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JAN 75 T L ISENHOUR, T J MEYER, S CHOI DAHC15-73-6-9

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MATERIALS SCIENCES OFFICE
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Materials Research Center
University of North Carolina at Chapel Hill

↙ This report describes

⑫ 39 p.

Relating work performed from 1 June 1974 to 30 November 1974

on projects as follows:

1. Application of Machine Decisions to Failure Analysis,
T. L. Isenhour
2. Homogeneous Catalysis of Net Electrochemical Reactions as Applied
to Fuel Cells,
T. J. Meyer
3. Theoretical Investigation of Solid Electrolytes; and
S. Choi
4. Electrocatalysis: Application of X-ray Photoelectron Spectroscopy
to Surface Composition of Electrode Materials,
R. W. Murray

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Grant DAHCL5-73-G-9

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R.W. Murray

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Application of Machine Decisions to Failure Analysis

Thomas L. Isenhour

1. Objective

The purpose of this work is the application of modern computer techniques to failure analysis. Particular emphasis is being placed on specific DOD problems involving sophisticated mechanical systems where analysis of lubricants and hydraulic fluids may allow prediction of impending failures.

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2. Background and Technical Need

The advent of high speed digital computers has allowed the development of empirical methods of problem solving which would have been prohibitively slow by non-computer methods. Recently, information retrieval and pattern recognition methods of data interpretation have emerged to allow the information contained in large data compilations to be applied to individual problems.

This research group was among the first to apply pattern recognition (including learning machines) to chemical problems. Also this group has made significant contributions to search and retrieval systems. One recent example is the development of a centralized mass spectral retrieval system for the Environmental Protection Agency. Remote laboratories can access this system by telephone line and have the benefit of the entire EPA data compilation for a cost of a few dollars per sample analyzed.

3. Accomplishments

For the past two years we have been supported by the University of North Carolina Materials Research Center on the Application of Machine Decisions to Failure Analysis. This support has been viewed as "seed money" and, we have made various contacts with DOD agencies involved in maintenance and failure analysis.

June 1, 1973 - May 31, 1974

During the first year of support four investigations - which are detailed below - were conducted:

i) Studies on Gas Chromatographic Liquid Phases; ii) Progressive Filter Network; iii) Bayesian Decision Theory Applied to the Multicategory Classification of Binary Infrared Spectra; and iv) Failure of Lubricants. i and iii were solutions of chemical classification problems involving the development and application of the type of general techniques we expect to find application in failure analysis, ii was the development of a general, easily applied classification technique which can be used without resort to a computer, and iv was a direct application of the methods we have been developing to the analysis of engine oil data from Navy aircraft.

(i) Studies of Gas Chromatographic Liquid Phases

Gas Chromatography has become, perhaps, the most frequently applied separation method in chemical analysis. This technique is capable of separating and identifying components of a great variety of complex samples. The selectivity of liquid phases is typically characterized on the basis of retention behavior, which is desirable because retention behavior directly reflects molecular interactions between liquid phases and test solutes (functional probes) under actual operating conditions. Keller (1) pointed

out, "It now seems desirable to characterize the selectivity of mobile and stationary phases in terms of chromatographic behavior, using a minimum number of probe solutes to elucidate the retention forces involved". He also suggested that the selection of these probes might be made by using the extended solubility parameters proposed by Snyder (2).

In a recent work (3) a nearest neighbor technique was used to group liquid employing retention data taken with the first five of McReynolds' solutes (benzene, 1-butanol, 2-pentanone, 1-nitropropane and pyridine) (4). Using these results and other criteria, the authors proposed a set of twelve preferred phases and presented a substitution table listing each of the 226 liquid phases reported by McReynolds with its nearest preferred phase as determined by a five-dimensional distance calculation. A major problem which remains, however, is the systematic characterization of McReynolds, as well as new phases to be reported in the future. Characterizing these phases using the five McReynolds probes would be a task of considerable magnitude. To reduce the amount of work involved the feasibility of using fewer than five of McReynolds probes for the characterization of liquid phases was studied using a nearest neighbor technique.

Two sets of three test probes and several sets of four probes gave results similar to those obtained using all five of the test probes evaluated by McReynolds. The interactive forces important in gas chromatography were related to those solutes present in the best sets of test probes. It is interesting to note that these results obtained using the nearest-neighbor method agree with the work of other researchers who used statistical methods to study retention data.

- (1) Leary, J. J., Justice, J. B., Tsuge, S., Lowry, S. R., and Isenhour, T. L., J. Chromatog. Sci. 11, 201 (1973).
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- (3) Snyder, L. R., "Modern Practice of Liquid Chromatography," J. J. Kirkland, ed., Wiley-Interscience, New York, 1971, p. 125.
- (4) McReynolds, W. O., J. Chromatog. Sci. 8, 685 (1970).

(11) Progressive Filter Network

With the ever increasing use of computers in all areas of science, applications of pattern recognition has become common in many diverse fields (1,2,3). The goal of any pattern recognition algorithm is to classify objects or patterns on the basis of certain attributes or parameters. Frequently, classification is accomplished by evaluating those parameters with a discriminating function. Unfortunately even after considerable effort and computation time have gone into developing a given discriminant function, still more lengthy calculations (often requiring a computer) are necessary to classify unknown patterns. Often the scientist who could benefit most, has neither the background nor the equipment to apply these techniques to his own research.

This work describes a pattern recognition algorithm which is conceptually simple and can be applied without resort to a computer. The technique employed is a sequential filter approach.

Each parameter (or dimension) of the data is investigated for an upper and lower threshold. Thresholds are defined as values which will classify only one class of data. The first filter is selected as that which has the two thresholds that classify the most members of the training set. (The thresholds need not classify into the same categories.) These patterns are then removed from the data set and the next best filter is sought.

The network can be applied, once developed, to classifying unknown patterns by following a simple filtering process of comparing the magnitudes

of individual parameters to the recorded thresholds. Successful applications were made to interpreting mass spectra and electrocardiograms.

- (1) Isenhour, T. L. and Jurs, P. C., Anal. Chem. 43 (10), 20A (1971).
 - (2) Rogers, O. S. and Tanimoto, T. T., Science 132, 1115 (1960).
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- (iii) Bayesian Decision Theory Applied to the Multicategory Classification of Binary Infrared Spectra

Pattern recognition techniques employed for the analysis of infrared spectra have been previously reported as acceptable alternatives to search and compare methods (1,2). The advantage of using pattern recognition is the ability to determine common characteristics of spectra from similar compounds. Other compounds displaying similar characteristics in their spectra can then be predicted to belong to the same class of compounds as the original set in which these characteristics were observed. Previous works in this field have reported results using binary classification techniques. This means that the answers were simply yes or no; e.g. yes, the compound was a carboxylic acid or no it was not. Similar questions were asked for esters, aldehydes, and each of the other classes of compounds being tested. For a given spectrum, if after all the questions were answered only one answer was yes, then a specific prediction could be made. Otherwise the prediction would merely be that the compound belong to one of the positive classes.

Another approach is to use multicategory classification techniques. In this case, rather than asking a number of yes/no questions, only one question is asked. To which class does the compound belong? Selection of the proper discriminant function results in a prediction for the correct answer to this question. This paper reports on an investigation of multicategory

predictions using binary data. With the knowledge that the spectrum belonged to one of fourteen possible classes, the goal was to select the proper class.

The recognition results obtained using a Bayesian approach were considerably better than the 1% figure expected from random guessing. Bayesian approaches are not used very often, usually due to the difficulty of obtaining $p(A|C)$, known as the a priori probability. However, in a situation such as the one described here, it is quite easy to determine the a priori probabilities from the training set. Given that $p(A|C)$ is obtainable, the Bayesian approach can then be viewed merely as a formalization of common sense (3). If the order 1, 2, 3, 4, 5 most frequently occurs when a compound belongs to class 1, then it is common sense to predict a spectrum giving that same order is of an acid. As was mentioned, the most likely next step for this type of approach would be to use very large training sets incorporating fewer restrictions. Also, the fourteen classes selected for this study would most likely not be the ones selected for a thorough investigation of a large data set. When using a table generated from a large data set, if the percentage of recognition still was near 90% then one would have a quick and accurate means of predicting the type of compound without having to search large numbers of spectra. This study demonstrated the feasibility of employing a Bayesian approach for the classification of infrared spectra, but varying degrees of utility should be found when using discriminant functions generated from other types of data.

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(2) Liddell III, R. W., Jurs, P. C., Appl. Spectrosc., 27, 371 (1973).

(3) Kelly, P. C., Anal. Chem., 44 (11) (1972).

(iv) Failure Analysis of Lubricants

A preliminary investigation of engine oil data was made with the cooperation of the Naval Oil Analysis Program under the Naval Air System

Command. The body of a report on that initial investigation follows.

The data set investigated consists of information taken from fourteen distinct aircraft engines. Samples of engine oil were analyzed for trace amounts of each of ten elements. The analyses were done by an emission technique. In each of the fourteen cases samples were periodically withdrawn and analyzed until a disabling malfunction occurred. The ultimate goal of this investigation is to determine if any factors involving the given concentration foretell engine malfunction. To insure practicality the factors need to be simple enough to be visually or graphically seen.

For the following discussion the set of concentration taken from one oil sample are called a pattern. Also the set of patterns for one engine are designated a subset.

Observations

Consider the nature of the data. The following observations may be made.

1. Some subsets are represented by too few patterns. To distinguish trends, enough patterns must be present to scan the functioning engine before the malfunction. Arbitrarily the four subsets with fewer than four patterns are excluded in data analysis.
2. Engine operation times are not included. For any analysis of concentrations versus time a measure of operation time is needed. Since only the Julian date is given for the patterns, derivative methods will be unreliable.
3. Oil changes appear to be made randomly and oil samples seem to be withdrawn the same way. Concentration profiles have gross jumps where oil is sampled close to the time of oil change.
4. The ultimate cause of engine failure is not given. There is little reason to expect factors indicating one type of failure to be the same as factors for a different cause of failure.
5. There is questionable accuracy in parts of the data. This may be illustrated by observing the set of concentration profiles for silicon. The maximum value for Si is 52 ppm, whereas the other values lie between 0 and 13 ppm.

6. Precision may also be a limiting factor in the emission output data. As a rule of thumb the absolute error may be considered the maximum of 3 ppm and 10% of the concentration.

Investigation of Data

Three methods of data analysis are applied to the data set. Motivation and expectation for each of the three methods are outlined below.

1. If any one element predicts malfunction, then something abrupt should happen to its concentration at the time of failure. Thus a simple look at concentration profiles seems reasonable. The difficulty here is sampling technique (as mentioned in observation three). Little illustrative should result from this look.
2. To overcome the sampling problem, perhaps one of the elements may be set as a standard. This suggests a ratio method--a look at concentration/concentration profiles. It is hoped that as an engine malfunctions, the value of the ratio reaches a maximum/minimum value and that the numeric value of the ratio is significant. A limit to this approach is the large relative error. This will be especially apparent for low concentration species. Ratios between "high" concentration species are preferred.
3. The third procedure assumes that getting to the extreme is less important than how the extreme is approached. Simply this implies a derivative or slope technique. For the given data set two immediate problems exist. Since the derivative operation is especially sensitive to noise, the large relative error eliminates the apparent utility of this method. Further there is no appropriate time function available for the ordinate.

A fourth procedure might be a spectral method. However the quantity of data required for each subset makes this impractical.

Trends

Considering the preceding argument the concentration ratio procedure (method two above) is preferred. Observation of concentration-concentration ratios are made for the elements of each subset. The denominator is limited to high concentration elements (Cu, Fe, Al, Mg) and all of the 36 remaining ratios are observed. A positive response occurs when for elements X and Y,

$$\left(\frac{[X]}{[Y]}\right)_{\text{malfunc. time}} = \max \left\{ \frac{[X]}{[Y]} \right\}_{\text{subset.}}$$

Using this criterion on the ten subsets, [Cu]/[Fe] and [Fe]/[Al] give five positive responses. [Cu]/[Al] and [Cu]/[Mg] give three positive responses.

Considering all the problems inherent in the data these results are encouraging. Unfortunately although the maxima appear, the value at these extremes do not seem to be significant.

At this point the analysis pleads for time factors and a curve smoothing algorithm. This would allow a derivative procedure to be attempted.

It needs to be emphasized that all the afore mentioned results only indicate possible trends. Until an investigation of a larger data set takes place all results are, at best, tentative.

Recommendations

In order to determine whether trends are present or, if present significant, other factors need to be included in the data. As mentioned previously the engine run times between sample withdrawals and the eventual cause of failure are needed.

Other suggestions concern, either directly or indirectly, the oil change itself. For data analysis it would be ideal if the oil were changed at regular run time intervals and oil sampled immediately before the oil change. It seems that the latter of these is a reasonable suggestion and that the former is an ideal expectation. Some of this problem could be aided by including "standard engines" in the data. The "standard engine" would have its oil changed regularly and sampled immediately before the oil change. Samples could also be taken as a function of time over the life of the engine oil. These would provide normal curves and standardizing curves to compare with curves near malfunction times.

These suggestions intentionally overlook the irreproducibility of the "coffee can" sampling technique. This is an obvious contributor to data scatter and need not be mentioned more.

Conclusions

A first analysis of the data appears to be rather inconclusive. Tentative trends appear, but noise factors impair certainty on such a small and incomplete data set. Before a final decision may be made more data per pattern and more patterns need to be investigated.

June 1, 1974 - December 1, 1974

During this period two additional studies - which are detailed below - have been completed and a third initiated: i) Density Estimations and Characterization of Binary Infrared Spectra, ii) A Comparison of Two Discriminant Functions for Classifying Binary Infrared Data; and iii) Development of a Computerized Retrieval System for Remote Maintenance and Failure Analysis. i and ii are further solutions of chemical classification problems involving the development and application of the type of general techniques we expect to find application in failure analysis and iii is the Investigation of the Development of a Model System for Remote Access to Maintenance Advice and Failure Analysis. The proposed future research is principally based on item iii.

(i) Density Estimations and the Characterization of Binary Infrared Spectra

Improved instrumentation has led to great quantities of data in the chemical literature. The instrumental output is often digitized, many parameters being used to describe each observed output pattern. Consequently, the interpretation of a set of data numbers may be a formidable task. If chemical structure information is suspected in the observations, this interpretation may be accomplished by *ab initio* theoretical calculations. More frequently, however, experience is the guiding tool.

In the presence of a set of well-defined data, computer-aided recognition techniques utilize the computer to rapidly acquire this experience. Two such approaches may be employed. The data file may be searched to find closest matches with the known observations. In this case the recognition will approach an optimum. Unfortunately, unless special techniques, such as inverted files and hash coding, are applicable, search time increases linearly with the size of the file and often becomes prohibitively long.

Second, an estimate of the true class probability density functions (pdf's) may be determined. As more terms are included in the pdf estimate, the recognition will improve. Also, however, the time of investigation will increase and the technique will more closely parallel a search.

A truncated orthogonal expansion has been used to represent binary data taken from a multidimensional file of infrared data. The expansion represents an approximation for the true class conditional probability density functions (pdf's). As a first approximation, statistical independence is assumed and the only terms necessary are the estimated class conditional probabilities for each peak. A more accurate estimation of the pdf is attained when a second term is included in the expansion, a correlation term.

The data set consists 2600 spectra in thirteen mutually exclusive classes with each spectrum consisting of 139 dimensions. Results are obtained for a maximum discriminant function case as well as for pairwise discrimination among the classes. The thirteen class problem is characterized 67.2% of the time by the class conditional probabilities and 87.3% of the time when the correlation terms are included. For pairwise discrimination, the results are 92.2% and 98.1% respectively.

(ii) A Comparison of Two Discriminant Functions for Classifying Binary Infrared Data

Some form of information compression is essential if one is to be able to utilize effectively the increasingly large data compilations. One approach is to eliminate the intensity information, leaving spectra packed in a peak/no peak format. This research investigated the comparison of two simple discriminant functions for classifying binary infrared data. For the multicategory problem of thirteen classes used in this investigation, random guessing would achieve about 8% correct classification. A dot product calculation produces 49.1% correct classification, while a distance measurement produces 58.7%. The results from this investigation are also qualitatively compared to previous work using infrared data which retained some intensity information. It is found that the binary packing of spectral data shows great promise in the area of infrared analysis.

(iii) Investigation of the Development of a Model System for Remote Access to Maintenance Advice and Failure Analysis

For several months we have been in contact with Mr. John Patton, Project Engineer, NOS Louisville, with respect to analysis of hydraulic fluids from gun mounts. On August 19 and 20, 1974. I attended a meeting at the Office of Naval Research at Mr. Patton's suggestion. This meeting was on the "Optimum Methodology for Interpretation of Wear and Wear Trends from Oil Analysis". The meeting hosted by Lt. Richard S. Miller, ONR, and included, among others: Mr. Mike Hoobchaak, Mgr. Hdqtrs; Mr. Joe Guite, NOAP manager for NAVSEA; and Mr. Peter Senholzi, Commander, Naval Air Engineering Center, Philadelphia. From these discussions I learned the variety of sophisticated approaches being applied to this particular problem in hydraulic fluid maintenance. It was clear that this project is viewed by those involved as an attempt to establish a model program for maintenance and failure control of complex systems for the Department of Defense. Central to this meeting was the establishment of mechanism for maintaining

a complete archive of analytical and historical information relating to hydraulic fluid maintenance for the 5"-38 gun mount.

The need for a central system of maintenance information with remote access capabilities for failure analysis became quite apparant. We have studied possible approaches to this problem and the result of our investigation is the proposed research.

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Homogeneous Catalysis of Net Electrochemical Reactions as
Applied to Fuel Cells

Thomas J. Meyer

1. Objective

The principal goal of the work is the rational design of metal complex catalysts for applications in potential fuel cell processes and in organic syntheses. Special emphasis will be placed on the oxidation of organic compounds which may prove useful as fuels in net electrochemical reactions. Collaborative studies will be carried out with Professor R. W. Murray on the attachment of potential catalytic groups to the surfaces of semiconductor electrodes.

2. Background and Technical Need

Fuel cells allow for the direct conversion of chemical energy into electrical energy. The direct oxidation of fuels in a fuel cell can lead to much higher efficiencies than indirect processes based on chemical combustion. For small-scale devices, fuel cells offer the further advantages of quietness of operation, compactness, and portability.

Fuel cells based on organic compounds as the fuel and oxygen as the oxidant have several advantages. The reactions are highly favored thermodynamically; the products of the reaction (CO_2 and H_2O) are innocuous ecologically, and oxygen is conveniently available. A promising organic fuel for fuel cell applications is methanol. The large-scale production of methanol from processes based on coal gasification and bacterial fermentation appears to be promising.

The oxidation of methanol by oxygen, $\text{CH}_3\text{OH} + 3/2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$, is favored by -1.2V in acidic solution. However, attempts to couple the two half reactions in electrochemical cells-- $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}$ and $\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightarrow 2 \text{H}_2\text{O}$ --are usually unsuccessful because of kinetic limitations.

The one-electron oxidation of organic compounds is in general a slow process. The products are often a complicated mixture because of the formation of intermediate, high energy radicals. The oxidation of organic compounds by appropriate, strong metal ion oxidants (e.g., MnO_4^-) can be facile, but is difficult to make catalytic in a useful way.

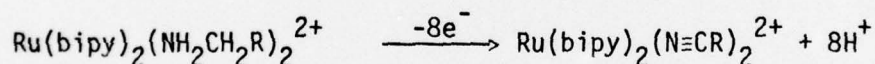
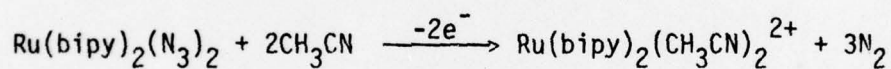
In developing catalysts for the oxidation of organic compounds, desirable features include: 1. The ability to oxidize organic compounds rapidly.

2. A lower thermodynamic oxidizing strength than MnO_4^- , for example. 3. The ability to be recycled at an electrode. Materials with the appropriate properties may, in fact, prove useful as redox catalysts operating either in homogeneous solution or when attached to the surfaces of semiconducting electrodes.

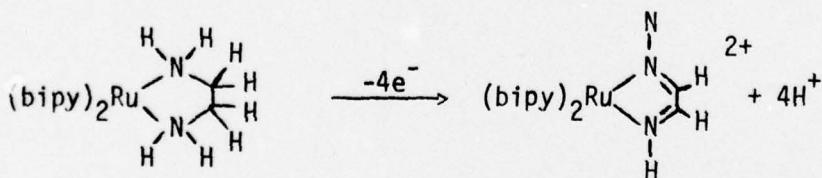
3. Accomplishments

From our work, one of the most versatile chemical approaches to the design of metal ion oxidation catalysts involves the use of polypyridine complexes of ruthenium(II)-ruthenium(III). For example, the complexes offer the following properties: 1. A wide range of redox couples exist, e.g., cis-Ru(bipy)₂Cl₂⁺⁰, having systematically variable redox potentials. 2. The complexes undergo facile electron transfer. 3. Potential multiple site oxidants have been prepared and characterized. 4. The basic molecular framework is exceedingly stable.

Using 2,2'-bipyridine complexes of ruthenium we have discovered a series of efficient oxidation reactions of inorganic and organic compounds.



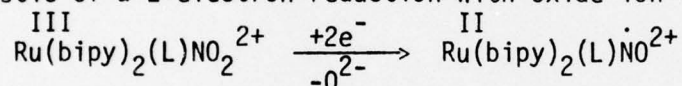
(R is -CH₂CH₂CH₃ and -C₆H₅)



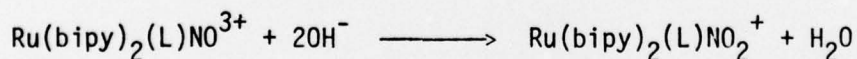
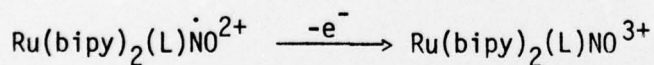
The reactions proceed via initial rapid chemical or electrochemical oxidation of Ru(II) to Ru(III), e.g., Ru(bipy)₂(N₃)₂ $\xrightarrow{-e^-}$ Ru(bipy)₂(N₃)₂⁺. The Ru(III)/Ru(II) couples undergo rapid, reversible reactions at electrodes.

The initial oxidation step is followed by a series of stepwise reactions involving oxidation of the coordinated ligand, e.g., $\text{Ru}(\text{bipy})_2(\text{N}_3)_2^+$ + $\text{CH}_3\text{CN} \rightarrow \text{Ru}(\text{bipy})_2(\text{N}_3)(\text{CH}_3\text{CN})^+ + 3/2 \text{N}_2$. The overall reactions are quantitative and rapid.

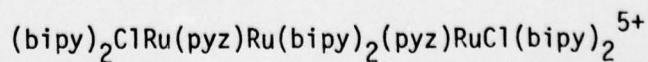
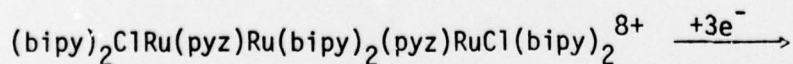
We have begun a study of the redox chemistry of Ru(II)-nitro complexes in an attempt to find reagents which mimic the ability of MnO_4^- and HCrO_4^- to accept two electrons and donate an oxide ion, e.g., $\text{MnO}_4^- + \text{RCHO} \rightarrow \text{Mn(V)} + \text{RCO}_2\text{H}$. Our initial work shows that Ru(II)-nitro complexes are rapidly oxidized to Ru(III), e.g., $\text{Ce(IV)} + \text{Ru}(\text{bipy})_2(\text{L})\text{NO}_2^+ \rightarrow \text{Ce(III)} + \text{Ru}(\text{bipy})_2(\text{L})\text{NO}_2^{2+}$. The reactions of the Ru(III)-nitro complex are characteristic of a 2-electron reduction with oxide ion transfer,



In contrast to permanganate ion, the two-electron reduction occurs at both the metal and the coordinated NO group. The reduced complexes $\text{Ru}(\text{bipy})_2(\text{L})\text{NO}^{2+}$ have been prepared and characterized. The Ru(II)-NO₂ complexes are promising as catalysts since they appear to be very reactive, they are less strongly oxidizing than MnO_4^- and HCrO_4^- by a considerable amount, and in slightly alkaline solution their reactions can be made catalytic using known reactions:



A series of ligand-bridged complexes have been prepared in which there are multiple oxidation sites, e.g.,



(pyz is pyrazine)

Theoretical Study of Ionic Transport
in Solid Electrolytes

Sang-il Choi

OBJECTIVES

Numerical computation of potential energy surfaces for the motion of carrier ions and calculation of frequency dependent electrical conductivity of some solid electrolytes are planned. Potential energy barrier heights and vibrational frequencies along the path can be obtained from ion-ion interaction energies and the Madelung energy.

Although there are theories on the dc conductivity and the ac conductivity, all of them are parameterized theories. Independent calculation of the parameters is necessary to test the theory and also to understand the effect of ion properties on the parameters. As an example, we may consider recent published results on the far infrared dielectric response of beta-alumina. Allen and Remeika¹ interpret their observation with the aid of the theory of Sato and Kikuchi.² They consider the barrier for hopping from the normal site to the interstitial site to be the activation energy and conclude that the nearest neighbor interaction energy and the site energy difference to be negligible. Our calculation shows their conjecture and conclusion to be incorrect. Actually the site energies differ by approximately 2 eV and the interaction energies are about 1 eV (this number is obtained by fitting S-K theory to the experimental temperature dependence of the dc conductivity).

ACCOMPLISHMENT

Our first effort in this project was to obtain the potential energy surface for the motion of silver ion in silver β -alumina from the silver ion electron density measurement by the x-ray diffraction study of Roth. We were successful in this attempt. Next step was to express the potential energy surface as a sum of ion-ion potential energy. The interaction potential energy between a pair of ions was written as the sum of the point charge-point charge interaction, the Born-Mayer repulsive potential, the Van der Waal's interaction, and the polarization effect term. Although we obtained the values of the parameters to produce the potential energy surface mentioned above, these values were extremely unrealistic in the sense that the values of ionic radii and polarizabilities of some ions have turned out to be unreasonably small or too large. We believe that such difficulty originates from the nature of silver ion distribution seen by the x-ray diffraction study. As proven by our latter investigation, at relatively small deviation of silver concentration from the stoichiometric compound, most silver ions are localized near the normal sites (Beavers-Roth Site) while some silver ions form interstitialcy pairs and tend to stay between the normal site and the interstitial site (Anti-Beavers-Roth Site). What is seen by the x-ray is, then, an average of these two kinds of silver ion distribution.

Next we proceeded to calculate the potential energy curves along the trajectory of silver ions as detected by the x-ray study. The trajectory of ion motion was taken as a network of regular hexagons whose vertices consist of the normal sites alternating with the interstitial sites. The silver density distribution detected by the x-ray study shows that the centers of silver ions are restricted on the vertices and the lines of

a hexagonal network in nonstoichiometric compound crystals. By including the Madelung energy, the repulsive energy, and the polarization energy, the change of the total potential energy as a function of the position of a silver ion between a normal site and an adjacent interstitial site has been calculated. Similar calculation for four other ion substituted β -alumina has been carried out. The resulting potential energy curves show that the normal sites correspond to deep but broad minimum. On the other hand the interstitial sites of all five β -alumina correspond to maxima of the potential energy curves. The difference of site energies between the normal site and the interstitial site ranges from 1.7 eV for Na^+ to 2.5 eV for Cs^+ . These numbers are an order of magnitude larger than the reported activation energies. In a nonstoichiometric β -alumina, there are more carrier ions than the number of normal sites. Therefore a fraction of interstitial sites are expected to be occupied. In our model we added one carrier ion to an interstitial site in an otherwise stoichiometric crystal. In this model, positions of the nearest five carrier ions are adjusted to minimize the total potential energy of the crystal as the interstitialcy ion is moved step by step toward a nearest normal site (which is occupied by a carrier ion). Except one normal site ion, all other ions remained in the vicinity of their original sites. The normal site ion which is "pushed" by the interstitialcy ion moved as "a pair." The potential energy barriers for such motion are found to be close to the measured activation energies except for Li^+ . If only the pair is moved while all other ions are fixed, the potential energy barriers are found to be considerably higher than the above calculations involving six ions (15 ~ 100% higher).

The equilibrium configuration of the interstitialcy pair is such that

both ions are located between the normal site and the interstitial site. Such configuration can explain the presence of ion density between the two sites detected in the x-ray study. Vibrational frequencies of interstitialcy pairs and single ions in the normal sites are obtained. For the pairs, $1.1 \times 10^{12} \text{ sec}^{-1}$ for Na^+ and $4.3 \times 10^{11} \text{ sec}^{-1}$ for Ag^+ . For single ions, $2.7 \times 10^{12} \text{ sec}^{-1}$ for Na^+ and $1.2 \times 10^{12} \text{ sec}^{-1}$ for Ag^+ . It is found that the potential energy barriers decreased with the increasing polarizability and increased with the increasing ionic radius. Energy barriers for K^+ and Na^+ ions in $\text{K}(\text{Na})$ beta-alumina and $\text{Na}(\text{K})$ beta-alumina have been calculated.

In the theory of Sato and Kikuchi², we have used our calculated site energy differences and the measured activation energies to deduce the nearest neighbor interaction energies for 5 different beta-alumina. The values range from - 1.18 ev for Li to - 1.61 ev for Rd. For beta double prime alumina, numerical computation has shown a peculiar result. With Mg ions uniformly distributed in the middle of the spinel block, we have calculated the potential energy curve for the migration of one vacancy with 11 carrier ions' positions adjusted to minimize the total energy at each step (small). The potential energy barrier found is approximately 0.05 ev which is considerably smaller than the reported activation energy. Since experimental data do not show a simple one activation energy but a strong deviation from an exponential behavior, it is difficult to compare our calculation with experimental data.

For calcia stabilized zirconia $\text{ZrO}_2(\text{CaO})$, we assumed a CaF_2 structure and calculated the potential energy curve for the motions of an oxygen ion vacancy along a straight line joining the two nearest neighbor oxygen

sites. The potential barrier is approximately 5 ev in the neighborhood of a Ca^{++} ion and ca. 4 ev in the absence of Ca^{++} . The potential curve is rather flat, in the absence of Ca^{++} , near the minimum. These numbers are considerably higher than the experimental activation energy. More detailed study is required.

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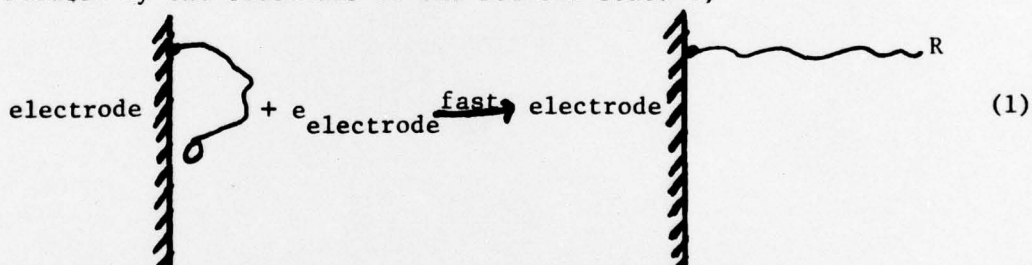
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ELECTROCATALYSIS: APPLICATION OF X-RAY PHOTOELECTRON
SPECTROSCOPY TO SURFACE COMPOSITION OF ELECTRODE
MATERIALS - R. W. MURRAY

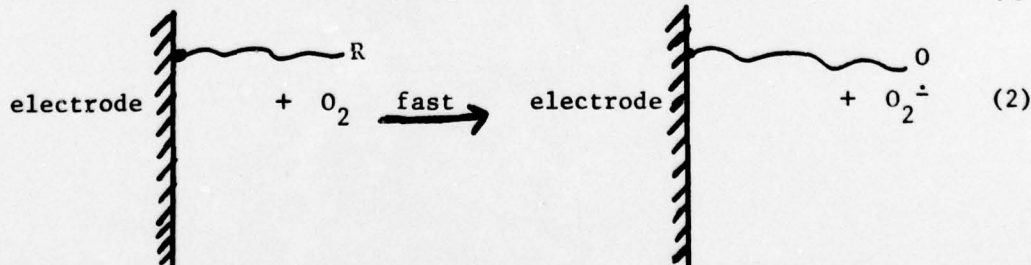
OBJECTIVES

The general objective of this research is to employ X-ray photoelectron spectroscopy (XPES) for the analysis and characterization of surfaces of materials useful as electrodes in electrochemical cells. Of particular interest are electrode surfaces which have been chemically modified so as to attach various functional reaction centers to the surface, including reaction centers which can be oxidized or reduced by the electrode and/or by a solution redox agent.

If a reaction center attached to the surface in its oxidized form O is rapidly reduced by the electrode to the reduced state R,



and the reduced center R reacts rapidly with a solution species, such as oxygen,



O_2 , then the normally slow direct reduction of the solution species, O_2 , at an electrode is replaced by an indirect but kinetically fast process. Deliberate covalent attachment of such electron transfer mediator couples O/R to electrode surfaces would open an entirely new and heretofore unexplored form of electro-

catalysis. Development of this concept of synthetic surface catalytic sites is a second general objective of this research.

Specific electrode materials to be chemically modified are doped tin oxide (SnO_2) and carbon (graphite).

BACKGROUND

Surface science is today one of the most vigorous and exciting areas of chemical science, substantially because of the development of techniques and instrumentation for a variety of surface sensitive experiments. Many questions can be asked about surfaces today which were impractical a few years ago. One important technique is X-ray photoelectron spectroscopy (XPES), which provides information on the elemental composition and chemical state of surface layers 10-50 Å in depth. That definitive information on the composition of electrode surfaces, and thus information on electrochemical reactions at and of those surfaces, can be obtained by XPES has already been demonstrated by Winograd and coworkers (1).

Another aspect of surface science which has also undergone a more diffuse revolution is that of covalent attachment of useful reagents or chemicals to surfaces. Bonded stationary phases are used in chromatography (2), peptides are synthesized in surface-bound states (3), enzymes are immobilized on silica surfaces (4,5), and dithiocarbamate groups have been attached to glass wool to scavenge trace metals for XPES measurement (6). Such situations are important in that, in them, the chemistry of a solid surface, which by itself has an unpredictable and heterogeneous array of defects, active sites, etc., is transformed into a surface having the chemical properties of a known reagent.

These developments have set the stage for the covalent attachment of homogeneous solution catalysts (7) to surfaces, resulting in preparation of

heterogeneous catalysts with a undreamed of level of chemical versatility and specificity. The chemical background needed to attempt the surface links exists, as do the methods (XPES) to monitor the preparation of the derivatized surface. A first step was recently taken by immobilizing homogeneous solution rhodium phosphine catalysts on silica for heterogeneous catalysis of hydroformylation reactions (8).

Deliberate covalent reagent attachment reactions have thus far not been reported for electrode surfaces. The dividends of such an electrochemical capability are potentially enormous, impacting on electrocatalysis (fuel cells), electrosynthesis, and fundamental surface-oriented electrochemical studies. Electrocatalytic activity of an electrode is sought today on mainly empirical grounds and often involves using finely divided metal particles. To make electrocatalysis into a predictive science through surface-modified electrodes also open the road to numerous new applications of electrochemical reactions. Solution (reactions 1,2) of the problems of slow kinetics of the oxygen electrode, important for fuel cells, would by itself be a very significant result.

This Principal Investigator believes it is realistic at this time to attempt a major program on covalent electrode surface modifications. This program is facilitated by the availability of an XPES spectrometer (DuPont 650) in the Principal Investigator's laboratory. The essential components of the program must be the following:

- 1) Selection of electrode materials whose surface chemistry is amenable to predictive covalent bond formation.
- 2) Develop chemistry for the attachment of a variety of functional groups and redox reagents to the electrode surface.

3) Investigate the electrochemical and chemical properties of the surface-bound reagent.

4) Couple the electrode to a solution reactant through electron transfer mediation by the surface-bound reagent, proving a new concept in electrocatalysis.

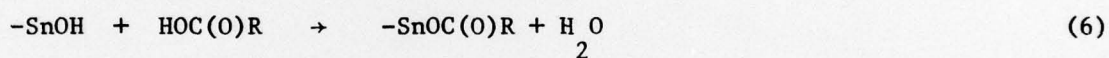
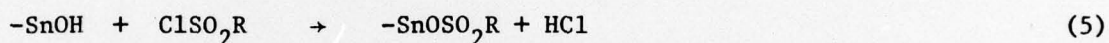
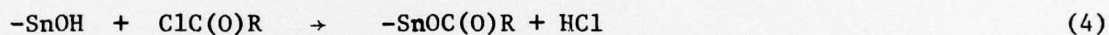
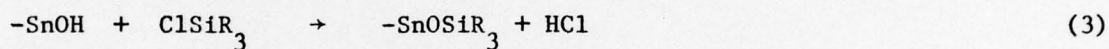
5) Utilize X-ray photoelectron spectroscopy, and other approaches as feasible, to characterize the chemically modified electrode surfaces.

Two electrode materials have been selected for XPES and chemical modification study. The first of these, tin oxide, SnO_2 , is a suitable electrode material when doped with antimony, has been explored for oxygen reduction in fuel cells (9), was introduced as an optically transparent electrode by Kuwana in 1966 (10) and used intensively since by him, and has been employed for several other electrochemical purposes (11-13). Little definitive is known about the chemical or electronic character of SnO_2 surfaces, or about the surface distribution of the antimony dopant.

The second electrode material selected is carbon, whose surface chemistry has been of interest for many years, and which is used extensively in industrial electrolysis. Carbon surfaces vary enormously depending on prior treatment and history, and have mostly been studied by classical methods such as chemical titration and IR spectroscopy. They are thus intrinsically prime candidates for XPES study. Two types of activated carbon are thought to exist (14,15), depending on previous treatment by exposure to oxygen and high (1000°C) or low (200-400°C) temperatures. Carbon surfaces have been postulated to have phenolic, quinone, carbonyl, and carboxyl surface groups. Low temperature carbon has an acidic, hydrophilic, and negative electrophoretic character, for example.

ACCOMPLISHMENTS

Most of the several months' effort since this program was begun has concentrated on the SnO_2 electrode material, which is available as a SnO_2 film on glass substrate. The key ingredient in derivatizing this (or any) electrode is the initial covalent link with a redox reagent or with a reagent which can be subsequently modified to a useful surface redox reagent. Our essential postulate in the surface-linking chemistry is that the Sn-O bond has considerable stability, that the SnO_2 surface is basic and can be protonated to form $-\text{SnOH}$ groups, and that these groups will react in a manner similar to $-\text{SiOH}$ groups. Thus we are interested in the reactions:

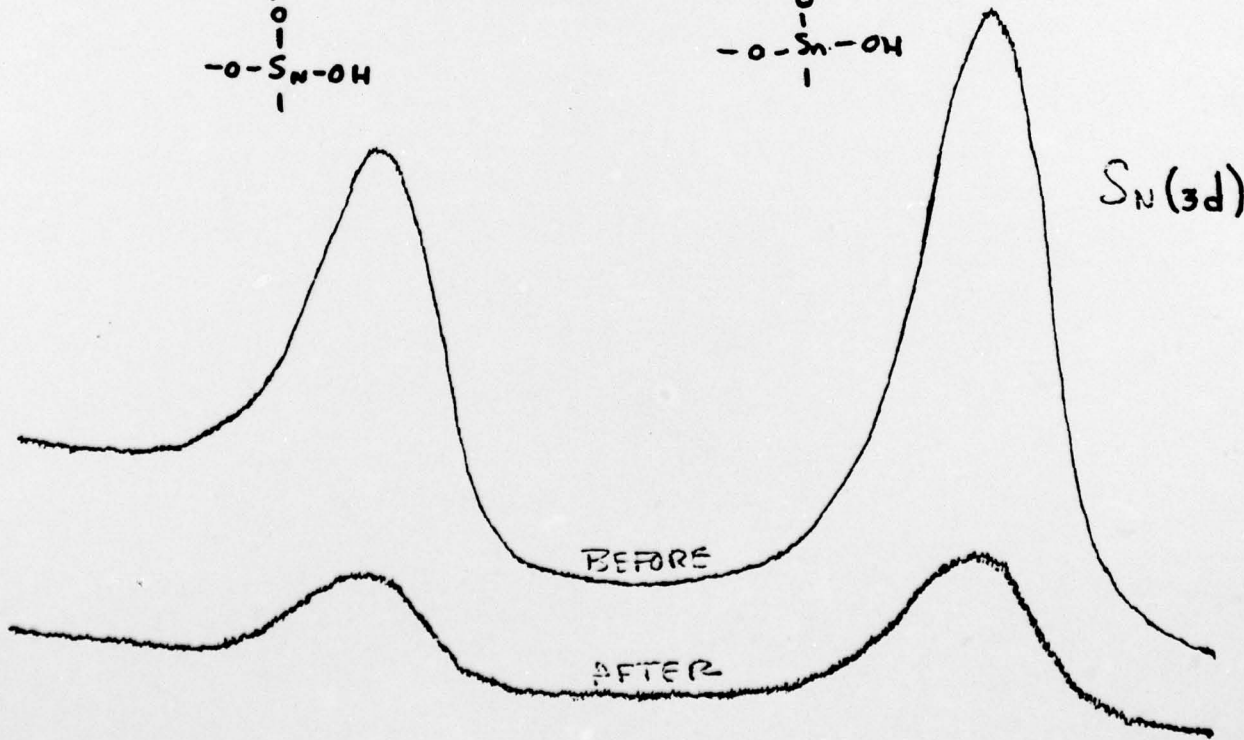
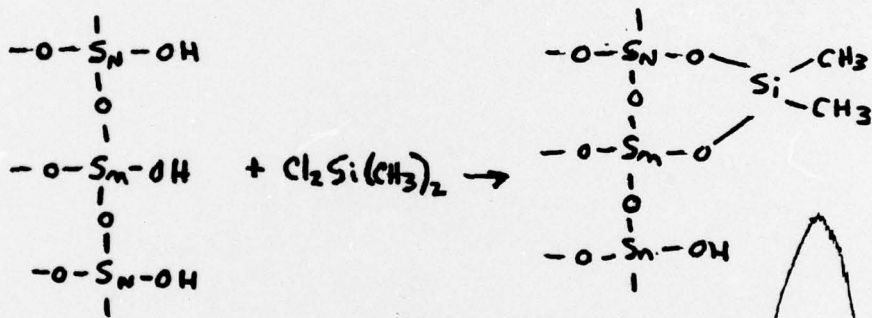
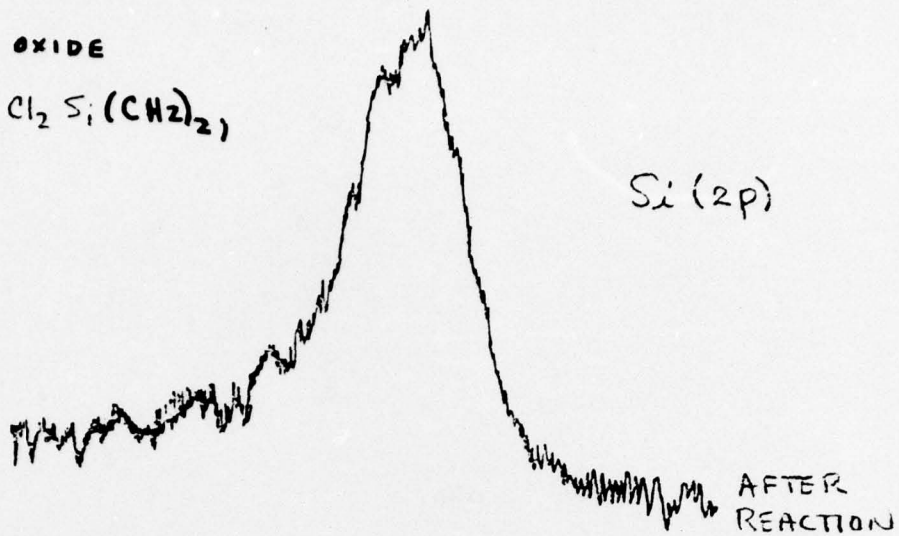


We have so far encountered considerable success with reactions of the type reaction (3). We find that ClSiR_3 , Cl_2SiR_2 , Cl_3SiR , $(\text{EtO})_2\text{SiR}_2$, and $(\text{EtO})_3\text{SiR}$ reagents all react with the $-\text{SnOH}$ surface, yields being greatest for the trichloro forms, as expected. The progress of the surface silanization reaction has been followed by XPES, for which typical sample spectra are shown in Figure 1. The acidified SnO_2 surface shows a strong Sn(3d) band and a weak Si(2p) band; the latter results from imperfections in the SnO_2 allowing exposure of some glass substrate. Upon silanization, the Si(2p) band becomes intense, and the Sn(3d) band decreases as the SnO_2 becomes covered with a film of $(\text{SnO})_2\text{SiR}_2$ groups. Estimates of the coverage of the surface with $(\text{SnO})_2\text{SiR}_2$ can be made from the Sn(3d) attenuation. Assuming an electron escape depth of 15 Å, such estimates give a (substantial) surface coverage in the 10^{-9} mole/cm² range.





FIGURE 1

REACTION OF TIN OXIDE
ELECTRODE WITH $\text{Cl}_2\text{Si}(\text{CH}_2)_2$

ESCA SPECTRA.



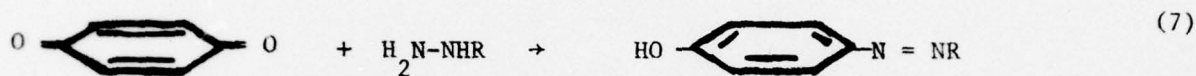
If the silyl "R" groups contain or are reacted with other elemental "tags", (e.g., N(1s), S(2p)), these appear in the XPES spectrum of the derivatized surface. This is quite useful for monitoring chemical elaboration of the surface sites. We are very interested in obtaining a series of ligand groups bound to the surface; these will be subsequently coordinated to metal ion redox centers to provide O/R surface redox reagents. A representative selection of the surface ligands we seek and the status of each follows:

<u>Group</u>	<u>Status</u>
-NH ₂	surface linked as -Si  NH ₂
-CH=CH ₂	surface linked as -Si 
*-R-Pφ ₂	surface linked as -Si  Pφ ₂
-Py	silane reagent available
*-dipy	silane reagent to be prepared
*-acac	silane reagent to be prepared
*-8-(OH)quinoline	to be attempted as sulfonyl chloride
*-en	silane reagent to be prepared
*-NHCS ₂ ⁻	surface linked as -Si  NHCS ₂ ⁻

Successful introduction of this entire group of ligands will yield a very broad range of coordinative reactivity. The XPES results serve to confirm the silanizations indicated. For the amine function, for example, N(1s) appears in the spectrum of the modified surface as well as the effects of Figure 1. Also treatment of the surface-bound amine to form the thiocarbamate function produces a S(2p) band, and a Na(1s) band which disappears upon treatment with metal counterions more strongly bound to thiocarbamate than sodium. Few of the coordinating silanization reagents are commercially available, and we are obliged to synthesize many ourselves (see stars in above table).

We view the above results on SnO_2 as exceedingly important, as they establish at least one rather general type of surface linkage ($-\text{SnOSi}-$) which can be used for surface modifications.

Some results have also been obtained with graphite electrodes activated at 600°C followed by exposure to air, postulating that these surfaces contain quinone groups which will react with hydrazines:



Graphite treated with 2,4 dinitrophenylhydrazone (DNPH) indeed yields two N(1s) XPS peaks of equal intensity and with chemical shift consistent with one being $-\text{N}=\text{N}-$ and the other being $-\text{NO}_2$. Longer reaction times with DNPH increase these peaks' intensities. When employed as electrodes in aqueous KNO_3 electrolyte, a large, irreversible cathodic current peak occurred on the first potential sweep and was absent thereafter. These encouraging but so far very preliminary results will be followed up.