt) reduce the oxygen at least partially to peroxide rather than to water. The working voltage for the peroxide reaction is lower than that possible with the water reaction, and therefore, the achievable efficiency of conversion of chemical to electrical energy is also lowered. The development of catalysts for oxygen reduction, particularly in the acid cell, that avoid the peroxide reaction or minimize it could result in significant increases in efficiency that may be necessary in the second-generation cells and beyond. It is interesting to note that some highly-conducting metal oxides (e.g., IrO_2, RuO_2) appear to catalyze oxygen reduction directly to water. Unfortunately, they are very unstable in acids, but may ultimately be useful with neutral (buffered) electrolytes.

Thus, it appears that in a very practical sense of application of fuel cells in the extensive way needed beyond 1980 may well depend upon progress in the science of electrocatalysis as applied to non-noble metal surfaces, with particular but not exclusive reference to the oxygen electro-reduction processes. Now this is a field at the boundary between two disciplines, electrochemistry on the one hand, and solid state physics and chemistry on the other.

Semiconductors have long been used as heterogeneous catalysts, especially for oxidation and reduction reactions [7]. Early uses of such materials as electrocatalysts included the oxides of Cu and Ag. Silver has found extensive use at the oxygen electrode in alkaline fuel cells, [9] and may well operate as an oxide. Lithiated NiO at temperatures above about 100 °C has also operated successfully as an oxygen electrode in alkaline media [10]. More recently, work has been done using spinels [10] such as $CoAl_2O_4$ and perovskites such as Sr-doped $LaCoO_3$. The latter use is obviously related to the use of the perovskites ABO_3, where A represents rare earth, Pb, or alkaline earth ions, and B is Co or Mn, for oxidation of CO and reduction of NO_x in automotive exhaust catalysts [12]. Some of the early, exciting non-metallic electrocatalysts, for both hydrogen oxidation and oxygen reduction were the tungsten bronzes and related compounds [13,14,15]. However, more recent work has shown that the observed high catalytic activity probably depends upon the presence of Pt, [16,17] which in some way activates the oxide in a synergistic fashion.

A fairly detailed body of theory has been worked out for electrochemical processes on semiconductors and insulators [5,6], but most of the application has been to very well-characterized semiconductors such as Ge, Si, GaAs, ZnO, and CdS. Recently, Tench and Yeager [18] have applied these ideas to a study of lithiated NiO.

With this as background, the time appeared ripe for a workshop on Electrocatalysis on Non-Metallic Surfaces, to review the most recent experimental and theoretical investigations, to consider what are the problems most important for scientific progress in this field, and to strive for some common understanding on how to approach those problems. A fundamental purpose of the workshop was to bring together electrochemists, surface scientists, and solid state physicists and chemists to stimulate as much interdisciplinary interaction as possible.

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2.4 Program and Abstracts

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2.4.1 Session 1 - Joint Session with Workshop on the Electron Factor in Catalysis on Metals

Chairman: Dr. Alan D. Franklin
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Plenary Lecture: Electron Transfer and Electrocatalysis
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Non-catalysed electron transfer is reasonably defined as an electron exchange between an electron donor or acceptor and an electrode under the condition of very weak interaction between the reactants and the electrode. The case of strong interaction between reactants and electrodes is analysed with respect to its catalytic effect on electron transfer. It is pointed out that strong interaction may often inhibit electron transfer for a single electron transfer step at its individual equilibrium potential. Electrocatalysis is, however, found in multistep electron transfer reactions when the adsorption of intermediates in the reaction path brings the individual standard potentials of the single electron transfer steps closer to that of the overall redox potential. Examples for this effect of adsorptive interaction are given for metal and non-metallic electrodes. It is further analysed where the electron energy levels of the adsorbed reactants are located with respect to the characteristic energy levels in the metallic or non-metallic electrodes and in the non-adsorbed species in solution. The important role of surface states at a non-metallic electrode for chemisorption and electrocatalysis is emphasized.

2.4.2 Session 2 - Theory of Electrocatalysis on Non-Metallic Surfaces

Chairman: Dr. John B. Goodenough, Lincoln Laboratory
Reporter: Dr. William J. Gadzuk, National Bureau of Standards

Plenary Lecture on Surface states, Chemisorption, and Catalytic Processes on Transition Metal Oxides (with F. J. Morin and R. Hurst).
Professor Thomas Wolfram
University of Missouri at Columbia

Contributed Papers and Discussion.

A. B. Kunz, M. P. Guse, and R. J. Blint
University of Illinois
"Hartree-Fock Calculations of Hydrogen Adsorption on Nickel, Copper, and Magnesium Oxide"

E. Siegel, Public Service Electric and Gas Co.
"Ten-Fold Degenerate Hubbard and Anderson Models of Chemisorption on Narrow Band Transition Metal Oxide, Carbide, and Nitride Surfaces"

H. J. Zeiger, Victor E. Henrich, and G. Dresselhaus
Lincoln Laboratory
"Stark Model of The Excitonic Surface States Observed on MgO"

Yu. I. Kharkats, Institute of Electrochemistry of the Academy of Sciences of the USSR, and J. Ulstrup, The Technical University of Denmark
"The Role of Intramolecular Quantum Modes in Electrode Reactions via Intermediate States"

R. P. Messmer, General Electric Co., and
K. H. Johnson, Massachusetts Institute of Technology
"Quantum Chemistry and Catalysis"

Plenary Lecture: Surface States, Chemisorption and Catalytic Processes on Transition Metal Oxides

T. Wolfram, F. J. Morin* and R. Hurst
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A discussion of the bulk and surface electronic states of transition metal oxides such as the perovskites is presented. The factors which determine the surface electronic structure are described and several examples of surface states and surface energy band models are presented using both cluster and energy band models.

The role of d-electron surface states in chemisorption and catalytic processes on transition metal oxides is considered. Several examples of surface reactions are given using a cluster model for the substrate. These examples include the chemisorption of OH^- ions, the dissociative adsorption of H_2 and the hydrogenation of ethylene.

A detailed description of a Green's function theory for surface reactions is given in which both the reacting molecule and the solid are described by local basis states. The concept of the spectral weight function (local density of states) is used to describe delocalized bonding of molecules to a solid surface. As an example of the application of the theory the formation of localized electronic states associated with the adsorption of OH^- ions is considered.

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Hartree-Fock Calculations of Hydrogen Adsorption on Nickel, Copper, and Magnesium Oxide[1]

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The potential energy curves for NiH, HNiH, CuH, and HCuH resulting from the ground and first excited state atomic configurations are calculated using the unrestricted Hartree-Fock and generalize valence bond methods. NiH bonding in the $3d^8 4s^2$ configuration and CuH bonding in the $3d^9 4s^2$ configuration is by means of an sp hybrid orbital, which comes from the 4s shell, leaving a singly occupied orbital free to bond to another hydrogen atom. The bonding in the $NiH3d^9 4s$ and $CuH3d^{10} 4s$ configurations is to the 4s orbital leaving in NiH a hole in the nickel

3d shell which interacts with another hydrogen only weakly and in CuH a closed 3d shell resulting in a repulsive potential energy curve. The interaction of hydrogen with a cluster representing a magnesium oxide surface V_1 center was calculated using UHF. The lowest energy results when the Mg and O are singly ionized rather than doubly as in the bulk, resulting in a surface radical. The hydrogen is bound over one of the oxygen atoms.

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[1] This research was supported by the National Science Foundation under Grant DMR 72-03026.

Ten-Fold Degenerate Hubbard and Anderson Models of Chemisorption on Narrow Band Transition Metal Oxide, Carbide and Nitride Surfaces

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The ten-fold degenerate Hubbard (TDHM) and Anderson (TDAM) models of true d-electron (hole) transition metals are applied to narrow band transition metal oxide, carbide and nitride surfaces. The gas (transition metal or hydrogen) chemisorption energy is calculated with this ten-fold degeneracy, Hund's rule correction and compared to that for a non-degenerate, s-electron (hole) treatment. With this model Hamiltonian approach, one can only calculate the trend in chemisorption energy as a function of d-band-filling $\Delta E\ (f_B)$ and not absolute magnitudes of chemisorption energy. The shift in $\Delta E\ (f_B)$ for transition metal oxides, carbides and nitrides from the parent transition metals $\Delta E\ (f_B)$ is calculated from the shift in lattice constant upon metalloid information. This is accomplished via a Heine-like prediction of d-bandwidth contraction upon metalloid formation which produces an effective increase

in d-band-filling, without necessarily a donation of charge from the metalloid anion to transition metal cation. Such an effect exists in alloy formation.

Stark Model of The Excitonic Surface States Observed on MgO*

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Using the energy and angle-of-incidence dependence of the electron energy loss spectra of MgO, we have separated the excitonic transitions from the Mg core levels to the excited states into those of bulk and surface origin. The bulk transitions are very nearly those of the free Mg^{2+} ion. The (100) surface-state transitions can be described by Stark-splitting of the energy levels of the surface Mg^{2+} ions in the intense Madelung electric fields at the crystal surface. The observations on other crystal faces of MgO and in amorphous MgO, however, suggest the possibility of the presence of surface Mg^{+} ions.

---

*This work was sponsored by the Department of the Air Force.

The Role of Intramolecular Quantum Modes in Electrode Reactions via Intermediate States

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The importance of intermediate electronic states of energy-non-conserving (virtual) nature in various molecular processes has been recognized recently. In homogeneous and heterogeneous electron transfer reactions such states participate effectively, when they provide good electronic and/or Franck Condon overlap integrals with both the initial and final manifold of vibrational states.

For weak interactions the electron transfer probability, averaged over all vibrational and electronic states, is calculated by second order quantum mechanical perturbation theory. Account can thus be taken of reorganization of both solvent (classical) and intramolecular modes (essentially quantum) resulting in physically transparent expression for the reaction probability. Also adiabaticity of the overall reactions can be incorporated in the theory. Explicit summation can be performed for various model systems (Fermi distribution functions, harmonic or Morse potentials etc.), which again leads to theoretical free energy relationships for direct reactions. The electrochemical reduction of molecular oxygen on various phthalocyanine catalysts is analyzed on the basis of the formalism presented.

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A number of recent theoretical calculations on model systems relevant to chemisorption and catalysis are discussed. The approach taken is basically chemical in nature, emphasizing the local active site concept and employing a cluster of atoms to represent the substrate which interacts with the molecular or atomic adsorbate. The computational procedure used in these studies has been the self-consistent-field Xα scattered wave (SCF-Xα-SW) method.

2.4.3 Session 3 - Characterization of Non-Metallic Electrocatalytic Surfaces

Chairman: Dr. Jerome Kruger, National Bureau of Standards
Reporter: Prof. Robert de Levie, Georgetown University

Plenary Lecture on The Study of Electrode Surfaces by Electrochemical Methods
Professor Brian Conway (with H. Angerstein-Kozlowska)
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Plenary Lecture on Electroreflectance Study of the Defect States in Reduced n-type Titanium Dioxide
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"Characterization of Semiconductor Electrodes in Nonaqueous Solvents"

S. Roy Morrison, Stanford Research Institute, and Thomas Freund,
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"Dislocations in ZnO as Channels for Electron Transfer from Surface Species"

The Study of Electrode Surfaces by Electrochemical Methods

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Electrochemical methods for the study of surfaces are reviewed. Unlike high-vacuum techniques, they measure changes in the state of surfaces by virtue of occurrence of electrode surface processes, rather than giving information on the state of the surface itself. However, electrochemical procedures have high sensitivity down to 2% of a monolayer and multiple states of chemisorption can be distinguished with an energy resolution of 100-200 small calories. Interactions in the ad-layer can also be derived from the form of electrical transients. Combination of electrochemical methods with optical techniques, such as relative reflectivity and ellipsometry, provides a new dimension for studies in electrochemical surface science.

Electroreflectance Study of the Defect States in Reduced n-type Titanium Dioxide*

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We have investigated the electroreflectance spectrum of reduced n-type TiO_2, particularly below the fundamental absorption edge ($\sim$ 3 eV), in aqueous electrolyte, metal-semiconductor and metal-oxide-semiconductor configurations. We have observed for the first time in electroreflectance features in the spectrum for $\hbar\omega < 3$ eV which are related to the defect states. It is found that this structure is strongly dependent on the applied bias electric field. One optical peak appears at about 1.7 eV, an energy region in which structure has been observed in various other measurements which are related to both bulk (optical transmission, photoconductivity) and surface (electrochemical, electron loss spectroscopy) states. The intimate relationship between the bulk defect levels introduced by reduction and surface states will be discussed. Our results will be interpreted in terms of a recent model of Morin and Wolfram for d-electron surface states in transition metal oxides.

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*Work supported in part by the National Science Foundation

Electron Energy Loss Spectroscopy of Surface States on Titanium and Vanadium Oxides*

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Using electron energy loss spectroscopy, we have studied the surface electronic structure of TiO_2, Ti_2O_3, $TiO_{0.87}$ and V_2O_3. A surface-state transition in the region of 1.5 to 2.5 eV is present in all of these materials when the surface is reduced by Ar-ion bombardment. Subsequent exposure of the surfaces to oxygen or water vapor reduces or completely eliminates this transition. The origin of the transition in terms of d-electron population of surface cations is discussed.

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*This work was sponsored by the Department of the Air Force.

Characterization of Semiconductor Electrodes in Nonaqueous Solvents

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The large number of simple and reversible redox couples available in nonaqueous solvents allows convenient investigation of the band structures of semiconductors using electrochemical techniques. Comparisons of the cyclic voltammetric behavior of these couples at platinum and a semiconductor permits estimation of the relative energy levels of the conduction and valence bands and provides a means of mapping the gap region for intermediate levels and surface states. This technique is demonstrated with TiO_2 and n-type Si semiconductors. In spite of the

large difference in band gaps between these semiconductors, their electrochemical behavior is similar and is ascribed to a similarity in the energies of their respective conduction bands and the energies of an intermediate energy level in TiO_2 and the valence band in Si.

Dislocations in ZnO as Channels For Electron Transfer From Surface Species[1]

S. Roy Morrison and Thomas Freund[2]
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The results reported show that dislocations strongly affect the properties of the ZnO electrode and that with the help of electrochemical measurements a fairly complete picture of the electrical and chemical behavior of dislocations can be developed. It is shown that dislocations in ZnO act as hole or electron traps in the space charge region, as recombination centers, as points of electric breakdown under anodic polarization, and as current paths leading to exchange current even in an indifferent electrolyte. The dislocations can be passivated by annealing or by precipitation of impurities. A qualitative model is presented that can account for the observed affects of dislocations on the solid state and electrode properties.

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[1] Supported in part by ARO-D.

[2] Now at Xerox Corporation, Webster, New York, 14580.

2.4.4 Session 4 - Electrochemical Process on Non-Metallic Surfaces I

Chairman: Dr. Ralph J. Brodd, Union Carbide Corp.
Reporter: Dr. Ugo Bertocci, National Bureau of Standards

Plenary Lecture on chemical theory of chemisorption and catalysis on the surfaces of non-metals

Professor Robert L. Burwell, Jr.
Northwestern University

Plenary Lecture on electrocatalysis at transition metal oxide and carbide surfaces

Dr. Paul Stonehart
United Technologies Corp.

Contributed Papers and Discussion

D. R. Jennison, D. L. Klein, A. B. Junz, K. M. Hall, and W. S. Williams, University of Illinois
"Relationship Between Electronic Structure and Catalytic Behavior of Transition Metal Carbides"

H. Yoneyama and H. A. Laitinen, University of Florida
"Adsorption and Oxidation of Bromide Ion on Tin Oxide Electrodes"

C. O. Huber, T. A. Berger, and R. E. Reim, University of Wisconsin-Milwaukee
"Cathodic Pyrophosphate-Lead Dioxide Electrode Reaction Properties:

Chemical Theory of Chemisorption and Catalysis On the Surfaces of Non-Metals

Robert L. Burwell, Jr.
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

This paper surveys chemisorption and catalysis on non-metals primarily from the point of view of localized, coordinatively unsaturated surface (cus) sites and with use of analogies to the chemistry of coordination and organometallic complexes. Topics covered include chemisorption on oxides of main group elements and of transition elements, heterogeneous catalytic hydrogenation and oxidation on oxides of transition elements, and chemisorption on group IV elements and group II-V compounds.

Electrocatalysis At Transition Metal Oxide And Carbide Surfaces

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Due to the cost of noble metal electrocatalysts, significant research has been carried out to find non-noble metal electrocatalytic materials. Transition metal oxides, usually doped tungsten oxides (bronzes), have been postulated previously due to their favorable electronic conductivity and stability in electrolytes. The surface chemistry of such electrocatalysts has been largely neglected but interesting parallels exist for the electron injection and extraction with heteropolyanions in solution. The heteropolyanions exhibit electrochemical properties of "bronze" crystals and can be considered to be microcrystallites. Optical studies show correlations between absorbance in the visible region and the electron density per transition metal atom. By and large, the transition metal oxide electrocatalysts have not fulfilled their expectations.

A related research direction has examined the activity of transition metal carbides for hydrogen oxidation in acid. Here it was found that tungsten carbide was the most active material but that it required a pretreatment. Surface studies established that the active form of the tungsten carbide electrocatalyst was slightly carbon deficient.

Relationship Between Electronic Structure and Cayalytic Behavior of Transition Metal Carbides[1]

Dwight R. Jennison, David L. Klein, A. Barry Kunz, Kent M. Hall, and
Wendell S. Williams
Department of Physics and Materials Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

We have studied the electronic structure of TiC within the unrestricted Hartree-Fock approximation. We find that strong covalent bonding occurs between the carbon 2s and 2p and the metal 3d orbitals. An absence of strong metal-metal bonding was noted. We tested various configurations on the metal atoms and found $4s^0 3d^n$ energetically favored. Thus, the formation of the carbon-metal bonds results in a loss of 4s character in the electronic structure. Cluster calculations confirm that the strength of the bonds is sufficient to prevent the reestablishment of 4s character on a surface. The recent studies of Kunz, Guse, and Blint indicate that H bonds strongly to the 4s level, but not to the 3d. Although Ti metal can dissociate H_2, our results explain why the carbide apparently can not. Similar results are anticipated on WC, suggesting a carbon deficient surface may have properties intermediary to W and WC.

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[1] This research was supported in part by the U.S. Energy Research and Development Administration under Contract E(11-1)-1198, and in part by the National Science Foundation under Grant DMR 72-03026.

Adsorption and Oxidation of Bromide Ion on Tin Oxide Electrodes

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Adsorption of bromide ion on a tin oxide electrode proceeded at such a slow rate that adsorption equilibrium took longer than two days to be reached. The electrode became active for oxidation of bromide ion depending on the extent of soaking in an acidic bromide solution. It was found that hydration of the electrode is an important factor to determine its activity for electro-oxidation of bromide ion. An electrode having a high activity lost its activity owing to surface oxidation upon polarization into the discharge potential region of bromide ion.

Cathodic Pyrophosphate Lead Dioxide Electrode Reaction Properties

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In the vicinity of +0.4 volts vs. S. C. E. in pH 8 solution pyrophosphate yields a cathodic current selective over orthophosphate at the lead dioxide electrode. Several aspects of this response were examined using α-electroplated lead dioxide on a platinum base and using mixed α-β wax-bound lead dioxide electrodes prepared from the powdered material. Scanning electron microscope results indicated the topographical nature of the wax-bound electrodes. Current-voltage plots indicated an absence of a limiting current and relatively high residual currents as the potential becomes cathodic. Scanning cyclic voltammetry suggested adsorption of reactive species. Capacitance and coulometric studies indicated clear evidence of adsorption and showed that the current was necessary to the desorption step. Current vs. concentration studies allowed fits to electrosorption models within certain concentration ranges. From these data estimates of some thermodynamic quantities were made. An electrode reaction process involving quasi equilibrium adsorption

of the electron transfer product followed by desorption of a plumbous-pyrophosphate complex is discussed.

2.4.5 Session 5 - Electrochemical Processes on Non-Metallic Surfaces II

Chairman: Prof. Allen J. Bard, University of Texas
Reporter: Dr. A. C. C. Tseung, The City University, London

Plenary Lecture on Mechanisms of Electrochemical Reactions on Non-Metallic Surfaces
Professor Ernest Yeager
Case Western Reserve University

Contributed Papers and Discussion

J. G. Mavroides, D. I. Tchernev, J. A. Kafalas, and D. F. Kolesar,
Lincoln Laboratory
"Photoelectrolysis of Water"

D. M. Tench and D. O. Raleigh, Rockwell International
"Electrochemical Processes on $SrTiO_3$ Electrodes"

A. J. Appleby and M. Savy, Laboratoire
d'Electrolyse du C.N.R.S., Bellevue
"Electrochemical Activity of Polymeric and Monomeric Iron
Phthalocyanines as a Function of Their Spectral Properties"

V. Z. Leger and R. J. Brodd, Union Carbide Corp.
"Electrocatalytic Activity of Phthalocyanines for Oxygen Reduction"

A. Damjanovic
"Continued Growth of Anodic Oxide Films at Platinum and
The Mechanism and Catalysis of Oxygen Evolution"

Mechanisms of Electrochemical Reactions on Non-Metallic Surfaces

Ernest Yeager
Chemistry Department
Case Western Reserve University
Cleveland, Ohio 44106

Non-metallic electrodes are of particular importance to oxygen electrocatalysis. This lecture will consider the mechanism and kinetics of the oxygen electrode reactions on various non-metallic surfaces and the relation of the kinetics to the properties of the surfaces.

Photoelectrolysis of Water*

J. G. Mavroides, D. I. Tchernev, J. A. Kafalas, and D. F. Kolesar
Lincoln Laboratory, Massachusetts Institute of Technology
Lexington, Massachusetts 02173

The photoelectrolysis of water has been investigated by experiments on cells consisting of an illuminated n-type semiconductor anode, an aqueous electrolyte, and a platinized-Pt cathode. It has been found that such cells operate either in the photogalvanic mode (no H_2 evolved) or in the photoelectrolytic mode (H_2 evolved at the cathode by decomposition of water), depending on whether or not the electrolyte surrounding the cathode contains dissolved oxygen. In both cases, current flows through the external circuit and O_2 is evolved at the anode. For operation in the photogalvanic mode, maximum values of 80-85% for the external quantum efficiency (η) for current production have been measured at $h\nu \approx 4$ eV with both single-crystal and polycrystalline TiO_2 anodes. Similar results have been obtained with $SrTiO_3$ anodes. The internal quantum efficiencies, corrected for reflection and absorption losses, are close to 100%, indicating that the band bending in both cases under photogalvanic conditions is sufficient to separate the electron-hole pairs generated by photon absorption and also that the oxygen overvoltage for charge transfer at the semiconductor-electrolyte interface is negligible for illuminated anodes. For operation in the photoelectrolytic mode, η is only 1-2% for TiO_2 and $\sim$ 10% for $SrTiO_3$ if the anode and cathode are shorted together, but the efficiency can be greatly increased by applying a bias voltage. All the observations, including the increased efficiency for $SrTiO_3$, can be given a straightforward explanation in terms of the energy levels of the electrodes and the electrolyte.

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*This work was sponsored by the Department of the Air Force.

Electrochemical Processes on Strontium Titanate Electrodes

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Thousand Oaks, California 91360

The electrochemical properties of n-type single-crystal $SrTiO_3$ electrodes (10^{18}-10^{19} carriers/cm^3) were investigated in acidic sulfate solutions, with special attention to the hydrogen evolution reaction. AC impedance measurements, together with the voltammetric behavior of the ferro-ferricyanide couple and the onset of anodic photocurrent, established that the flat band potential, U_{fb}, lies about 250 mV cathodic to the reversible hydrogen electrode potential.

Slow-sweep cyclic voltammetry with a rotating electrode assembly established several hydrogen discharge mechanisms in moderately acidic solutions. Anodic to U_{fb}, chemical desorption ($H_{ads} + H_{ads} \rightarrow H_2$) appears to be rate limiting. At more cathodic potentials, electrochemical desorption ($H_3O^+ + e^- + H_{ads} \rightarrow H_2 + H_2O$) dominates. At still more cathodic potentials, where proton discharge becomes diffusion-limited, hydrogen discharge from H_2O appears to dominate. Anomalous current behavior at low pH values ($\sim$0.5) suggests possible proton diffusion into the electrode. ESCA measurements showed that the first few atomic layers of the $SrTiO_3$ surface, when brought in contact with aqueous solutions, become depleted in Sr.

Electrochemical Activity of Polymeric and Monomeric Iron Phthalocyanines as a Function of Their Spectral Properties

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Samples of monomer and polymer iron phthalocyanines, prepared both in situ on carbon supports or in the form of thin films, using a gas-phase synthesis method, and by dissolution of liquid-phase preparations in sulfuric acid followed by reprecipitation on carbon, were examined by optical and Mössbauer spectroscopy. Their electrochemical activities for oxygen reduction were examined under steady-state conditions using the ultra-thin porous electrode technique, as a function of O_2 partial pressure, pH (11.8 - 16.4) and H_2O_2 additions. In addition, rotating ring-disk electrode experiments were conducted. Analysis of reaction orders and comparison of activities with those of the support have allowed the most probable mechanism to be determined, in which the rate-determining step is a chemical dissociation of the 0 - 0 bond. Correlations between electrochemical activities and spectral properties indicate the role of polymerization and of the spin configuration of the central iron atom in promoting catalysis. These effects result from reoxidation of Fe^{II}iS to Fe^{III}HS or iS, which is favored by interaction between the polymer π electrons and the d-electrons of the iron.

Electrocatalytic Activity of Phthalocyanines For Oxygen Reduction

V. Z. Leger and R. J. Brodd

A survey of the activity of phthalocyanines for oxygen reduction in saline solutions is described. The central metal ion evidently controls

the overall activity of the phthalocyanine for oxygen reduction. Ferric phthalocyanine has the best overall activity and approaches platinum in activity for oxygen reduction. Structure also influences the activity. The order of activity for the central copper ion is poly copper phthalocyanine > copper phthalocyanine > copper porphyrazine. The substrate also influences the activity of the phthalocyanine as does the solution composition.

Continued Growth of Anodic Oxide Films at Platinum and the Mechanism and Catalysis of Oxygen Evolution

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It is shown on the example of oxygen evolution at platinum that thin anodic oxide films may profoundly affect kinetics and mechanism of an electrochemical reaction. At any potential above 1.0V an "insulating" oxide film grows over the electrode surface. The potential difference across the anode is then divided into potential difference across the oxide film and that across the electrolyte double layer. The film is a barrier to electron transfer and together with the reaction across the double layer controls the kinetics and mechanism of the reaction. The exchange current density of the reaction decreases exponentially with thickness of the film. Only when the distribution of potential across the oxide film and double layer is taken into account it is possible to explain the observed fractional reaction order with respect to activity of hydrogen ions and to propose a mechanism of the reaction that explains this reaction order. In the proposed mechanism a chemical step that follows first electrochemical step controls the rate in the double layer.

2.4.6 Session 6 - Electrochemical Processes at Non-Metallic Surfaces III

Chairman: Professor Norman Hackerman, Rice University
Reporter: Dr. Sigmund Schuldiner, Bureau of Mines

Plenary Lecture on Electrochemical Surface Reactions on Non-Metals
Dr. R. Memming
Philips Forschungs Laboratorium, Hamburg

Contributed Papers and Discussion

A. C. C. Tseung and S. Jasem, The City University, London
"Oxygen Evolution on Semiconducting Oxides"

G. Singh, M. H. Miles, and S. Srinivasan
Brookhaven National Laboratory
"Mixed Oxides as Oxygen Electrodes"

M. F. Weber and H. R. Shanks, Iowa State University
"Surface and Electrocatalytic Properties of Tungsten Bronzes"

Jean Horkans, M. W. Shafer, and R. Peekma,
International Business Machines Corp.
"The Electrochemistry of Molybdenum Oxides"

U. Bertocci, M. Cohen, J. Mullen, and T. Negas,
National Bureau of Standards
"Titanates as Oxygen Electrodes"

Electrochemical Surface Reactions on Non-Metals

R. Memming
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Various surface reactions of semiconductors during electrochemical polarization are investigated which are of interest in connection with catalytic and photo-electrocatalytic processes. Examples for the anodic and cathodic decomposition are given and discussed with regard to the stability of electrode materials. In addition the formation of semiconducting layers on metal electrodes is described and their analysis and characterization investigated as far as electron transfer is concerned. Reactions at bronze electrodes leading to semiconducting surface films are included.

Oxygen Evolution on Semiconducting Oxides

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The oxygen evolution reaction is of particular interest to secondary metal air batteries and water electrolysis plants. However, most of the earlier work has been on precious metals and there are no guidelines for the choice of semiconducting oxides as oxygen evolving electrodes. In this study, the role of the metal/metal oxide or the lower metal oxide/higher metal oxide couple in determining the minimum voltage required for the evolution of oxygen is emphasized, together with other essential requirements such as electrical resistivity, electrode microstructure, corrosion resistance and catalytic properties. A survey of various metal oxides based on the above criteria suggested that $NiCo_2O_4$ is of particular interest and teflon bonded electrodes based on this material gave over 13,000A/m^2 at 1.63 V vs DHE, 70°C, 5N KOH.

Mixed Oxides as Oxygen Electrodes

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The irreversibility of the oxygen electrode reaction on metals and alloys is the main cause of efficiency losses in fuel cells, water electrolysis cells and some battery systems. Oxygen evolution always occurs on oxide covered surfaces while the reduction reaction generally takes place on bare metallic surfaces but can do so on oxides. Since the most likely candidates for reversible oxygen electrodes are oxides, mixed oxides or compound oxides, three types of oxides - NiO_x, $NiCo_2O_4$ and $RuO_2|TiO_2$ were examined as oxygen electrodes in KOH solution. When these oxide electrodes were prepared by thermal decomposition of their salts on a substrate, ratios of true to apparent surface areas of the electrodes were quite high (over 200) and the transfer coefficients, obtained from the Tafel lines for oxygen evolution in the temperature range 25 - 100 °C, were 1.5, as compared with about half that value on nickel electrodes. Above 100 °C $NiCo_2O_4$ and $RuO_2|TiO_2$ electrodes corroded in the strong (50%) KOH environment. Mixed oxides are more stable than simple oxides in the region of potential where oxygen reduction occurs. From the values of the Tafel slopes and exchange current densities for oxygen evolution and reduction on $NiCo_2O_4$ (a spinel) and $RuO_2|TiO_2$, it is clear that reversibility of this electrode reaction was not obtained. Other mixed oxides (including spinels and perovskites) will have to be investigated with the aim of developing reversible oxygen electrodes.

Surface and Electrocatalytic Properties of Tungsten Bronzes[1]

M. F. Weber and H. R. Shanks
Energy and Mineral Resources Research Institute
Iowa State University, Ames, Iowa 50010

Tafel plots have been obtained for the oxygen reaction in acid solution on several alkali tungsten bronzes having different crystal structures. Platinum-doped sodium tungsten bronze crystals were studied and the results compared with those of platinum-free crystals of the same composition. In both cases sodium tungsten bronzes were found to be poor electrocatalysts for the cathodic reduction of oxygen. Similar

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[1] This work was supported in part by a grant from the National Science Foundation.

results are reported for other alkali tungsten bronzes and for tungsten trioxide. Anodic treatment of the crystals affected the electrocatalytic activity of only the sodium tungsten bronze and the effect was a negative one. Cyclic voltammetry was employed to study the effects of the anodic treatment which created a sodium depletion layer on the sodium tungsten bronze surface. The existence and depth of the sodium depletion layer was determined by an Auger Electron Spectroscopy depth profile.

The Electrochemistry of Molybdenum Oxides

Jean Horkans, M. W. Shafer, and R. Peekema
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The general electrochemistry of four oxides of molybdenum, MoO_2, Mo_4O_{11}, Mo_8O_{23}, and Mo_9O_{26}, and the reduction of oxygen on these oxides in 1 N H_2SO_4 have been investigated on natural faces of single crystals. These compounds are found to undergo electrochemical oxidation and reduction in the potential range between 0.13 and 0.73 V vs. NHE. Oxygen does not influence the oxidation of MoO_2 and Mo_4O_{11}, but promotes the anodic dissolution of Mo_8O_{23} and Mo_9O_{26}. Oxygen reduction is supported on all these oxides at low currents and high overpotentials. Large effects of crystal orientation are observed. The chemical composition of the crystal has a much smaller effect. This is apparently due, at least in part, to a change of surface composition with changing electrode potentials. Thus, at a given potential, the compositions of the surface layers of all samples may be similar.

Titanates As Oxygen Electrodes

U. Bertocci, M. I. Cohen, J. L. Mullen and T. Negas
National Bureau of Standards
Washington, D.C. 20234

Single crystal or polycrystalline compacts of five, TiO_2-based, oxide materials were investigated as oxygen electrodes. Potentiostatic and potentiodynamic measurements were accomplished at room temperature using neutral borate or 5M H_3PO_4 and inert (Ar) or oxygen environments. Observations of electrochemical behavior during illumination also were made.

These materials display slow, but continuous, changes in features of potentiodynamic scans, as well as changes in current with time at constant potential. Failure to attain steady-state conditions is attributed to specimen mechanical/chemical inhomogeneities and changes prior to and during measurement, variable surface conditions, together with electrode pre-treatment. For example, cathodic currents for O_2 reduction tend to increase after cathodic polarization, while H_2-evolution is hindered by dissolved O_2. Illumination increases the current density for O_2 reduction at very negative potentials while current decreases are apparent during H_2-evolution in Ar.

Results indicate that these oxides are not promising as electrocatalysts for O_2-reduction, although for a definitive assessment, well-defined and closely controlled surface conditions are necessary.

2.4.7 Session 7 - Electrochemistry at Solid Electrolyte Interfaces, etc.

Chairman: Professor J. Ross MacDonald, University of North Carolina
Reporter: Dr. Douglas O. Raleigh, Rockwell International

Plenary Lecture on Ionic Transport and Electronic Exchange at Solid Electrolyte Interfaces

Dr. Manfred W. Breiter and Gregory C. Farrington,
General Electric Company

Contributed Papers and Discussion

Gregory C. Farrington, General Electric Co.
"Influence of Water on Beta Alumina Interfacial Ion Transport"

Wayne L. Worrell, University of Pennsylvania
"Overvoltage Phenomena in Solid Oxide Electrolyte Cells
at Elevated Temperatures"

R. R. Adzić, A. R. Despić, D. N. Simić, and D. M. Drazić,
Institute of Electrochemistry, Belgrade
"Electrocatalysis by Foreign Metal Monolayers"

Ionic Transport and Electronic Exchange at Solid Electrolyte Interfaces

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Interest in highly conductive solid electrolytes, compounds that display conductivities comparable to aqueous electrolytes at room temperature, is great because of their many potential applications. This paper reviews conduction mechanisms and charge transfer at solid electrolytes having fast ionic transport. For the discussion, solid electrolytes have been grouped into stoichiometric compounds, doped compounds and non-stoichiometric compounds; interfaces are classified as two-phase and multi-phase boundaries.

Influence of Water on Beta Alumina Interfacial Ion Transport

Gregory C. Farrington
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Water, adsorbed on a beta alumina surface, significantly influences the nature of Na^+ ion transport across a non-aqueous electrolyte/beta alumina interface and the behavior of a Pt/beta alumina interface. Na^+ interfacial exchange current at 23 °C between beta alumina and propylene carbonate decreases with increasing surface hydration. Adsorbed water undergoes a number of faradaic reactions at a Pt/beta alumina interface, which otherwise should approximate an ideally polarizable or "blocking" electrode. This paper discusses the effects of adsorbed water on ion and electron transport at these two interfaces.

Overvoltage Phenomena in Solid-Oxide Electrolyte Cells at Elevated Temperatures

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To develop a more quantitative understanding of the factors which establish overvoltages in solid-oxide electrolyte cells, constant currents have been passed through two types of symmetrical cells. At temperatures between 800 and 1000 °C, constant and reproducible cell overvoltages are obtained when the imposed current is less than 50 μA. The cell overvoltage (η) is directly proportional to the current (I), and the interfacial resistance, defined as equal to η/I, is constant for each cell at constant temperature. Assuming that oxygen concentration gradients in the metal portion of the electrodes establish the cell overvoltages, a quantitative expression has been derived to calculate the interfacial resistance for each cell. Reasonable agreement between calculated and experimental values of the interfacial resistance is obtained for cells having two-phase metal-metal oxide electrodes. This agreement indicates that oxygen is transferred between metal particles and the electrolyte rather than through oxide particles in the electrodes. For cells with oxygen-saturated copper electrodes, the solubility-diffusivity product of oxygen in solid copper has been calculated from the overvoltage data.

Electrolysis by Foreign Metal Monolayers

R. R. Adzić, A. R. Despić, D. N. Simić and D. M. Drazić
Institute of Electrochemistry, ICTM and
Faculty of Technology and Metallurgy,
Belgrade, Yugoslavia

Catalytic effects of foreign metal monolayers deposited at underpotentials have been found in the case of Fe^{2+}/Fe^{3+} redox reaction on gold, oxygen reduction on gold, and oxidation of some small organic molecules on platinum. It was found that the catalytic effects of foreign metal monolayers originate in the change of surface electronic properties and the change of energy of adsorption of oxygen or oxygen-containing species for Fe^{2+}/Fe^{3+} and oxygen reduction respectively. In the case of formic acid oxidation foreign metal monolayers decrease the hydrogen adsorption on platinum, thus preventing the formation of the main poisoning species.

2.4.8 Session 8 - Panel Report and Discussion on Major Problems, Advances, and Opportunities Revealed by Workshop

Chairman: Professor Dr. Heinz Gerischer
Fritz Haber Institute der Max Planck Gesellschaft, Berlin
Reporter: Dr. Alan D. Franklin, National Bureau of Standards

Panelists:
Dr. John B. Goodenough, Lincoln Laboratories
Dr. William Gadzuk, National Bureau of Standards
Dr. Jerome Kruger, National Bureau of Standards
Prof. Robert de Levie, Georgetown University
Dr. Ralph J. Brodd, Union Carbide Corp.
Dr. Ugo Bertocci, National Bureau of Standards
Prof. Allen J. Bard, University of Texas at Austin
Dr. Sigmund Schuldiner, Bureau of Mines
Prof. J. Ross MacDonald, University of North Carolina
Dr. Douglas O. Raleigh, Rockwell International
Dr. A. C. C. Tseung, City College, London

Summary of Discussion

Theory - The theoretical papers read at the Workshop dealt mainly with chemisorption rather than with electrocatalysis as such. Because of the great complexity of real catalytic systems, it cannot be expected that theory at present will be able to deal in detail with catalytic problems. Rather, theory can develop ideas and concepts which can guide researchers in developing strategies for investigating and understanding real catalytic systems.

Two trends in chemisorption theory are evident. On the one hand, calculations are being made of the electron states of clusters of atoms that represent small particles, including adsorbed species. Molecular orbital theory plays a dominant role here. Electron energy spectra can be calculated and compared to experimental observations, especially for energy differences. Of particular interest would be calculations on alloy clusters, to explore size effects on alloy catalytic properties, and on clusters containing lattice defects, although clearly the cluster size would have to be large enough to make a lattice defect meaningful.

This kind of theory is closely related to the chemists' view of specific chemical bonds between adsorbate molecules and atoms of the catalyst surface. Such theory is useful for understanding mechanisms and reaction paths, but is not reliable for predicting energy levels of electrons in surfaces and chemical bonds because of neglect of delocalizing effects of the electron states in the solid.

On the other hand, band theory has been extensively used to describe electrochemical reactions on semiconductors based on experimental analyses of the energetic position of band edges at the interface between semiconductors and electrolytes. Specific adsorption sites are introduced as surface states, and the nature of these states is the probable meeting ground for the molecular orbital and band approaches. Indeed, Wolfram showed that the two descriptions converge when considering surface states in the energy gap of the semiconductor, both giving localized electron states capable of interacting strongly with anti-bonding states of adsorbed species. That this kind of theory is applicable to electrochemical situations is demonstrated by the observation in Wolfram's calculations of a group of surface states about 1.5 eV below the conduction band in n-type TiO_2, agreeing well with a peak at the same energy in the electron energy loss spectrum for reduced TiO_2 *in vacuo*, reported in the paper by Henrich, Zeiger, and Dresselhaus, and with a peak found by Lu, Pollak, and Raccah near 1.7 eV in the electro-reflectance spectrum of reduced TiO_2 in contact with 1 M aqueous KCl solution. In addition, Frank, Laser, Hardee, and Bard in their paper report a concentration of surface states about 1.2 eV below the conduction band in n-type TiO_2 from redox behavior of a number of redox couples in acetonitrile in the presence of the TiO_2 as a working electrode.

Characterization - Adequate characterization of electrocatalyst specimens, like the characterization of materials in many other kinds of studies, involves determining a number of things. The specimen purity and stoichiometry must be determined, as the potential role of lattice oxygen in the activity of WC for the electrochemical oxidation of H_2 shows. The paper of Morrison and Freund demonstrates that lattice defects can be important, and Tseung showed that activity for O_2 reduction may correlate with magnetic susceptibility.

Analytical chemistry techniques for measuring very low concentrations of reactants and products in the electrolyte near the electrocatalyst can be helpful in sorting out the reactions taking place and the concentration levels at which impurities might become important. An example is found in the oxygen electroreduction, where a variety of intermediate oxygen-containing species occur, and the problem occurs of assessing the balance between the reduction paths leading to H_2O and H_2O_2.

Techniques for probing the nature of the surface and the species formed on it by chemisorption fall into two classes. On the one hand, there are very sensitive and powerful methods for studying surfaces under high vacuum or other ultra-clean conditions, such as LEED, ESCA, Auger spectroscopy, etc., while on the other hand, there are now a number of techniques capable of studying the surface *in situ*, in contact with an electrolyte and with an applied potential. These include optical techniques such as internal reflection absorption and Raman spectroscopy and electroreflectance, and also include electrochemical methods like linear sweep voltammetry and a.c. impedance. The paper by Conway reviews the tremendously useful information available from linear sweep voltammetry, and Bard and coworkers, in their paper quoted above, use linear sweep voltammetry with a series of redox couples in a non-aqueous solvent to probe the surface states of the electrode material.

The problem with applying the ultra-clean techniques to understanding electrochemical processes is how to assess the correspondence between the nature of the surface as seen by the measurement and the surface as it exists in the electrochemical situation, in contact with the electrolyte and under the influence of the applied potential. In general, changes undoubtedly do take place on the surface as the sample is removed from the electrolyte and prepared for and transferred to the ultra-clean environment. However, examples do exist in which good correspondence has been seen between measurements made under electrochemical conditions and those on ostensibly the same surfaces under high vacuum or controlled gas environments. For instance, the phenomena of underpotential deposition discussed in the paper by Adzic and co-workers arises because the substrate-adsorbate interaction is energetically stronger than is the self-interaction of the adsorbate. In effect the heat of adsorption of the first monolayer is larger than the heat of vaporization of the bulk. It is therefore expected, provided that the surfaces are essentially the same, that the amount by which the underpotential for monolayer deposition differs from the thermodynamic potential for bulk deposition should correlate with the difference between the temperature for flash desorption of bulk deposited layers and that for the last layers of adsorbate to vaporize, and indeed such a correspondence is observed for metals on metals.

Optical techniques, such as internal reflection infrared or Raman spectroscopy, offer the hope of probing in a fundamental way the nature of surface species in situ in the electrochemical environment. A cautionary note must be sounded, however. Even such a seemingly simple system as CO adsorbed from the gas phase on Ni surfaces has yet to be unscrambled in spite of work over three decades using highly sophisticated optical techniques.

Characterization of non-metallic electrocatalytic surfaces and materials may require measurements not always used in electrochemical studies. An example arises from the work reported in this Workshop by Morrison and Freund, pointing out the role dislocations may play in determining the electrochemical behavior. Characterization with respect to dislocations and similar lattice defects may be very important in some cases. Similarly, the discussion brought out that the actual composition of WC electrocatalysts may be quite complex, involving perhaps excess W, substitutional oxygen, or dissolved gases, and that these compositional anomalies may be very significant in determining electrochemical behavior. The paper by Tseung and Jasem brought out a possible correlation between electrocatalytic activity and magnetic susceptibility in some of the transition metal oxides, opening up the possibility of using magnetic measurements as a tool of characterization.

From another standpoint, very sensitive analytical chemistry techniques for the quantitative assessment of very low concentrations of reactants and products can be valuable in sorting out actual reaction mechanisms at various potentials. Such chemical studies in situ during the course of electrochemical reactions on the surface can help elucidate the role of impurities. Because of the variety of oxygen species possible, they may be particularly valuable for studying oxygen reduction.

In situ studies under electrochemical conditions are particularly important for oxide semiconductors or metallic compounds. These materials are apt to be relatively strong Lewis acids or bases and, as mentioned above, to interact strongly with H_2O. Furthermore, as often demonstrated (e.g., the paper by Weber and Shanks on sodium tungsten bronzes in this Proceedings), the nature of the surface is influenced by the electrochemical reactions being catalyzed. Extrapolation from the bulk properties to the surface is seldom possible, and the surface must be studied under dynamic conditions to understand how it influences the electrochemical reactions.

Influence of the Support on the Catalytic Activity of the Electrocatalyst, and Vice Versa - The paper by Stonehart reviewed some of the evidence for the so-called "spill-over effect," in which the support appears to take a more active catalytic role with the catalyst present than it is capable of in the absence of the catalyst. Several mechanisms for this effect appear possible. Examples are Pt on graphite and the earlier work of Hobbs and Tseung on Pt on WO_3.

One possibility is that the support acts as a cocatalyst. In this mode, the support possesses some catalytic activity that operates in a way synergistic to that of the catalyst itself. By shifting concentrations of reactants or products critical to the main reactions, the support may be able to affect the overall reaction rates in a way not possible in the absence of the supported catalyst. A possible example of this mode is the enhancement of the oxygen reduction activity of graphite by the addition of phthalocyanines on the surface. One suggestion is that the role of the phthalocyanine may be to decompose H_2O_2 produced by the reduction of oxygen on the graphite surface, but note evidence to the contrary in the paper of Appleby and Savy. This catalytic activity for oxygen reduction is observed when the phthalocyanine is added to a graphite surface, but not when it is deposited on surfaces of NiO or Au. The presence of the phthalocyanine also enhances the life of the graphite, which again may be due to the removal of H_2O_2.

A second mechanism possible for this apparent synergistic effect between catalyst and support is the modification of the catalyst properties by the support. For instance, it is well known that the different crystallographic faces of a given substance possess different catalytic activities. Deposition of the catalyst on a given support may result in a preponderance of particularly favorable crystal faces exposed to the electrolyte and therefore catalytic activity enhanced over that of the same catalyst on other supports or unsupported. Similarly, favorable structural defects may be stabilized by deposition of the catalyst on a given substrate.

A third mechanism that might in some cases explain an apparent influence of the substrate on the catalyst is the storage or enhanced dissemination of reaction products. By reducing the back reactions, the rate of the overall catalyzed reaction can be increased.

Finally, there may be some similarity between the interaction of, e.g., Pt and graphite and that of Pb adsorbed on Pt. The paper by Adzic and colleagues shows that in the latter case, the adsorption of H on the Pt is inhibited, and reactions such as the oxidation of formic acid, with which adsorbed H interferes, are enhanced.

Photoelectrolysis - Since the work of Fujishima and Honda (Bull. Chem. Soc. Jap 44, 1148 (1971); Nature 238, 37 (1972)) demonstrating direct decomposition of water in a photocell, there has been interest in the possibility of energy conversion using the electrochemical activity induced by the absorption of light at the electrocatalytic surface.

Scientifically, there is interest because the phenomena appear to be amenable to treatment by rather well-established solid state concepts and it appears to be a reasonable testing ground for the applicability of such theory to electrochemical reactions. As a practical source of hydrogen or a practical means of converting solar to electrical or chemical energy, it is still uncertain. Too much energy is wasted with such a wide band gap semiconductor as TiO_2 for practical application, but other, better materials may be found.

"Engineered" Surfaces - A concept that is being actively explored is to attach molecular compounds of known catalytic activity to substrates capable of acting not only as supports but also as electronic connectors with external circuitry. Not only must the substrate be a good conductor but the fixing of specific functional groups must allow rapid electron transfer to the substrate. Graphite has been a favorite substrate to which to fix various polycyclic compounds with controlled functional groups, particularly in a search for oxygen reduction catalysts. One apparent problem is to maintain stability in the presence of the reactive species formed during the electrochemical reactions. A three-dimensional structure with self-renewing surface might work.

Catalysts for the direct reduction of hydrocarbons and for the reduction of oxygen to water rather than hydrogen peroxide might be sought in this way. The suggestion was made that the splitting of the oxygen-oxygen bond needed for reduction to water might go well with coordination compounds involving low-valence states of second and third row transition elements, e.g., Ir^+. In such studies, the mode of adsorption should be determined, whether it involves isolated molecules, clusters, or monolayers of adsorbate. By observing the change in activity of the adsorbate in going from the solution to the adsorbed state, one might obtain some information on the mutual interaction between the adsorbate and substrate.

Interfaces Involving Solid Electrolytes - In a very general way, electron exchange of reactants/products with the electrodes and ion exchange with the electrolyte appear to be very rapid, and early fears of large activation barriers, particularly with respect to the ion exchange with the electrolyte, appear to be unfounded. Indeed, examples of slow processes of this kind are hard to find. The electroreduction of CO_2 with Pt on a stabilized zirconia electrolyte is one possibility. The paper by Farrington in this Proceedings suggests that the transfer of Na^+ between β-Al_2O_3 and propylene carbonate when H_2O (or other protonated species) is present may be another.

Most theories of the development of electrode polarization involve the concept of the blocking electrode. Like the perfect insulator, the completely blocking electrode is an idealization, not really reproduced by any real electrode. A very useful form taken under simplified conditions by the theories of electrode polarization is the equivalent circuit, and it must be remembered that these are idealizations so that complete correspondence with experimental data must not be expected.

As work on solid electrolytes and their interfaces with various electrodes has proceeded, it has been found that the concepts and instrumental methods of aqueous electrochemistry have been very useful.

2.5 Proceedings

A Proceedings of the workshop will be published as an NBS Special Publication. It will contain all the full papers presented, plus a number of comments and a summary of the Panel Report and Discussion.

The requisite number of copies will be forwarded to the sponsoring organizations. Additional copies will be available from the superintendent of documents, U.S. Government Printing Office, Washington, D.C. 20402, under the title Proceedings of the Workshop on Electrocatalysis on Non-Metallic Surfaces. This Proceedings is expected to appear by October 1976.

NBS-114A (REV. 7-73)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBSIR 75-1049	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

THE ELECTRON FACTOR IN CATALYSIS ON METALS
ELECTROCATALYSIS ON NON-METALLIC SURFACES

5. Publication Date
May
March 1976

6. Performing Organization Code

7. AUTHOR(S)
L. H. Bennett and A. D. Franklin

8. Performing Organ. Report No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.
3000110

11. Contract/Grant No.

12. Sponsoring Organization Name and Complete Address *(Street, City, State, ZIP)*
Division of Materials Research
National Science Foundation
Division of Conservation Research and Technology
Energy Research and Development Administration

13. Type of Report & Period Covered
Final

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Two related workshops were held at the National Bureau of Standards in Gaithersburg, MD, December 9-12, 1975, in topics of importance for energy conversion. These topics, concerned with some of the science underlying the development of fuel cells for electric utility use, are: (1) The Electron Factor in Catalysis on Metals; and (2) Electrocatalysis on Non-Metallic Surfaces.

This report includes discussions of the needs and expected benefits, lists of attendees, descriptions of the programs, and summaries of the major problems, advances, and opportunities revealed by the workshops.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Catalysis; electrocatalysis; surface physics and chemistry; electrochemistry; fuel cells; electrodes

18. AVAILABILITY ☐ Unlimited

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19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED	21. NO. OF PAGES 70
20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	22. Price

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