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FINAL TECHNICAL REPORT

TRANSPORT STUDIES OF DEFECT STRUCTURE
INORGANIC COMPOUNDS

SEPTEMBER 30, 1965 through
MARCH 31, 1965

TRANSPORT STUDIES OF DEFECT STRUCTURE OXIDES

Reference: Contract Nonr-3800(00)
 Authority NR359-444
 ARPA Order No. 300, A. No. 3,
 Program Code No. 4980
Final Technical Report,
 Sept. 30, 1964 thru March 31, 1965
 Transport Studies of Defect
 Structure Inorganic Compounds
 Period of Performance:
 April 1, 1964 thru March 31, 1965
 Amount: \$245,282.00
 Project Scientist: R.R. Heikes,
 Telephone 412-242-1500
 Ext. 682-683

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Introduction

In this report we summarize the research on oxygen-ion conducting electrolytes and chemisorption studies performed on the contract. Extended abstracts are presented of the projects or papers completed in the past half year.

The solid electrolyte studies were made on oxides based on three related crystal structures, the fluorite, the pyrochlore and the c-type rare earth. The fluorite-type consists of an essentially simple cubic packing of oxygen ions with metal ions at alternate interstices, while the pyrochlore and c-type rare earth structures have one-eighth and one-fourth of the oxygens absent, respectively, with some accompanying lattice distortions. The oxides actually studied are defective forms of these structures formed by addition of metal ions with a valence different from that of the host cations.

Addition of a few mole percent Y_2O_3 or CaO to ThO_2 or ZrO_2 at temperatures of $1300^\circ C$ or below results in substitution of Y^{+3} or Ca^{+2} for Th^{+4} or Zr^{+4} in the crystal and the presence of an appropriate number of vacancies at oxygen ion sites to preserve electrical neutrality. At much higher temperatures, however, some metal ion interstitials in addition to the vacancies may occur. Temperature and time dependent conductivity changes reflect some of the structural and diffusional changes which occur in these systems.

Thoria systems, e.g. $(ThO_2)_{1-x}(YO_{1.5})_x$, at oxygen pressures below about 10^{-7} mm have lower conductivities but similar thermal emf characteristics to calcium or yttrium oxide doped zirconia with O^{2-} being the principle charge carrier. At oxygen pressures near atmospheric, on the other hand, the conductivity of $(ThO_2)_{1-x}(YO_{1.5})_x$ is partially electronic, and thermal emf evidence indicates that an additional ionic species O^- , may perhaps be present.

In the pyrochlore structures studied, $Cd_{2/3}Nb_{2/3}O_7$ and $Pb_{1.5}Nb_{2/3}O_{6.5}$, and solid solutions of these, metal interstitials occur, and we obtain mixed ionic-electronic conduction properties.

Y_2O_3 and Sc_2O_3 have the c-type rare earth structure and with one exception will not form appreciable solid solutions with the alkaline earth oxides. Scandium oxide at about $2150^\circ C$ will form a solid solution with 20 to 30% magnesium oxide. At temperatures of the order of $1000^\circ C$, these solutions are unstable with possibly less than 1/2% solubility. The high temperature solid solutions appear to have Mg^{2+} ions partially at interstitial positions. Conductivities of the metastable solid solutions are more than hundred times those of the pure oxide but lower in magnitude near $1000^\circ C$ and have a higher activation energy than the zirconia calcia system.

Mössbauer studies were made of $(ZrO_2)_{1-x}(YO_{1.5})_x$ containing 1% or less of Fe^{57} added as a probe nucleus to obtain information on charge symmetry around the individual ions. The field gradient showed no temperature or vacancy concentration dependence indicating that only near neighbor vacancy distortions are detected and that vacancies may be bound to Fe^{+3} pairs. If the Fe^{+3} is on substitutional sites, the results may also apply to vacancy interaction with Y^{+3} .

The modes of chemisorption of oxygen on silver and platinum and their effects on oxygen reduction at oxygen electrodes at room temperature were studied. At ambient temperatures oxygen electrodes are not reversible and weak (presumably molecular) structure-sensitive, chemisorptions are of particular importance. The detailed state of the surface such as exposed crystal planes, imperfections and impurities, affects the mode of chemisorption, and vice versa, the ambient gas can change the structure of the surface. Studies of gas-solid interactions were carried out first in a dry system and common characteristics with electrode properties were used to aid the interpretation of the more complicated electrode systems.

The catalytic properties of the surface for the isotopic oxygen exchange reaction $O_2^{16} + O_2^{18} \rightarrow 2O^{16}O^{18}$ and the oxygen chemisorption were investigated. The oxygen chemisorption is shown to be energetically very heterogeneous; this well demonstrates that the concept of oxide

"phases" like PtO or PtO₂, as commonly used by electrochemists, has little reality. The most strongly chemisorbed oxygen suppresses the catalytic activity at low temperatures. In a paper concerned with the electrochemical characteristics of the platinum electrode in an acid electrolyte (presented in the previous semi-annual report) it is shown that some of the changes in electrode activity with pretreatment, potential, and time can be interpreted in the same manner as in the gas-solid studies.

Long term experiments with the silver-magnesium oxide electrodes confirm that this electrode maintains a lower polarization than pure silver. Other impurity additions were also studied. These experiments were accompanied by studies of (1) the $O_2^{16} + O_2^{18}$ exchange reaction on Ag-MgO powder which showed a reversible oxygen chemisorption and high catalytic activity at room temperature and (2) diffuse reflectance of pretreated Ag and Ag-MgO in the ultra-violet region. Ag-MgO showed an absorption characteristic of the silver oxide phase although prepared at oxygen pressures at which silver oxide is not stable. Pure silver surfaces showed a strong resistance to nucleation of the oxide phase where its formation is thermodynamically possible.

The electrochemical oxygen reduction and hydrogen peroxide decomposition at silver electrodes in basic solutions was examined experimentally and theoretically. Using reaction rate theory, the intermediate peroxide scheme was shown to provide an internally consistent scheme. The intermediates O_2^- , OH and HO₂ must be in the chemisorbed state.

Work on desorption and isotopic exchange of oxygen on silver and low temperature orthopara conversion of hydrogen on silver was completed on the present contract. (Most of the experimental work on this particular phase of the work was done under a previous contract A-36-039 AMC-00136E.)

VACANCIES IN SUBSTITUTED ZIRCONIA -- A MÖSSBAUER STUDY

A. J. Panson
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R. J. Ruka

Abstract

A Mössbauer study was made of Y_2O_3 stabilized cubic ZrO_2 with Fe^{57} added as a probe nucleus. Spectra of samples containing 7.5 and 16.5 atm percent anion vacancies showed the Fe to be trivalent and in a significant electric field gradient. The field gradient showed no dependence on temperature or vacancy concentration in this range. The results are interpreted as indicating that only near neighbor vacancy distortions are detected and that vacancies may be bound to Fe pairs. If the Fe is present on substitutional sites the results for the Fe apply to vacancy interaction with Y^{3+} in pure Y_2O_3 stabilized ZrO_2 .

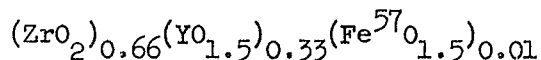
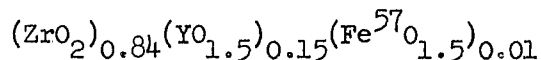
Recently there has been considerable interest in zirconia as an ionic conductor useful as a solid electrolyte for oxygen transport in high temperature fuel cells. The purpose of this Mössbauer study was to gain information concerning the state of anion vacancies in the fluorite lattice of substituted zirconia. At present a description of the vacancy state is not available, but would be highly desirable in order to gain insight into conduction mechanisms.

Experimental

In pure ZrO_2 the fluorite structure is unstable at room temperature with respect to formation of a monoclinic phase. The high temperature structure may be stabilized, however, by suitable lattice substitution. In the case of Y_2O_3 stabilization, a minimum of 9 atom percent is required, while the maximum solubility is 15 atom percent. The Y^{3+} is incorporated substitutionally on the cation sublattice and accordingly one half an O^{2-} vacancy is added for each substitution.

In the system studied an Fe^{57} Mössbauer active probe was incorporated into a Y_2O_3 stabilized fluorite lattice.

The compositions:



were prepared by coprecipitating iron and zirconium from HCl solution with NH_3 , firing at 900°C , and mixing with Y_2O_3 . Pellets 1/4 inch in diameter containing 0.001 mole of the compositions were placed in covered ZrO_2 crucibles and sintered close to their melting point in an arc image furnace. The compounds were then reground and pressed into 1/2 inch disks and used in this form as Mössbauer absorber samples. The Mössbauer apparatus employed a constant velocity pendulum drive similar to that described by Flinn.

Results and Discussion

Spectra were obtained at room temperature and elevated temperatures up to 400°C.

An isomer shift of 0.55 mm/sec was observed in all cases indicating that only Fe^{3+} was present. A significant quadrupole splitting of 0.5 mm/sec was observed in all spectra independent of the vacancy concentration. Observation of a quadrupole splitting indicates that a significant local field gradient exists at the Fe^{3+} nucleus so that it resides in a non-cubic local field. The cubic fluorite structure, however, was observed in x-ray diffraction patterns of all samples. This result is not inconsistent since Mössbauer measurements are far more sensitive to local distortions about an active nucleus than x-ray diffraction.

When this study was undertaken an experimental relationship was sought between vacancy concentration, N_V and the quadrupole splitting or field gradient at the iron nucleus, $\nabla \cdot E / \text{Fe}$. It was our judgment that $\nabla \cdot E / \text{Fe}$ would be a function of the vacancy concentration. Thus a systematic study of this relationship was anticipated which would allow inferences to be made about details of the vacancy structure in substituted zirconia.

The results of our measurements, however, were that variation of N_V did not alter the quadrupole splitting of $\nabla \cdot E / \text{Fe}$. Thus we were not successful along our original lines of investigation. An unequivocal explanation of the results is not available; however, certain implications appear which deserve consideration.

If our original judgment that $\nabla \cdot E / \text{Fe} = f(N_V)$, is correct, a logical interpretation appears. The dependence of $\nabla \cdot E / \text{Fe}$ on N_V is dominated by nearest neighbor vacancies. Also, the nearest neighbor vacancies are not randomly distributed about the probe Fe^{57} nuclei but are bound to them. Since each substitutional Fe creates one-half a vacancy, the Fe substitutes as pairs bound to a single oxygen ion vacancy.

The precise location of probe Fe nuclei in the lattice, however, is not determined. If substitutional sites are occupied a model of anion vacancies bound to Y^{3+} is likely for pure Y_2O_3 stabilized ZrO_2 . The 0.56 Å Fe^{3+} radius, however, could readily be accommodated by interstitial sites.

THE SEEBECK COEFFICIENT OF $(\text{ThO}_2)_{1-x}(\text{YO}_{1.5})_x$

J. E. Bauerle
R. J. Ruka
J. Hrizo

A theoretical treatment of the thermal emf of solid ionic conductors has been given by Holtan, Lidiard and others. Some terms in these equations can be directly evaluated but others represent heats of transport for which no adequate theory exists for their evaluation. Consequently, to obtain interpretable data from experimental measurements, it is generally desirable to make changes in the systems which have important effects on the calculable terms or to compare changes in systems which are chemically and structurally similar.

It has previously been shown experimentally that the effect of a change in gas atmosphere can be correctly evaluated for the zirconium-calcium oxide systems and that values for the absolute Seebeck coefficient of this and the zirconium-yttrium oxide system are relatively insensitive to change over a wide temperature range. Since the thorium-yttrium oxide system and the two zirconium oxide systems both have a fluorite-like structure and similar chemical characteristics, it is of particular interest to note the different qualitative character of the Seebeck coefficient vs. temperature curves shown in Fig. 1 for the two types of systems. Other authors have shown that the transference number for ions in the $(\text{ThO}_2)_{1-x}(\text{YO}_{1.5})_x$ system is much less than 1 in gas atmospheres greater than about 10^{-6} atm. and it has been suggested that O^- rather than O^{2-} may be a major charge carrier at the higher pressures, but that at the low pressures O^{2-} is the only important charge carrier. This suggests that the use of reducing atmospheres of hydrogen-water may result in a Seebeck coefficient with a smaller and more uniform temperature coefficient as is the case with the zirconia systems. Figure 2 shows that this is the case with $(\text{ThO}_2)_{.95}(\text{YO}_{1.5})_{.05}$. The differences in Seebeck coefficient between the different gas atmosphere experiments is also about that calculated from the theoretical Holtan relations, except for the point at 1150°C representing the .34% H_2 mixture. In the latter instance, the atmosphere may not be sufficiently reducing.

The data for the $(\text{ThO}_2)_{1-x}(\text{YO}_{1.5})_x$ system are then consistent with the presence of different or additional charge carriers, electrons and perhaps O^- , in the oxygen atmospheres and a single important charge carrier O^{2-} in the reducing atmospheres.

The authors express thanks to D. Watt who made many of the measurements.

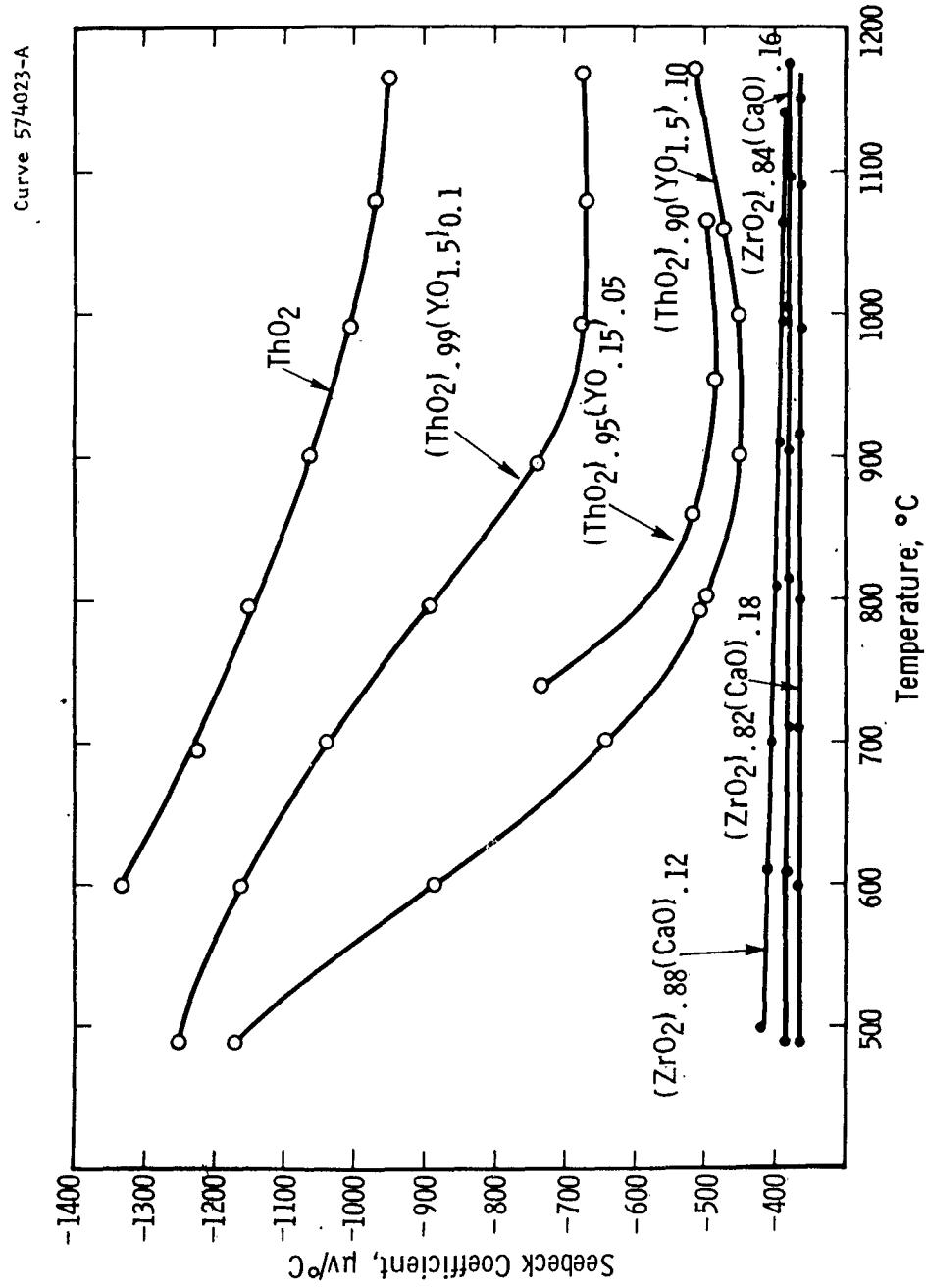


Fig. 1—Seebeck coefficient as a function of composition and temperature

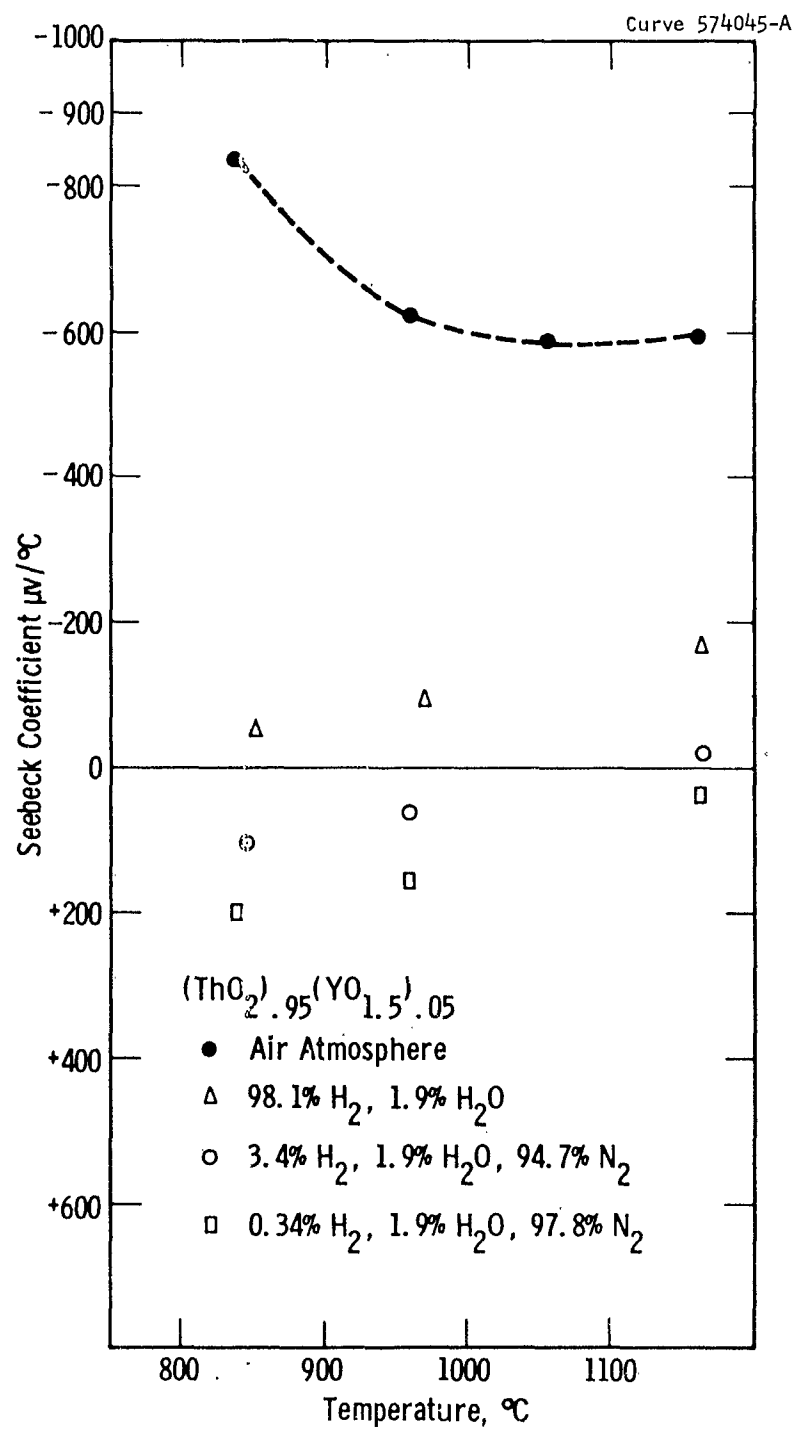


Fig. 2—Effect of gas atmosphere on the Seebeck coefficient of $(\text{ThO}_2)_{0.95}(\text{YO}_{1.5})_{0.05}$

CONDUCTIVITY AND TRANSFERENCE NUMBER IN
SCANDIUM-MAGNESIUM OXIDE SOLID SOLUTIONS

J. E. Bauerle
J. Hrizo
R. J. Ruka

Solid solutions of scandium oxide with alkaline earth oxides have been studied only briefly by previous investigators. Of these mixed oxides an appreciable solid solution is known to exist only for the Sc_2O_3 -MgO system at high temperatures. Tresvjalskii¹ and co-workers report a maximum solubility of nearly 30 mole % MgO at the eutectic temperature of 2150°C.

The purpose of the present work is to investigate the conductivity and defect structure of the scandium oxide rich solid solution region at lower temperatures.

Experimental

Conductivity measurements were made by the AC method using frequencies up to 100 KC. Transference number measurements were made by using the oxide pellet as electrolyte of an oxygen concentration (galvanic) cell, with oxygen partial pressures of 1 atmosphere at the cathode and 1/5 atmosphere (oxygen-argon mixture) at the anode. Density was measured pycnometrically and compared with values determined from x-ray diffraction data for substitutional or interstitial models. Specimens were fired at temperatures between 1650°C and 2000°C in the arc image furnace, zirconia-susceptor high frequency furnace or in a platinum rhodium resistance element furnace.

Results

At compositions between 1/2 and 5% the specimens showed initial resistance values which were lower by two orders of magnitude or more than the values for pure scandium oxide. However, holding the specimens at 850°C to 1100°C for several hours resulted in irreversible resistance

increases which were greater with larger MgO contents. Figure 1 shows results for specimens with 1 and 3 mole percent MgO in Sc_2O_3 . The results indicate that the solid solutions as quenched are in a metastable state.

Transference number measurements show that conductivity is largely ionic, but the experiments cannot distinguish between anion and cation diffusion. Density measurements on quenched specimens suggest that part of the Mg^{+2} may reside at interstitial sites. This point is still in question, however, due to an apparent loss of part of the MgO during firing of the specimens. Further analytical and micrographic work are needed to clarify these questions.

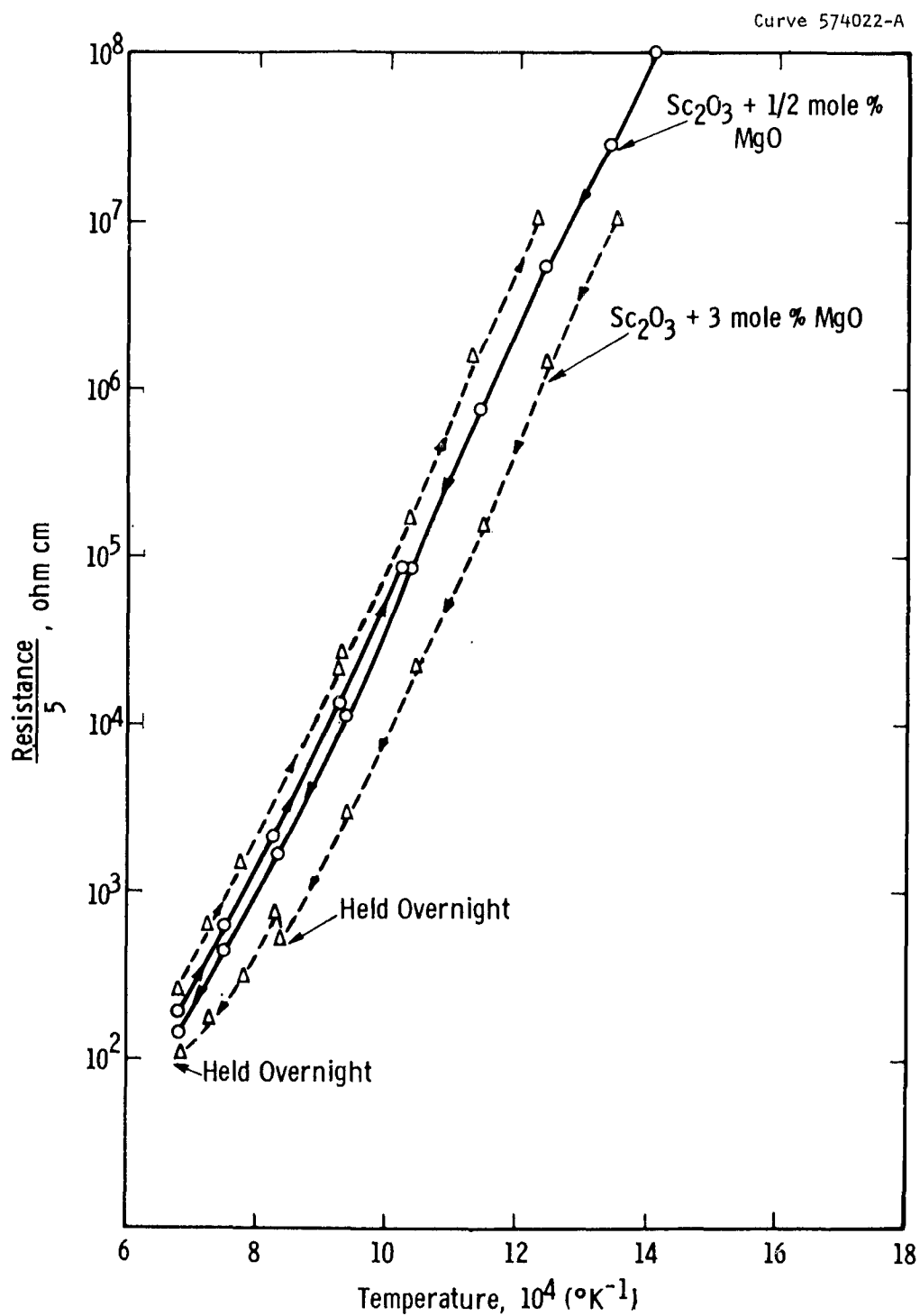


Fig. 1—Resistance changes in metastable solid solutions of MgO in Sc_2O_3

CONDUCTIVITY BETWEEN 350° and 1250°C
OF HIGH PURITY, STABILIZED ZrO₂

J. E. Bauerle
J. Hrizo

The purpose of this work was to take a closer look at the conductivity of cubic ZrO₂-CaO, i.e. ZrO₂ containing 14 to 20 mole % CaO, employing

- A. High purity specimens (sintered under contamination-free conditions in an arc image furnace);
- B. High resolution conductivity measurements (impedance comparator, 0.01% precision, frequencies from 0.1 kc to 100 kc);
- C. An extended temperature range, especially toward lower temperatures.

We particularly wished to investigate previously reported anomalies in this system (Tien and Subbarao, 1963) to determine if they were present also in specimens of high purity.

Our results may be conveniently divided into a high temperature region and a low temperature region.

High Temperature Region (850 to 1250°C)

In this region our results were qualitatively similar to those of Tien and Subbarao. When a specimen was held at temperatures in the range of 850 to 1000°C for a week, the conductivity decreased by 5 to 50% corresponding to specimens having CaO contents of 14 to 20 mole %, respectively. Each point of a given conductivity curve (below the aging temperature) was shifted downward by the same percentage. By raising the temperature gradually to 1250°C, these conductivities were observed to increase to their original value. Four-terminal DC measurements ruled out the possibility that these effects might have arisen from electrode changes.

All of these effects are consistent with the idea of a "precipitation-like" process occurring between 850 and 1000°C, and a dissolving of the "precipitate" at higher temperatures. It should be noted, however, that no x-ray evidence for the existence of a second phase could be found, even though a sensitive Guinier focussing technique was used.

Low Temperature Region (350 to 850°C)

In this region time dependent conductivity effects are either absent or very small; consequently our data here are reliable enough to warrant some comparisons with theory.

It has been fairly well established that in the $\text{ZrO}_2\text{-CaO}$ (14 - 20 mole %) system, the CaO is incorporated into the lattice along with equal numbers of oxygen vacancies (Hund, 1952). Furthermore, it has been established that conduction in this system takes place exclusively by means of oxygen ion vacancy diffusion (Kiukkola and Wagner, 1957; Weissbart and Ruka, 1961; Kingery et al., 1959). The appropriate expression for the conductivity in this case is

$$\sigma T = A e^{-E/KT}$$

with

$$A \cong \frac{8 c e^2 v}{a k} e^{\Delta S/K} = \text{const. for a given composition}$$

and where σ = conductivity, T = absolute temperature, c = fraction of oxygen lattice sites which are vacant, e = electronic charge, v = Debye frequency (approximately 10^{13} sec^{-1}), k = Boltzmann constant, a = lattice parameter ($5.13 \text{ \AA}$), and $e^{\Delta S/K}$ = entropy factor, related to ion vibrational frequency changes in the neighborhood of a vacancy during a jump. The most reasonable high estimate for this last factor is 10.

If our data is plotted as $\ln \sigma T$ vs. $1/T$, one may attempt to fit straight lines to the data and hence obtain experimental estimates of the activation energy E for a vacancy jump, and the pre-exponential factor A . The results are as follows:

<u>% CaO</u>	<u>E (exper.)</u>	<u>A (exper.)</u>	<u>A (theor., $e^{\Delta S/K} = 10$)</u>
14	1.285 e.v.	$13.8 \times 10^6 \Omega^{-1} \text{ cm}^{-1} \text{ } ^\circ\text{K}$	$2.0 \times 10^6 \Omega^{-1} \text{ cm}^{-1} \text{ } ^\circ\text{K}$
15	1.313	11.0×10^6	2.2×10^6
17	1.327	5.3×10^6	2.4×10^6
18	1.338	2.7×10^6	2.6×10^6
20	1.344	2.2×10^6	2.9×10^6

It should be pointed out that at temperatures above 550°C , the experimental points for the 14 and 15% compositions showed an increasing deviation below the initial straight line.

It is interesting now to consider two possible interpretations of the data:

Interpretation I:

With this viewpoint one assumes that the above experimentally determined parameters for A and E are the correct ones, and that the deviations observed for the 14 and 15% compositions are due to the presence of a second phase having quite different properties from the bulk of the sample. The large variation of A and the small variation of E with composition is taken as further evidence of this. One difficulty with this viewpoint is that one would not predict any of the A's to be larger than the theoretical values (as is observed) but only equal or smaller than theoretical. To salvage this viewpoint one must assume an entropy factor $e^{\Delta S/K}$ equal to 70, a suspiciously high value compared to those found in existing experiments and theory for vacancy motion.

Interpretation II:

With the second viewpoint one assumes that in the 14 and 15% compositions, a diffusionless phase transformation of the order-disorder type occurs below 550°C . If the vacancies were much less mobile in the ordered state, one would expect a slope change in the $\ln \sigma T$ vs. $1/T$ curve

at 550°C which would be qualitatively similar to that actually observed. This would automatically lead to anomalously high values for A. As far as the other compositions are concerned, one would have to assume that they underwent the transformation at higher temperatures, say about 750°C .

In conclusion, it should be remembered that although the addition of CaO to ZrO_2 stabilizes it against the well-known monoclinic and tetragonal transformations, more subtle traces of distortion may still occur, especially in the oxygen sublattice, where they would not be easily detectable by the usual x-ray techniques. Carter has found some evidence for such oxygen distortions in the ZrO_2 -CaO system by means of neutron diffraction measurements (private communication).

THE INTERACTION OF OXYGEN WITH PLATINUM

Y. L. Sandler and D. D. Durigon

The lack of reproducibility of the surface properties of platinum in the oxygen adsorption in catalytic oxidation reactions and in the electrochemical reduction of oxygen on the platinum electrode has often been noted.

In order to study the cause of these effects, the catalytic activity for the reaction $O_2^{16} + O_2^{18} \rightarrow 2O_2^{16}O^{18}$ was determined on sintered platinum powders with the simultaneous determination of the adsorption as a function of pressure, temperature, time, and prehistory.

An example of the results obtained is given in the accompanying figure. The logarithm of the rate at which equilibrated oxygen molecules leave the surface is plotted versus the inverse absolute temperature for ascending and descending temperatures after degassing the metal at 600°C.

A sample of highest available purity (99.999%) was used. It had previously been annealed at 800°C and was treated in situ with low-pressure oxygen at 600° for several days for degassing and removal of carbon. As a result of this, the defect structure was reduced to a minimum and the results are characteristic of true surface changes.

It may be seen that there is an appreciable activity at relatively low temperatures which, however, decreases with time. On increasing the temperature, at about 250°C, a higher slope is reached corresponding to an activation energy of about 30 kcal/mole. The amount adsorbed here becomes a maximum of about 0.7 monolayers and decreases again with temperature.

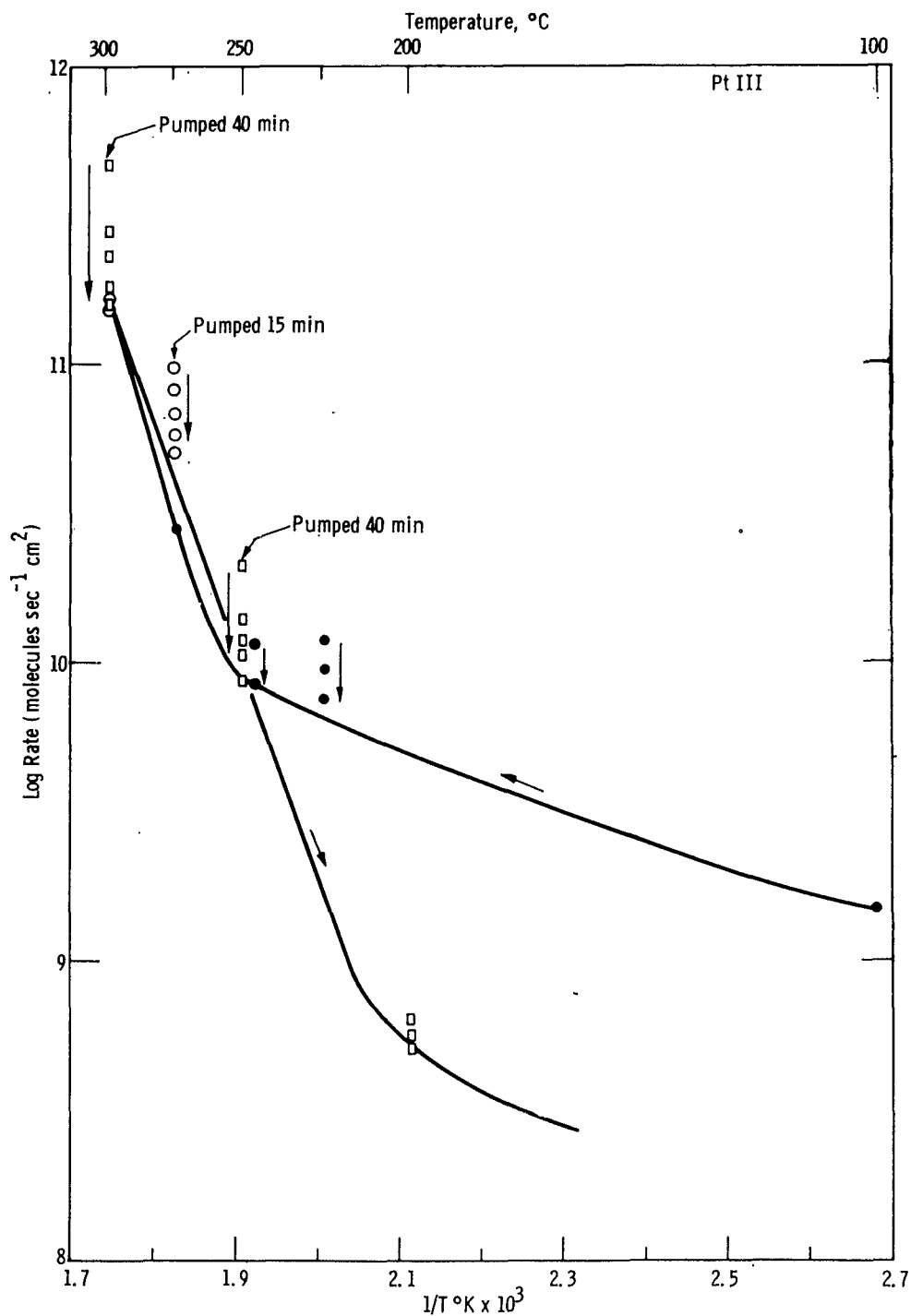
The important points are the following:

- (1) On decreasing the temperature, the low-temperature activity is very strongly reduced. (After pumping at 600° the cycle can be reproduced.) Presence of oxygen adsorbed at a high temperature, inhibits the catalytic activity at low temperatures. The marked effect of high-temperature oxygen on the oxygen reduction at a platinum electrode was previously discussed (cf. First Semi-Annual Report; J. Electrochem. Soc., in press).

- (2) A decrease in activity with time, as indicated by several points on the curve, was observed throughout the temperature range. A slow change in the mode of adsorption is taking place which presumably involves a rearrangement of the platinum surface. Changes of this type may explain the reduction in activity of the platinum oxygen electrode without invoking the presence of impurities or poisoning by intermediates. The surface is strongly heterogeneous. This also follows from measurements of the rate desorption as a function of coverage.

The study shows the complexity of the oxygen chemisorption on the heterogeneous platinum surface. A discussion of the kinetics of the oxygen electrode usually given in terms of phases like Pt, PtO, and PtO₂ does not seem meaningful.

Curve 573250-B



A SURVEY OF THE ACTIVITY OF SILVER-BASED ALLOY ELECTRODES
FOR THE OXYGEN REDUCTION IN KOH SOLUTION

Y. L. Sandler
E. B. Ashcraft
D. W. Beckett
E. A. Pantier

A study of the effect of the addition of a few percent of thorium, barium, magnesium, lanthanum, iridium, antimony, beryllium or manganese to silver on the oxygen reduction reaction in 1 N KOH was carried out. The alloys were abraded with MgO and washed, but not thermally treated. No significant changes were observed as compared to the pure metal, except that the alloy electrodes gave better reproducible characteristics than the pure silver.

Silver-magnesium alloys showed superior electrode characteristics after treating them in low-pressure oxygen at 500° to 570°C (cf. Report No. 4). The thermal pretreatment allows magnesium atoms to diffuse out to the surface where they are oxidized. Systematic experiments on a large number of samples from two different sources under different conditions of preparation and thermal pretreatment were carried out. Cathodic potentials were 0-120 mv higher than for pure silver between open circuit and the sharp drop to the hydrogen potential.

To establish the advantage of the alloy electrode for practical purposes, several long-term experiments were carried out in which pure silver and a silver-magnesium oxide electrode were alternately dipped into 1 to 3 M KOH electrolyte at intervals of 6 to 48 hours and the potential of the electrode was recorded at currents between 2 and 6×10^{-4} A. The potential was 15 to 35 mv higher for the alloy electrodes for the entire period after the first two hours, corresponding to a 2-3 x higher current at constant voltage. (Larger long-term differences may be achievable; the electrodes used for the tests did not show a large initial improvement over silver.) Again, pure annealed silver showed considerably larger potential fluctuations with time than the metal containing MgO as an "impurity". Thermally pretreated electrodes containing Be or Mn showed no improved characteristics.

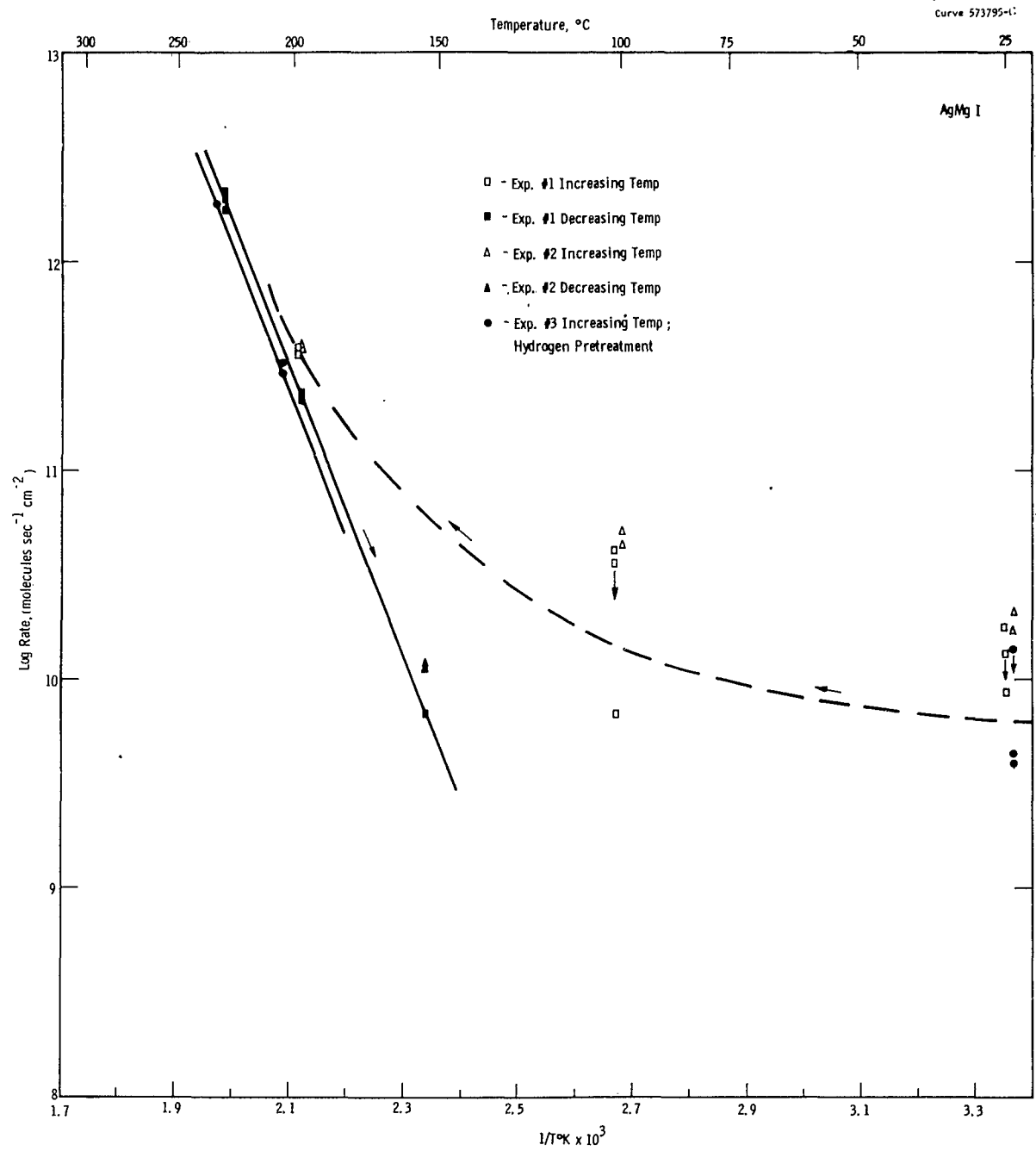
THREE NOTES ON THE SURFACE CHEMISTRY AND
CATALYTIC ACTIVITY OF SILVER-MAGNESIUM OXIDE SURFACES

Y. L. Sandler
D. D. Durigon
A. Langer
E. A. Pantier

The higher activity of the silver-magnesium electrode as compared to the silver electrode in the electrochemical reduction of oxygen was established in a previous paper.

In order to investigate the nature of the surfaces and their catalytic properties, the following studies were carried out:

- (1) The exchange reaction $O_2^{16} + O_2^{18} \rightarrow 2O_2^{16} O_2^{18}$ was studied on Ag-MgO powder. Contrary to what was found on pure silver, an exchange occurred at room temperature showing the existence of a reversible oxygen chemisorption and a high catalytic activity of the material.
- (2) The catalytic decomposition of hydrogen peroxide was studied on several Ag and Ag-MgO foils. No significant differences were found. The reason appears to be that the activity of Ag is very high and the decomposition is therefore diffusion limited.
- (3) The diffuse reflectance of a variety of differently pretreated Ag and Ag-MgO samples was studied in the visible and ultra-violet region. Silver shows a strong absorption peak at 3200 Å. With silver oxide, this peak is shifted to 3000 Å. Ag-MgO samples when white or metallic in appearance showed the absorption at 3200 Å like metallic silver, while brown surfaces, often obtained after high temperature pretreatment of the Ag-MgO even at a very low oxygen pressure, showed the absorption peak at 3000 Å. The presence of MgO appears to stabilize the silver in the oxide form. Contrary to Ag-MgO, very pure silver surfaces show a strong resistance to nucleation of the oxide phase and could not be oxidized at atmospheric oxygen pressure at any temperature. Even oxygen treatment at 250°C for two hours at 70 atmospheres still gave a bright metallic surface with an absorption peak at 3200 Å.



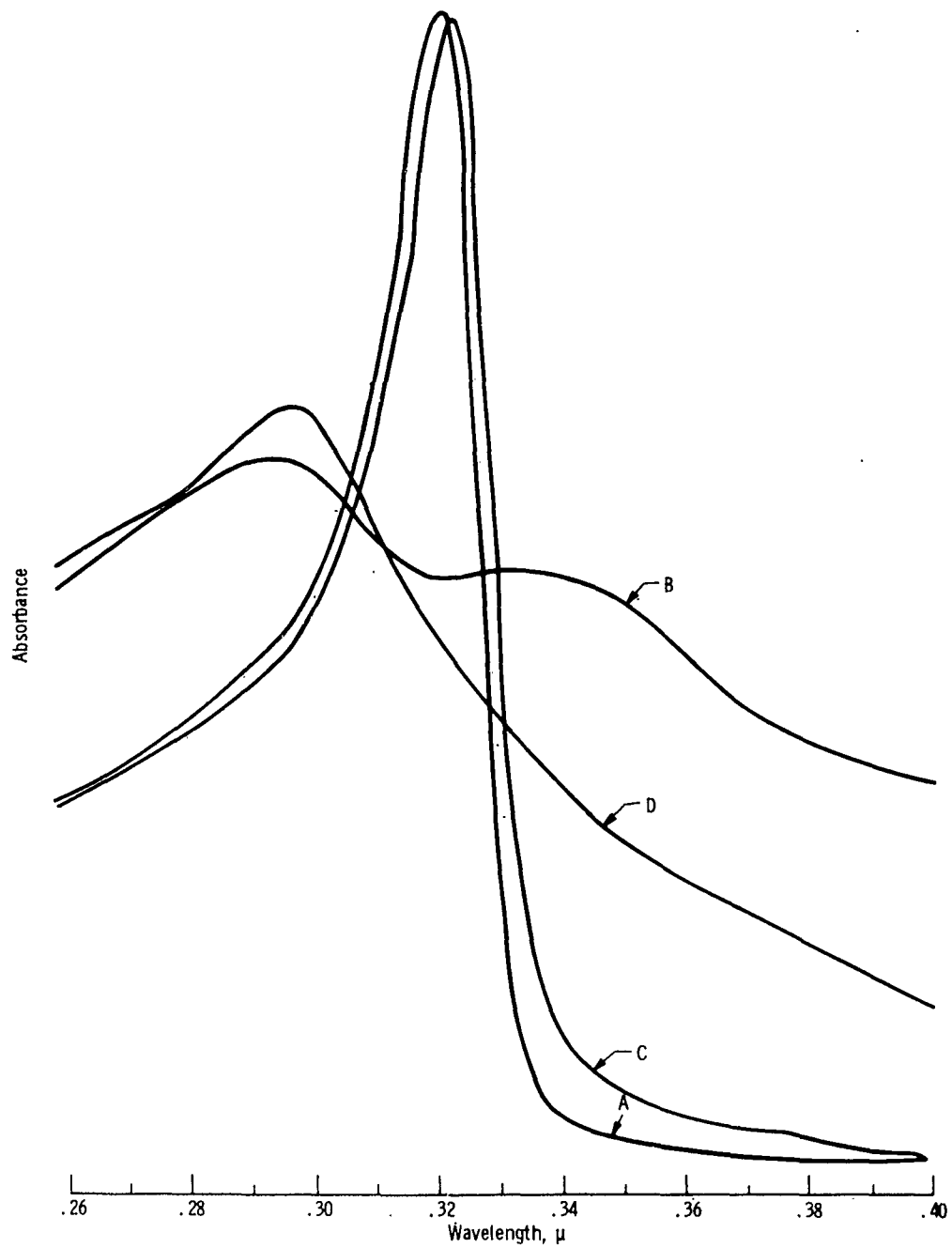


Fig. 2—Absorbance after pretreatment of (A) Ag heated in 0.01% O_2 at 500°C, (B) Ag MgO heated in 0.01% O_2 at 500°C, (C) Ag etched in 10% HNO_3 , (D) Ag thermally oxidized at 260°C, 40 atms, 24 hours

REACTIONS OF OXYGEN AND HYDROGEN PEROXIDE
AT SILVER ELECTRODES IN ALKALINE SOLUTIONS

T. Hurlen
Y. L. Sandler
E. A. Pantier

The intermediate peroxide scheme for the oxygen electrode was tested by experiments on oxygen reduction and hydrogen peroxide decomposition at silver electrodes in potassium hydroxide solutions (0.1, 1.0, and 5.0 M) at 25°C. This scheme was found appropriate in interpreting the observations made, and data were obtained for the specific rate of three of the four one-electron steps involved in the reduction of oxygen to water. From the magnitude of the exchange currents and the activities, it is seen that the intermediates O_2^- , OH and HO_2 must be in the chemisorbed state. A comparison of the polarization behavior in oxygen and in hydrogen peroxide shows that the scheme is internally consistent. The decomposition of hydrogen peroxide occurs at a diffusion-limited rate and gives a mixed potential of $0.94 - 0.059 \text{ pH}$ in V on the standard hydrogen scale when the peroxide concentration exceeds a rather low limit. The silver dissolution reaction exhibits an essentially pure diffusion polarization and mixes with the oxygen reduction reaction to determine the open-circuit potential of silver in solutions of low hydrogen peroxide content (below about 10^{-7} M in 1 M KOH).

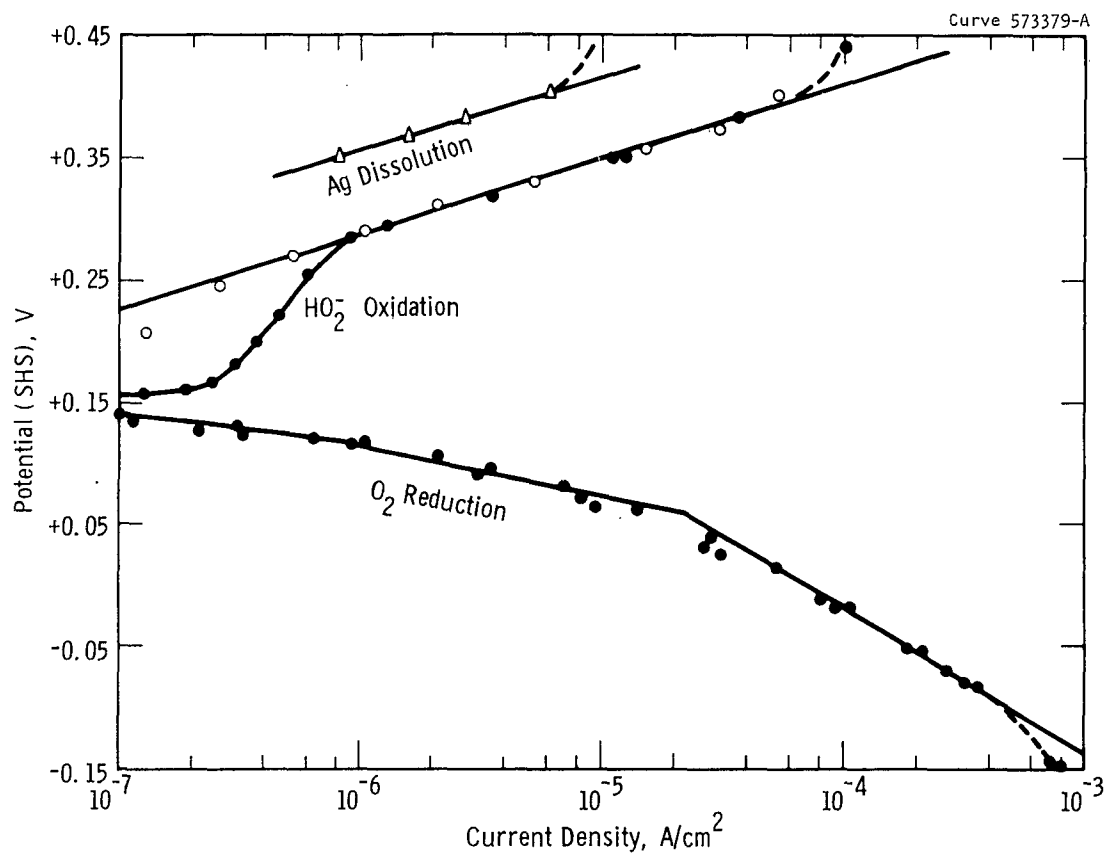


Fig. 1

THE LOW-TEMPERATURE ORTHO-PARA CONVERSION OF HYDROGEN ON SILVER^{1a}

Y. L. Sandler
D. D. Durigon

Abstract

A study of the low temperature ortho-para conversion of hydrogen on sintered silver particles was carried out to probe the surface for paramagnetic chemisorbed species. No paramagnetic structure of chemisorbed oxygen was found. Hydrogen chemisorbs on silver below room temperature only in the presence of adsorbed oxygen, presumably in molecular form. No paramagnetic surface structure results. On the other hand, hydrogen chemisorbed at high temperature gives a strongly paramagnetic surface; it appears to be chemisorbed in atomic form at centers containing firmly bound residual oxygen atoms and is not easily removed. This may explain the reported existence of a strongly bound paramagnetic form of oxygen and generally must be considered in adsorption studies on "bare" surfaces produced by hydrogen reduction.

^{1a} Work supported by the Advanced Research Projects Agency through the U.S. Army Electronics Laboratories and the Office of Naval Research.

THE DESORPTION AND ISOTOPIC EXCHANGE OF OXYGEN AT A SILVER SURFACE^{1a}

Y. L. Sandler
D. D. Durigon

Abstract

Pressure-temperature scans with oxygen on porous silver, as well as the onset of the homonuclear exchange O_2^{16} and $O_2^{18} \rightarrow 2 O^{16} O^{18}$, show that the chemisorption becomes reversible at about 160°C. Measurements of the exchange rate were carried out at 160° - 180°C, followed by fast removal of the gas phase and determination of the desorption rate and of the isotopic composition of the desorbing gas. It is thus shown in two independent ways that the desorption rate is equal to the rate of exchange. The chemisorbed oxygen exists in two binding states, but no evidence is found that one of these is in undissociated form. Increase in the proportion of the firmly bound form reduces the desorption rate but causes no change in the activation energy of desorption which is 32.5 kcal/mole O_2 . The results show that while rapid diffusion and exchange takes place over the entire outer surface, desorption occurs only from those regions which are free of the firmly bound oxygen.

^{1a} Work supported by the Advanced Research Projects Agency through the U.S. Army Electronics Laboratories and the Office of Naval Research.

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