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ENERGY CONVERSION AND UTILIZATION TECHNOLOGIES PROGRAM

Electrocatalysis Research — Final Report for the Period August 25, 1982, through December 30, 1983

L.F. Warren
(Rockwell International, Science Center;
Report No. SC5343.28FR)

August 1984

Sponsored by:
Energy Conversion and Utilization Technologies Division
Office of Energy Systems Research
U.S. Department of Energy

Through an Agreement with
National Aeronautics and Space Administration

Prepared for:
Biocatalysis Research Project
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91109

By:
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1049 Camino Dos Rios
Thousand Oaks, CA 91360

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The Biocatalysis Research Project is managed by the Jet Propulsion Laboratory, California Institute of Technology, for the United States Department of Energy through an agreement with the National Aeronautics and Space Administration (NASA Task RE-152, Amendment 307; DOE Interagency Agreement DE-AI01-81CS66001).

The Biocatalysis Research Project focuses on resolving the major technical barriers that impede the potential use of biologically-facilitated continuous chemical production processes.

PREFACE

The work described herein was conducted by the Rockwell International Science Center for the Jet Propulsion Laboratory, California Institute of Technology, under JPL Subcontract 956343.

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1.0 ABSTRACT

The general field of electrocatalysis, from both the technical and business standpoints is accessed and research areas and approaches most likely to lead to substantial energy/cost savings are identified. Our overall approach was to compile and evaluate available information, relying heavily on inputs/recommendations of research managers and technical personnel in responsible positions in industry and at universities. Some promising approaches identified to date include the use of transition metal compounds as electrocatalysts and the use of the new electrochemical photocapacitance spectroscopy (EPS) technique for electrocatalyst characterization/development.

For the first time, an oxygen electrocatalyst based on the K_2NiF_4 structure was synthesized, investigated and compared with a perovskite analog. Results show that this class of materials, based on Ni^{3+}, forms very efficient and stable O_2 anodes in basic solution and suggest that other structure-types be examined in this regard.

The very difficult problem of dinitrogen and carbon dioxide electroreductions is addressed through the use of biological model systems which can mimic the enzyme processes in nature. While the electrolytic reduction of N_2 and CO_2 is not likely to be applied on a large commercial scale, it may prove to be of great importance for manned space vehicle applications. Our approach was to apply to the electrode surface model systems which complex N_2 and/or CO_2; these would then be reduced in an aqueous or protic environment to generate N_2H_4, NH_3, CH_3OH, etc. Transition metal phosphine complexes were chosen as the models.

2.0 INTRODUCTION AND BACKGROUND

Electrocatalysis is a very broad field offering numerous opportunities for the development of more energy-efficient ways of producing a wide variety of inorganic and organic materials and it plays a central role in the operation, and thus the development, of such promising devices as fuel cells and photoelectrochemical cells. For example, a dimensionally-stable Ti/RuO_x anode [1] developed in recent years (as a replacement for carbon) is now used to produce practically all chlorine generated in the United States, resulting in large energy savings because of the low overvoltage derived from the catalytic properties of the metal/oxide electrode. For organic synthesis, electrocatalytic processes usually operate at relatively low temperatures and offer high yields of a specific product with minimal side reactions, and are consequently used to produce such important products as adiponitrile, a precursor for Nylon 6,6 and 6,12. Fuel cells also have demonstrated potential, as the primary electrical power source for our manned space flight program, and could provide clean, efficient power for terrestrial applications if appropriate catalytic electrodes, more economical than platinum and/or permitting utilization of fuels other than hydrogen, were available. Photoelectrochemical cells, which utilize sunlight to drive chemical reactions, are in the early stages of development but, with appropriate catalytic semiconductor materials, could ultimately provide an inexhaustible source of fuels, i.e., hydrogen from water, methanol from carbon dioxide, or hydrazine from nitrogen.

Such a broad field with demonstrated potential obviously represents a fruitful area for both fundamental and applied research, but a critical comparison of the various opportunities in terms of technical feasibility and potential payoff is presently lacking. At least part of the reason is that much of the work in this field has been done by private industry and detailed information is not readily available. Also, electrochemistry and related disciplines have been advancing rapidly so that many recently-developed ideas/approaches have not been thoroughly evaluated, and close examination of information from various sources/fields is likely to lead to new discoveries/ approaches.

We have proposed to access the field of electrocatalysis, from both the technical and business standpoints, to identify research areas and approaches most likely to lead to substantial energy/cost surveys. A key area identified is the use of transition metal compounds as electrocatalysts, and experiments designed to evaluate concepts and identify promising approaches have been performed. The use of electrochemical photocapacitance spectroscopy for electrocatalyst characterization/development is also addressed.

3.0 TECHNICAL RESULTS

3.1 Preliminary Opportunities/Impact Analysis for ECUT Electrocatalysis Project

Major technological areas in which advances in electrocatalysis could have a large impact on the national energy picture include energy production, inorganic electrosynthesis (including electrowinning), organic electrosynthesis, and energy storage. A summary of key issues and expected impact for each area is given below. Inorganic electrosynthesis is discussed first since a recent breakthrough in catalytic electrodes for the chlorine-caustic process serves to illustrate the important considerations and potential impact for developments in electrocatalysis. A summary and rationale for this ECUT project is given at the end of the write-up.

Inorganic Electrosynthesis

Practically all chlorine (15 million metric tons per year) and primary aluminum (13 million metric tons per year) produced in the United States comes from electrosynthetic processes, which together consume about 5% of the total electrical energy output of the country. Annual world wide production for these processes is currently about 40 and 13 million metric tons, respectively. Other inorganic chemicals, including caustic potash, soda ash and sodium chlorate, are also produced by electrosynthesis, but the quantities are typically too small to be of interest from an energy standpoint. An exception is electrolytic hydrogen which is expected to play an increasingly important role in the overall hydrogen production picture as a function of time.

In the chlorine-caustic process, aqueous sodium chloride solutions are electrolyzed to yield chlorine, sodium hydroxide (caustic soda), and hydrogen (as a by-product). For more than 50 years, the only available anode material was graphite, which is inefficient as a chloride oxidation catalyst and deteriorates rapidly during use. Consequently, the overall process was grossly inefficient because of the high overvoltage for chlorine evolution and excessive resistance losses in the solution resulting from the variable (unnecessarily large) anode to cathode spacing.

In the mid-1970's the chlorine-caustic industry was revolutionized by the introduction of a new mixed oxide (titanium-ruthenium) anode, which is a good chloride oxidation catalyst and dimensionally stable. Use of this anode has resulted in a reduction in cell voltage of 0.7 V, almost equally attributable to the catalytic properties of the electrode (overvoltage reduction) and the electrode dimensional stability (closer anode-cathode spacing permitted). The net energy savings for the process is 25-30%, which translates to an annual energy savings of 20 billion kWhr (equivalent of 12 million barrels of oil) in the United States alone (about 3 times this amount worldwide).

This example serves to illustrate the energy benefit that can be derived from advances in electrocatalysis. A comparable improvement (25% in energy efficiency for the aluminum production process), which would result in even greater energy savings (70 billion kWhr/year), should be attainable via an analogous electrocatalytic electrode development. This opportunity will not receive further attention here, however, since aluminum production involves a high-temperature (1000°C) molten electrolyte which presents unique problems that are outside the scope of the ECUT program (which addresses issues having wider implications).

The key inorganic electrosynthetic reaction that is of interest from an ECUT standpoint is water electrolysis to produce hydrogen. Because of its relatively high cost compared to hydrogen produced from fossil fuels, electrolytic hydrogen is currently used only in applications requiring high purity, e.g., food processing and semiconductor manufacture. However, as fossil fuels become more scarce, electrolysis will probably assume a lead role in hydrogen production for the fertilizer, metallurgical and petrochemical industries. Annual hydrogen produced in the USA is currently the energy equivalent of 1×10^{15} Btu, and this figure is expected to be 3 times greater by the end of the century at the present rate of increase. If, as appears likely, hydrogen becomes widely used as a clean fuel for fuel cells and gas turbines, and as a natural gas substitute, this estimate would have to be significantly increased.

Present water electrolyzers, even those that utilize noble metal catalysts and exploit the advantages of high pressure operation, are only 65-75% efficient and operate at relatively low current densities (200 mA/cm^2). These poor operating parameters are primarily associated with the oxygen electrode. Thus, improvements in the efficiency and stability of electrocatalysts for oxygen evolution would greatly improve the energy efficiency and reduce the costs of water electrolyzers.

Some electrowinning processes, in which a metal is extracted from its ore by electrodeposition from either aqueous or nonaqueous solutions, are also of some interest from an energy standpoint. In particular, deposition from aqueous solutions generally involves considerable overvoltage (>0.3 V) at the poorly catalytic anode (lead) at which oxygen is evolved. Thus, the development of efficient catalysts for oxygen evolution would also have an impact in this area. Production of metals (Zn, Cu and Ni) by electrowinning from aqueous solutions amounts to about 5 million metric tons/year.

Organic Electrosynthesis

In principle, electrosynthesis is a more energy efficient way of producing organic compounds since, compared to thermal conversion processes, reactions can generally be performed at lower temperatures and more reversibly, and are more product specific (fewer side reactions). In spite of these apparent advantages, however, only one organic chemical, adiponitrile, is presently produced on a large scale (200,000 metric tons/uear) by electrosynthesis. This is primarily because capital costs for electrochemical processes increase sharply with scale-up whereas, the opposite is true for thermal processes.

High capital costs for organic electrosynthetic processes are to a large extent attributable to the ineffectiveness of the electrocatalyst, which results in poor selectivity at higher current densities. Presently available electrocatalytic electrodes are also prone to poisoning and often have insufficient lifetimes. More effective catalysts must be developed before organic electrosynthesis can become widely used.

A direct evaluation of the energy benefits of electrosynthesis is difficult to make since its commercial application is limited to those few instances for which the thermal route is precluded, usually by selectivity considerations. However, generalization of one recent study indicates that energy savings in excess of 20% can reasonably be expected for electrosynthesis compared to conventional thermal processes. Potential overall energy savings for organic electrosynthesis can be estimated by considering that USA production of organic chemicals consumes about 10^{15} Btu/year (10^7 Btu/metric ton × 10^8 metric tons/year); 20% of this number is 2×10^{14} Btu/year (equivalent of 40 million barrels of oil). Annual production of a typical bulk chemical in the USA is about 2 million metric tons and consumes 10^{10} Btu; a 20% energy savings on one typical big bulk chemical would then amount to 2×10^9 Btu/year.

Energy Production

Photoelectrochemical cells are in the early stage of development but represent an attractive long-term means of solar energy conversion. Such cells utilize semiconductor electrodes in contact with a liquid electrolyte; the electric field generated within the semiconductor effectively separates electron-hole pairs produced by incident light so that electrochemical redox reactions can be performed at the semiconductor-electrolyte interface. Cells can be designed to produce electricity, fuels (e.g., hydrogen), or both. The catalytic properties of the electrodes, especially in the case of fuel generation, are of paramount importance. In particular, the role of interface states and adsorption processes, which are widely recognized to be critically important, are poorly understood. A hand-in-hand approach involving new in situ, surface characterization methods and the development of new catalytic semiconductor electrode materials is necessary for significant progress toward a practical system.

The energy impact of any economical solar conversion process would be very large. Estimates vary, but as much as 10% of the energy needs of the country may ultimately be provided by solar energy.

Energy Storage

Electrocatalysis also plays an important role in the performance of most battery and fuel cell systems, but particularly those involving gas producing/consuming electrodes, e.g., air or oxygen cathodes and hydrogen anodes. New high energy batteries and fuel cells are now being developed for vehicular propulsion and utility load leveling applications. The energy impact of such systems is difficult to access but will undoubtedly be significant.

Summary and Rationale

It is evident that ample opportunities exist for significant energy savings, both immediate and long-term, via advances in electrocatalysis. Not surprisingly, there is considerable ongoing R&D effort at both industrial and academic institutions directed toward taking advantage of these opportunities. However, the tendency at most industrial laboratories is to focus on specific problems and to operate in secrecy, whereas, academic work is usually focused on "model" systems chosen to provide answers to fundamental questions (rather than for their practical significance). As a result, new developments are often not readily available or sufficiently relevant to impact the fundamental practical issues common to several areas within the field.

In my view, the function of the ECUT program is to help bridge the gap between industrial and academic research by focusing incisive research effort, from an overview standpoint, on fundamental problems that are key to overall progress in the electrocatalysis field. The necessary overview is derived from both the literature and inputs from eminent scientists and managers in responsible industrial and academic positions.

The key overall problem currently hindering progress in the development of practical electrocatalytic systems is the present lack of knowledge concerning the role of interface states and adsorption processes which, as readily ascertained from the recent literature, are so critically important. Presently available in situ techniques, including optical spectroscopies, ellipsometry, Mossbauer spectroscopy, acoustoelectrochemical methods, and electron spin resonance, have proven useful in providing information about adsorbed species and films in some systems, but they generally are of limited applicability, have insufficient sensitivity, and most unfortunately, cannot detect the charge residing on interface species. New in situ techniques for characterization of interface states and adsorbed species are badly needed. Some promising methods include extended x-ray absorption fine structure (EXAFS) and nuclear magnetic resonance (NMR) techniques for detection of adsorbed species at dispersed porous electrodes, and electrochemical photocapacitance spectroscopy (EPS), which is unique in providing direct information about the energetic location, densities and state of charge of interface states and adsorbed species.

A specific problem of general importance in electrocatalysis is the oxygen electrode whose irreversibility at practical electrodes leads to large energy inefficiencies in a large number of presently-used and potential systems throughout the field. Considerable progress has been made in attaining the faster (more reversible) "four electron" oxygen redox reaction in laboratory systems but considerable additional effort will be required to attain a sufficiently stable, practical oxygen electrocatalyst. Some promising materials in this respect include mixed transition metal oxides and various semiconductors whose surfaces are chemically modified with metal organic compounds, e.g., phthalocyanines, or chemical/morphological variations of metals or semiconductors prepared by novel means, e.g., electrodeposition or decomposition of organic cluster compounds.

3.2 The K_2NiF_4 Family of Compounds as Oxygen Electrocatalysts

Addressing the oxygen electrode problem discussed above, we responded to some recent literature claims (1,2) which introduced the favorable electrocatalytic behavior of the perovskite-type, lanthanum nickelate, $LaNiO_3$, for oxygen evolution. Although it was stated that nickel on the surface was present as Ni^{2+}, doubtless, during use of the anode, the interconversion $Ni^{2+} \rightleftarrows Ni^{3+} + e^-$ readily occurs on the surface, which, in the bulk, confers on these compounds high electronic conductivity (3,4). Other solid state structures are capable of this effect, notably, the K_2NiF_4 group (3). To test if the latter class of structures would also be effective electrocatalysts (possibly better), we chose a composition $La_{1.5}Sr_{0.5}NiO_4$ (5), which formally contains equal quantities of Ni^{2+} and Ni^{3+}. The precursor powder was made by reacting $La(OH)_3$ and $SrCO_3$ in a blender with warm nickel nitrate (6), drying in vacuo and prefiring in air to 700°C to denitrate. The powder, lightly ground, was fired to 1000°C in oxygen. After isostatic compaction at 350 MPa, the specimen was sintered, in a bed of the same powder, to 1200°C in oxygen overnight and then annealed in oxygen at 1000°C for 8 hours. XRD indicated a single phase material; Table 1 shows the cell parameters for the body centered tetragonal unit cell; the value of a is smaller than either of the end member compounds shown for comparison; c is larger, however (5).

The black ceramic had an electrical resistivity of 0.2 Ω-cm measured by the four-point probe technique, but this is subject to wide variation depending upon preparation conditions. For comparison, we prepared, in a similar manner, the $LaNiO_3$ perovskite compound (1,2) which gave a resistivity of 0.004 Ω-cm, but was not quite pure single phase.

Table 1. Unit Cell Parameters (Å); K_2NiF_4 Structures

	La_2NiO_4(8)	$La_{1.5}Sr_{0.5}NiO_4$ (this work)	$LaSrNiO_4$(7)
a	3.855	3.818	3.826
c	12.652	12.730	12.450
c/a	3.282	3.335	3.254

Electrodes were prepared of area 1 cm^2 and 0.3 mm thick; electrical contacts were made with silver epoxy. The Tafel plot in Fig. 1 indicates that the catalytic activities for oxygen evolution in 1 M NaOH are comparable for $La_{1.5}Sr_{0.5}NiO_4$ and $LaNiO_3$. Tafel slopes for both samples were ~100 mV/decade. This further demonstrates the effectiveness of low spin Ni^{3+} (7) as an oxygen catalyst in basic media. The catalytic activities remained unchanged after several days of testing.

Other hosts are available for the $Ni^{2+} \rightleftarrows Ni^{3+} + e^-$ type reaction; for example, the Ruddleston-Popper phases of the $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ variety are likely candidates. The relative amounts of Ni^{3+} and Ni^{2+} can be controllably varied for basic studies in these phases.

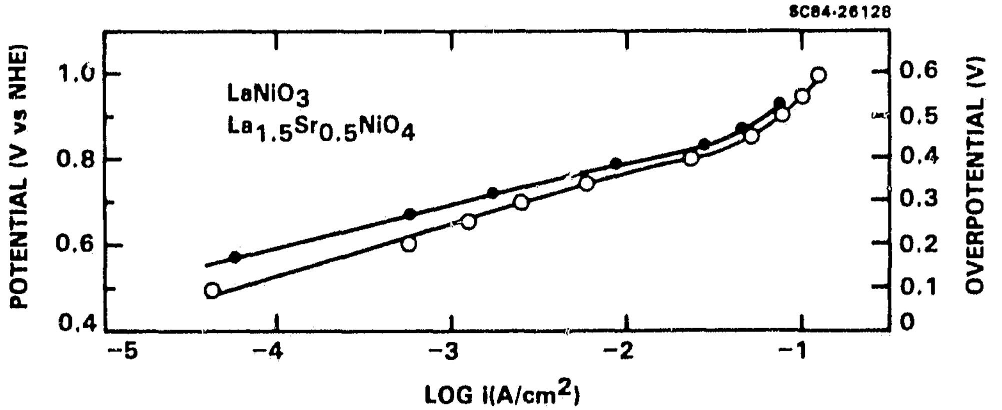


Fig. 1. Potential vs log i plots for oxygen evolution on $La_{1.5}Sr_{0.5}NiO_4$ and $LaNiO_3$ in 1 M NaOH at 25°C; measurements IR compensated.

References

1. T. Otagawa and J. O'M Bockris, J. Electrochem. Soc., 129, 2391-2 (1982).

2. J. O'M. Bockris, T. Otagawa, and V. Young, J. Electroanal. Chem., 150, 633 (1983).

3. P.E.D. Morgan, "Highly Conducting Oxide Materials," Proc. Workshop on High Temperature Solid Oxide Fuel Cells," 54-55, BNL-50756, (May 1977).

4. D.M. Tench and L.F. Warren, J. Electrochem. Soc., 130, 869 (1983).

5. J. Gopalakrishnan, G. Colsmann and B. Reuter, J. Solid State Chem., 22, 145-149 (1977).

6. P.E.D. Morgan, "Chemical Processing of Ceramics," in Processing of Crystalline Ceramics, 67-77, Ed. H. Palmour III, Plenum (1978).

7. G. Demazeau, M. Pouchard and P. Hagenmuller, J. Solid State Chem., 18, 159-162 (1976).

8. Von A. Rabenau and P. Eckerlin, Acta. Cryst., 11, 304-306 (1958).

3.3 The Design of a Biological Model Electrocatalyst

The ability of biochemical enzyme-based systems to effectively carry out fundamental, yet difficult, chemical processes under ambient conditions, e.g., the carbon dioxide and dinitrogen (N_2) reductions, has generated interest in some of these materials as potential electrocatalysts for those transformations. Studies in this direction have been conducted under the heading of bioelectrocatalysis (1) and electroenzymology (2) and have been directed toward the formation of possible biofuel cells. A primary impediment to the exploitation of such systems, however, is the frequent instability of cell-free enzyme preparations. Far easier to handle under typical electrochemical conditions are model systems which mimic the essential features of the enzymes. Examples of such mimicry are the synthetic models of the ferredoxins (electron transfer proteins) (3) and dioxygen-carrying proteins, out of which a porphyrin-based electrocatalyst for the difficult four-electron reduction of dioxygen (O_2) to water has evolved (4). Advantages of utilizing these models are their greater robustness and simplicity relative to their biological counterparts.

Particularly challenging to chemists today is to carry out the reductions of N_2 and of CO_2 under ambient conditions (25 C, 1 atm., aqueous environment), much as the bacteria and plant systems do in nature. Considerable effort in fact has been made to exploit some biological models toward these ends (5). Some of the more studied of these systems are based on transition metal phosphine complexes which chemically bind N_2 and CO_2, usually at a low valent (< 2+) metal atom site (6). There is now a considerable body of evidence that demonstrates the enhanced reactivity of these coordinated molecules. For example, a promising nitrogen fixing model exemplified by the Mo(0) complex, $Mo(N_2)_2(dppe)_2$, where dppe = $Ph_2PCH_2CH_2PPh_2$, is capable of forming ammonia in a cyclic chemical sequence (7). Note that there is a long-established belief that molybdenum provides the site where dinitrogen is attached to the nitrogenase enzyme and reduced.

A few attempts to capitalize on this reactivity electrochemically have been made, but these efforts failed apparently from the modes of attachment of the complexes to the electrode surface. In one case (8), an anchored $\mathrm{Mo(N_2)(dppe)_2}$ moiety detached from a surface-bound axially coordinated nitrile upon reaction. In another instance where methacrylamide polymers containing phosphine pendants coordinating the $\mathrm{Mo(N_2)_2}$ unit were applied to p-silicon and carbon electrodes (9), no electrocatalysis of N_2 reduction was reported. This is possibly due to the poor electrical conduction through such insulating polymer materials. In order to successfully examine such metal phosphine systems as electrocatalysts, a reliable means of anchoring these complexes cleanly to electrode surfaces must be identified, and we have initiated a study towards this end.

Electrocatalytic Sequence

An anticipated reaction sequence at an electrode-attached metal phosphine complex is exemplified in the following scheme for N_2 reduction to hydrazine in an acidic aqueous electrolyte. The complex in this case would be bound to the surface (vide infra) through a coordinated diphosphine, designated $\mathrm{dppe}{\sim}$, thus avoiding dissociation of the complex observed with the non-phosphine surface-bound system (8). (Note that aqueous solution electrochemistry of this class of metal phosphine complexes is not generally possible due to their insolubility in that medium.)

$$\begin{tikzcd}
{[\mathrm{M(N_2)_2(dppe{\sim})_2}]} \arrow[r, "2\ \mathrm{HX}"] & {[\mathrm{MX(NNH_2)(dppe{\sim})_2}]^+} \arrow[d, "\substack{2e^- \\ -X^-}"] \\
{[\mathrm{M(N_2)(NNH_2)(dppe{\sim})_2}]} \arrow[r, shift left, "-N_2"] \arrow[d, "\substack{2e^- \\ 2H^+}"] & {[\mathrm{M(NNH_2)(dppe{\sim})_2}]} \arrow[l, shift left, "+N_2"] \\
{[\mathrm{M(N_2)(H_2NNH_2)(dppe{\sim})_2}]} \arrow[r, "+N_2", "-N_2H_4"'] & {[\mathrm{M(N_2)_2(dppe{\sim})_2}]}
\end{tikzcd}$$

The overall reaction in this specific case is:

$$N_2 + 4H^+ + 4e^- \longrightarrow N_2H_4 \quad ,$$

and the proposed mechanism has considerable precedence in light of the chemistry of these systems (6,10).

Mode of Anchoring Phosphine Complexes to an Electrode Surface

An appealing mode of attaching reactants to electrode surfaces was developed by Anson and co-workers (11,12). This technique involves the irreversible adsorption on graphitic surfaces of water-soluble molecules containing sufficiently large aromatic pendant groups. Attachment by irreversible adsorption is far simpler and more rapid and cleaner than most of the other procedures, although the attachment is usually less long-lived. (In general, the larger the aromatic pendant, the stronger the adsorption, e.g., pyrene > phenanthrene > naphthalene). However, this technique does permit rapid electrochemical screening of the potential catalytic usefulness of transition metal complexes (12). In addition, with graphite being a relatively poor hydrogen electrode, studies of reduced systems in aqueous electrolytes are made easier.

With this objective in mind, we sought to devise a synthesis scheme incorporating a large pendant aromatic group on a phosphine ligand. A chelating bidentate diphosphine would ultimately be desired, not only as an analog to the much studied dppe systems, but also due to the robustness of their complexes relative to monodentate phosphine counterparts (e.g., Ph_3P). Attachment of such a system to graphite, in particular pyrolytic graphite (PG), electrodes is envisioned in Fig. 1. The PG can be mounted in an electrode so as to expose either the basal planes of the layered graphitic structure or the edge planes to the solution, as depicted in the Figure.

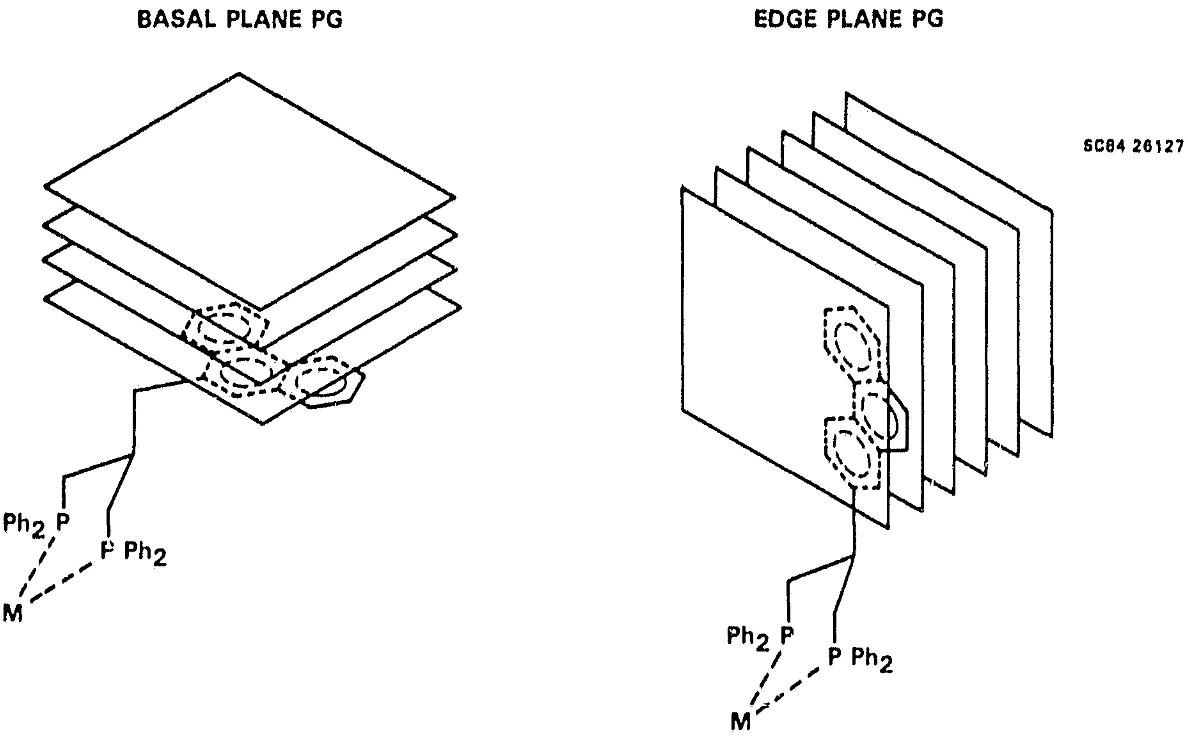
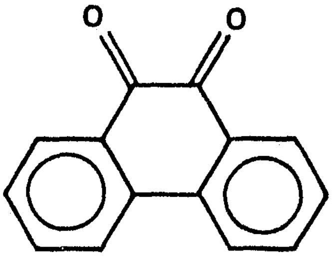


Fig. 1 Anticipated electrocatalyst adsorption modes on PG electrode surfaces.

Special pyrolytic graphite electrodes were produced by Pine Instrument Co., Grove City, PA. A rotating Pt ring-PG disc was considered most appropriate for electrocatalytic studies, where any electrolysis products from the disc (e.g., hydrazine) may be readily analyzed voltammetrically at the Pt ring. A further useful feature incorporated into the design enables the graphite disc to be moved so that it can be made flush with the ring. This is important, inasmuch as the graphite is slowly consumed during cleaning (polishing) of its surface prior to adsorption of catalysts. Both basal plane (C-axis normal to electrode surface) and edge-plane (B-axis normal to surface) disc inserts were obtained (13).

The quality of the PG disc materials was evaluated with phenanthrenequinone. This large, totally planar aromatic system is sparingly soluble in water and adsorbs onto the immersed PG electrodes. Potential cycling in an aqueous solution containing only a supporting electrolyte afforded a symmetrical redox wave corresponding to surface attached $PQ^0 \rightleftarrows PQ^-$ (11). (The analogous voltammogram of phenanthrenequinone adsorbed onto a glassy carbon electrode showed the same wave but immersed in a very much larger background current envelope, making electrochemical analysis more difficult.)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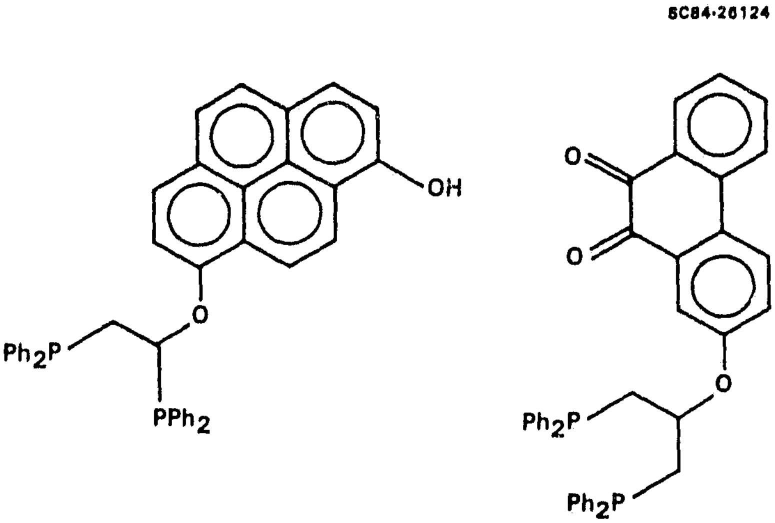
Phenanthrenequinone

Choosing a Suitable Aromatic Pendant

Identification of an appropriate large aromatic pendant which can be synthetically incorporated into a phosphine molecule is a necessary (non-trivial) first step toward the development of a general electrocatalytic phosphine system. A simple monodentate phosphine was deemed suitable to screen the adsorption capability of the pendant and to access the validity of our concept. In particular, tertiary diphenylphospino-pendant molecules should be relatively easily synthesized, relatively air-stable, and crystalline solids at room temperature. (Liquid phosphines are notoriously air-sensitive and would be impossible to purify by distillation if they contained very large aromatic groups.) In addition, the preparation of a water-soluble adsorbable phosphine complex which possesses a reversible one-electron redox reaction is highly desirable. The characteristic wave shape expected from such a system on PG would provide information regarding electron-transfer kinetics through the pendant, background currents of the electrodes, and adsorption lifetimes during potential cycling. A particular complex-type which fits the description is the $[Fe(CN)_5(phosphine)]^{3-}$ family of complexes (14), which possess reversible iron(2+) $\rightleftarrows$ iron(3+) redox couples, tertiary phosphines, such as triphenylphosphine, readily form these pentacyanoiron derivatives. Polar aromatic quinone-type pendant groups, such as phenanthrenequinone, would also display reversible one-electron couples as well as rendering a degree of water solubility.

Design of a Potential Nitrogen-Fixing Phosphine-Based Electrocatalyst System

Ideally, a molybdenum complex of a chelating bidentate diphosphine (analogous to dppe) would appear to be the most promising candidate as a N_2-fixing electrocatalyst. Electrode attachment via an aromatic pendant must take place through the diphosphine ligand itself; this is due to the lability of the non-phosphine coordination sites on Mo (8). Other crucial features to be incorporated into the molecule are diphenylphosphino groups and an appropriate "bite" angle ($-CH_2CH_2-$ or $-CH_2CH_2CH_2-$ bridged diphosphines, e.g., dppe or 1,3-bis(diphenylphosphino)propane form stable dinitrogen complexes with molybdenum (5)). With these criteria in mind, potential ligand systems can be envisioned, such as those shown below.



Possible bidentate phosphine ligands for adsorption onto PG.

Note in these compounds that the oxopyrene and the oxophenanthrenequinone pendants can present totally planar aspects to the graphite electrode surfaces. The synthesis of such molecules is, however, a non-trivial task and would entail several reaction steps (15) (vide infra).

An appropriate molybdenum complex may be easily prepared with a suitable pendant-diphosphine ligand by conventional displacement reactions on Mo-phosphine systems (5). It is important here to note that we need not adsorb directly an air-sensitive Mo(0) dinitrogen complex on the electrode surface; rather a more stable, higher oxidation state species, e.g., a $MoCl_2(phosphine)_2$ type complex, may be adsorbed and subsequently reduced under a N_2 atmosphere to form the Mo(0) complex in situ. Should the Mo-precursor not be water soluble for adsorption purposes, it may be possible to coat the PG surfaces by a simple evaporation technique (16).

Synthetic Studies

An effort was made to access the suitability of a particular aromatic pendant, the 9-anthrylmethyl group, for adsorption onto PG. In a straightforward single-step procedure, the reaction of 9-chloromethylanthracene with sodium diphenylphosphide afforded 9-anthrylmethyldiphenylphosphine as a pale yellow (due to the anthracene chromophore), microcrystalline solid in 70% yield. Sparingly soluble PPh_2An (where An = 9-anthrylmethyl) behaves as a normal tertiary phosphine, reacting with $NiCl_2$ in glacial acetic acid (17) to form red-brown, presumably diamagnetic (18), $NiCl_2(PPh_2An)_2$ (as opposed to blue, paramagnetic $NiCl_2(PPh_3)_2$). Attempts to prepare a water-soluble $[Fe(CN)_5(PPh_2An)]^{3-}$ complex under the same conditions that $[Fe(CN)_5PPh_3]^{3-}$

$$\text{An-Cl} + \text{Na}^+\text{Ph}_2\text{P}^- \xrightarrow{\text{dioxane}} \text{PPh}_2\text{An} + \text{NaCl} \qquad (1)$$

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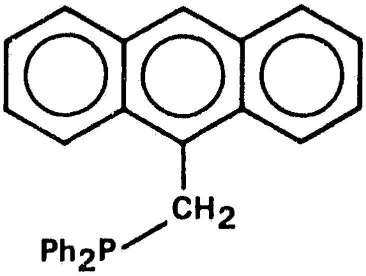

9-Anthrylmethyldiphenylphosphine

forms (14) were unsuccessful however, apparently due to the low-solubility of PPh_2An in methanol. Preparation of another class of redox active phosphine complexes, $K^+[Co(mnt)_2(PR_2)]^-$, where mnt = maleonitriledithiolate (19), was successful with both PPh_3 and PPh_2An, yet these ionic complexes were surprisingly insoluble in water. Despite repeated efforts to adsorb PPh_2An complexes onto PG by solution evaporation or adsorption from non-aqueous solvents, no definitive surface-bound electrochemistry of these systems was observed. As a result of these studies, we cannot completely rule out the possibility that the 9-anthrylmethyl pendant will not irreversibly adsorb onto PG surfaces. However, our feeling is that there are much more suitable candidate pendants available, in particular, systems which will provide greater solubilities in polar solvents, e.g., polar aromatic quinone groups.

In an ambitious effort to synthesize a diphosphine pendant system utilizing the 9-anthrylmethyl group (which is now questionable), the following reaction scheme was developed and carried to near completion. A major stumbling block was encountered in this sequence at the diol to dihalide conversion, reaction (5), where conventional reagents for this conversion (e.g., thionyl chloride) led to complex mixtures being formed; proceeding through the ditosylate appeared reasonably successful, although at a lower-than-desired yield. In any case, meaningful results derived from this exercise are (i) the successful use of the malonate moiety to form the symmetrically substituted propylene system, and (ii) awareness of potential problems which can be encountered during the use of electrophilic reagents with certain large aromatic groups. In addition, we successfully utilized a new method of generating the diphenylphosphide ion which avoids the complications of liquid ammonia manipulation required in "conventional" preparations. Synthetic procedures and characterization data on new compounds are presented in the Experimental Section.

$$\mathrm{AnCH_2OH} \xrightarrow{\mathrm{SOCl_2}} \mathrm{AnCH_2Cl} \qquad (2)$$

9-anthracenemethanol 9-chloromethylanthracene ≡ An-Cl

$$\mathrm{CH_2(CO_2Et)_2} \xrightarrow[\text{b) An-Cl}]{\text{a) NaOEt/EtOH}} \mathrm{AnCH(CO_2Et)_2} \qquad (3)$$

diethylmalonate

$$\mathrm{AnCH(CO_2Et)_2} \xrightarrow{\mathrm{LiAlH_4/Et_2O}} \mathrm{AnCH(CH_2OH)_2} \qquad (4)$$

$$\mathrm{AnCH(CH_2OH)_2} \xrightarrow[\text{b) LiBr/acetone}]{\text{a) tosyl chloride}} \mathrm{AnCH(CH_2Br)_2} \qquad (5)$$

$$\mathrm{AnCH(CH_2Br)_2} \xrightarrow[\text{dioxane}]{\mathrm{Na^+Ph_2P^-}} \mathrm{AnCH(CH_2PPh_2)_2} \qquad (6)$$

Conclusions

The principal of adsorption of transition metal complexes containing large aromatic pendants onto pyrolytic graphite electrode surfaces is well established (11,12,16) and should be equally applicable to phosphine complexes, in particular to enzyme model systems which coordinate dinitrogen, carbon dioxide, oxygen, etc. The rotating Pt ring-PG disc electrode arrangement can be employed for catalyst evaluation/product analysis. The molybdenum-dppe class of N_2 complexes represent particularly attractive candidates for nitrogen-fixing electrocatalysts in light of the exciting solution chemistry of these systems (6,7). Means of selecting a suitable phosphine-based aromatic pendant group via the $[Fe(CN)_5(phosphine)]^{3-}$ complex is described; in order to render some degree of water solubility to its metal complexes (for adsorption), the pendant should probably incorporate polar quinone moieties in the aromatic portion, e.g., in phenanthrenequinone.

Experimental Section

Preparation of Compounds. Na_2mnt was prepared by the published procedure (20) using the modification of McCleverty (21). $Na_3Fe[(CN)_5NH_3]$ was synthesized from sodium nitroprusside (22). Dioxane was distilled from sodium and stored under an inert atmosphere; diethylmalonate was purified by vacuum distillation (ca. 1 mm); diethyl ether was distilled from $LiAlH_4$. Pyridine was dried over 4A molecular sieves.

(9-anthrylmethyl(diphenylphosphine), $(9\text{-}C_{14}H_9CH_2)(C_6H_5)_2P$, or $AnPh_2P$. A dioxane solution containing 5.1 g of diphenylphosphorus chloride was refluxed overnight with one equivalent, 1.05 g, of sodium metal under an argon atmosphere. To the resulting cooled yellow slurry of $Na^+Ph_2P^-$ and NaCl was added chloromethylanthracene, one equivalent, 5.0 g, and the mixture heated to reflux for 30 min. The solvent was removed *in vacuo*, the solid washed well with deaerated water and filtered under argon on a Schlenk apparatus. The pale yellow solid was rinsed with deaerated i-propanol and argon-dried. The yield of the phosphine was 6.1 g, 70%. The compound is sparingly soluble in alcohols and aromatic solvents, but dissolves readily in dichloromethane.

Complexes of 9-anthrylmethyl(diphenylphosphine), $NiCl_2(AnPh_2P)_2$. The nickel chloride was prepared by the method of Browning et al. (17) in glacial acetic acid and also in refluxing i-butanol (dried over 4A mol series) from 0.15 g of $NiCl_2$ (dehydrated at 100°C) and 0.73 g of $AnPh_2P$. The latter procedure produced the purer material, 0.70 g (82%), as a red-brown crystalline powder. The complex is soluble in dichloromethane and decomposes in hot toluene.

$K^+\{Co[S_2C_2(CN)_2]_2(PR_3)\}^-$ Complexes. The triphenylphosphine and the 9-anthylmethyl(diphenylphosphine) complexes of $Co(mnt)_2^-$ were prepared by mixing equivalent amounts of $NaCo(mnt)_2$ (23) and the phosphine in ethanol. On gentle warming, the reactants, which are all sparingly soluble in the alcohol, slowly dissolved to give a deep purple solution. The mixture was cooled, filtered, and water was added to the filtrate (ca. 50 ml water/25 ml ethanol). An excess of potassium chloride was added, and water was slowly dripped into the mixture with continuous stirring. Dark purple microcrystalline solids separated in each case in ca. 80% yield. Both $K^+[Co(mnt)_2PPh_3]^-$ and $K^+[Co(mnt)_2(PPh_2An)]^-$ were insoluble in water, but very soluble in alcohols, acetone, and acetonitrile.

$Na_3[Fe(CN)_5)PR_3]$ Complexes. The triphenylphosphine complex was readily synthesized from methanol as described by Nast et al. (14). Attempts to prepare the $AnPh_2P$ analog, however, were unsuccessful, with the phosphine remaining largely unreacted after 3 days. This may be attributed to the insolubility of $AnPh_2P$ in methanol, and efforts to enhance its solubility by adding toluene to the reaction mixture were similarly without success.

9-Chloromethylanthracene, $9\text{-}C_{14}H_9CH_2Cl$. To 170 ml of dioxane under argon was added 23.0 g (0.111 moles) of 9-anthracenemethanol followed by dropwise addition of 14.5 g (0.121 moles) of thionyl chloride in 30 ml dioxane. The solution was stirred at ambient temperature for 1 h then refluxed for 1 h, cooled, and evaporated to dryness in vacuo. The residue was dissolved in a minimum of hot toluene, and filtered hot to remove a black, tarry residue. The dark brown solution was cooled and the yellow crystalline product filtered. Two additional crops were obtained by reducing the volume of the filtrate, cooling and filtering. Yield, 21.1 g (84%); melting point, 137.5-138.5°; ^1H-NMR ($CDCl_3$): 5.59 (s,2,$-CH_2$); 7.3-8.5 (m,9,arom CH).

9-Anthrylmethylmalonate diethylester, $(9\text{-}C_{14}H_9CH_2CH)CO_2C_2H_5)_2$.

Absolute ethanol, 300 ml, was treated with 2.06 g sodium (0.09 moles). When the sodium had dissolved, 14.35 g (0.09 moles) of diemethylmalonate were added and stirred for 15 minutes. 9-chloromethylanthracene, 20.3 g (0.09 moles) was added and the mixture refluxed for 5 hours. The yellow suspended solid was filtered (the filtrate saved) and washed repeatedly with water to remove sodium chloride; the residue was then dissolved in warm ethanol and added to the ethanol filtrate above. The ethanol was removed in vacuo, affording 27.2 g (87% crude yield) of a light yellow powder. The product was recrystallized from hot ethanol. Melting point, 77-80°; ^{1}H-NMR ($CDCl_3$): 0.92, 1.04, 1.16 (t,6-CH_3); 3.7-4.6 (m,7,-CH,-CH_2-); 7.2-8.4 (m,9, arom CH).

2-(9-anthrylmethyl)-1,3-propanediol, $(9\text{-}C_{14}H_9CH_2)CH(CH_2OH)_2$.

Anthrylmethylmalonate diethylester, 9.5 g (0.027 moles), was dissolved in 200 ml diethyl ether under an argon atmosphere; 2.2 g (0.058 moles) of $LiAlH_4$ were added in small increments, and the solution was refluxed for 16 hours. The mixture was treated with dilute sodium hydroxide solution, ca. 7 ml, stirred for 1 hour and then filtered (the filtrate being saved). The pale yellow residue was treated with 50% aqueous HCl to remove aluminum hydroxide and dissolved in ethyl acetate and added to the ether filtrate above. After removal of the solvents in vacuo, the residue was recrystallized from ethyl acetate/toluene to produce 5.4 g (75% yield) of the diol, melting point 131-133°C; ^{1}H-NMR ($CDCl_3$): 2.10 (br s,3,-OH, methine CH); 3.79 (t,6,-CH_2-); 7.2-8.4 (m,9,arom CH).

2-(9-anthrylmethyl)-1,3-dibromopropane, $(9\text{-}C_{14}H_9CH_2)CH(CH_2Br)_2$

Into 25 ml of pyridine was dissolved 1.0 g (0.0038 mole) 2-(9-anthrylmethyl)-1,3-propanediol. After cooling in ice 2.99 g of tosyl chloride (2-fold excess) was added and the solution stirred for 2 hours. The solution was refrigerated for 4 days, whereupon crystals of pyridinium hydrochloride separated. The mixture was added dropwise with vigorous stirring to 400 ml of ice water. After stirring for 1/2 hour, the solid was filtered and air dried. The crude ditosylate was immediately added to acetone (100 ml) which was saturated with anhydrous lithium bromide and stirred for 2-3 hours at room temperature. The solution was evaporated to dryness, the residue extracted with water, filtered, air-dried, stirred with warm hexane, cooled and filtered to yield 0.86 g (59% yield from the diol) as a fine white powder. Melting point 108.5-109.5°C. ^{1}H-NMR($CDCl_3$): 2.62 (m,1,methine CH); 3.57, 3.66, 3.77, 3.89 (dd,6,CH_2); 7.35, 8.45 (m,9,arom CH).

References

1. H.A.O. Hill and I.J. Higgins, Phil. Trans. R. Soc. Lond. A. 302, 267 (1981).
2. I.J. Higgins, R.C. Hammond, E. Plotkin, H.A.O. Hill, K. Vosaki, M.J. Eddowes, and A.E.G. Cass, "Electroenzymology and Biofuel Cells," in Hydrocarbons in Biotechnology, Harrison, Higgins, Watkinson, London, 1979, p. 181.
3. J.A. Ibers and R.H. Holm, Science, N.Y., 209, 223 (1980).
4. J.P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, and F.C. Anson, J. Am. Chem. Soc., 102, 6027 (1980).
5. J. Chatt, J.R. Dilworth, and R.L. Richards, Chem. Revs., 78, 589 (1978).
6. T.A. George and L.M. Koczon, J. Am. Chem. Soc., 105, 6334 (1983).
7. J.A. Baumann and T.A. George, J. Am. Chem. Soc., 102, 6153 (1980).
8. G.J. Leigh and C.J. Pickett, J.C.S. Dalton, 1797 (1977).
9. D.L. DuBois and J.A. Turner, J. Am. Chem. Soc., 104, 4989 (1982).
10. C.J. Pickett and G.J. Leigh, J.C.S. Chem. Comm., 1033 (1981).
11. A.P. Brown, C. Koval, and F.P. Anson, J. Electroanal. Chem., 72, 379 (1976).
12. A.P. Brown and F.C. Anson, ibid., 83, 203 (1977).
13. The Pine Instrument Co. has designated numbers ACDI4780PG and ACDI4780PGC to the Pt ring/PG disc edge-plane exposed and basal (C)-plane exposed electrode designs, respectively.

14. V.R. Nast and K.W. Kruger, Z. anorg. allegem. Chem., 341, 189 (1965).

15. See, for example, synthetic schemes for similar diphosphines: (a) V. Baltensperger, J.R. Gunther, S. Kagi, G. Kahr, and W. Marty, Organometallics, 2, 571 (1983); (b) J.P. Amm and J.K. Stille, J. Org. Chem., 47, 468 (1982 ; (c) M. Ding and J.K. Stille, Macromol., 16, 839 (1983).

16. R.R. Durand and F.C. Anson, J. Electroanal. Chem., 134, 273 (1982).

17. M.C. Browning, R.F.B. Davies, D.J. Morgan, L.E. Sutton, and L.M. Venanzi, J. Chem. Soc. 4816 (1961).

18. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th ed., Wiley-Interscience, New York, 1980, p. 789.

19. J.A. McCleverty, Progress in Inorg. Chem., 10, F.A. Cotton, ed., Interscience Publishers, New York, 1968, p. 49.

20. A. Davidson and R.H. Holm, Inorg. Synth., 10, 11 (1967).

21. J. Locke and J.A. McCleverty, Inorg. Chem., 5, 1159 (1966).

22. D.J. Kenney, T.P. Flynn, and J.B. Gallini, J. Inorg. Nucl. Chem., 20, 75 (1961).

23. J.F. Weiher, L.R. Melby, and R.E. Benson, J. Am. Chem. Soc., 86, 4329 (1964).

3.4 EPS Evaluation of Electrocatalysts

The potential utility of electrochemical photocapacitance spectroscopy (EPS) for characterization of electrocatalyst systems has been considered. EPS, which was described in detail in a recent publication (1) is an *in situ* method which can provide quantitative information about interface states (as well as bulk levels) residing at the semiconductor electrolyte interfacial region, i.e., where catalysis takes place. These states, which may be intrinsic or arise from lattice defects, are believed to act as active catalytic sites upon which reactants are adsorbed, facilitating formation/dissociation of reaction intermediates. They can be characterized in an electrolyte solution at various bias potentials before and after adsorption of reactants and/or intermediates. EPS has been shown to be particularly sensitive to interface states, which, because of their location, produce a disproportionately large effect on the measured capacitance upon ionization/neutralization. Note that interface states associated with oxygen adsorption at defect sites on n-CdSe have been detected by EPS at concentrations in the $10^{11}/cm^3$ range (1). The availability of this technique represents an exciting new opportunity for following the electronic structure of the interface *in situ* as catalytic reactions proceed. For example, shifts in the energy of specific interface states caused by adsorption of a given solution species, e.g., N_2, CO_2, H_2, NH_3, etc., should provide valuable insight into the chemical nature of the intermediate species involved in the important reactions of nitrogen and carbon dioxide reduction. Adsorbed species may also introduce new EPS spectral features by injecting photoexcited electrons or holes into the semiconductor bands so that a charged interface state is produced.

EPS is most readily applied to bulk semiconductor materials although semiconducting layers, e.g., oxides, on conducting substrates can also be investigated by this technique. The first choice for studies of electrocatalysts would be a large-gap semiconductor, e.g., n-TiO_2 or n-$SrTiO_3$, for two reasons: (1) the sub band-gap spectral region is sufficiently large, encompassing much of the visible spectrum, and (2) these semiconductors are stable to photodecomposition in aqueous electrolytes. Metal oxide electrocatalysts are the most obvious candidates to examine by EPS, inasmuch as they be readily applied to, say, n-TiO_2 by precipitation from solution photoelectrochemically (i.e., anodically) (2,3) or cathodically by reduction in the dark (2).

Other metal compound films may be prepared directly on the semiconductor surface, e.g., metal phthalocyanines can be evaporated or incorporated in the matrix of a conducting polymer film, e.g., polypyrrole. Care must be taken, however, that the light absorption by the catalyst be considered in the analysis of the EPS spectrum. Some catalysts may possess an affinity for particular reactants, e.g., O_2, N_2, CO_2, etc., at certain bias potentials and *in situ* EPS studies may be able to detect this and thus identify new potential electrocatalysts for particular transformations. An EPS comparison of CoPc (Pc = phthalocyanine), which reduces O_2 by 2 electrons and FePc, which is a 4 electron O_2 reducer, would be of particular interest in this regard. Even large biological enzyme systems adsorbed on the semiconductor surfaces may be amenable to EPS characterization.

References

1. R.P. Haak and D.M. Tench, J. Electrochem. Soc., 131, 275 (1984).

2. D.M. Tench and L.F. Warren, ibid., 130, 869 (1983).

3. D.P. Anderson and L.F. Warren, ibid., 131, 347 (1984).