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An Investigation of Mixed Conduction in Solid Electrolytes

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TECHNICAL PROGRESS REPORT

An Investigation of Mixed Conduction in Solid Electrolytes

Robert A. Rapp

Since the previous annual report of August 1969, further progress has been made in the theoretical and experimental investigation of mixed conduction in solid oxide electrolytes. The review paper, "Solid Electrolyte Cells," by R. A. Rapp and D. A. Shores has now been published in Volume IV of Techniques in Metals Research for which R. A. Rapp is the editor. A paper entitled, "Solid Bielectrolyte Cells for Thermodynamic Measurements," (by D. A. Shores and R. A. Rapp) which has been sent to the AEC as report number COO-1440-20 in May 1970, has been accepted with minor revisions for publication in Journal of the Electrochemical Society. The paper should appear in the Journal in a few months.

Three papers resulting from previously reported AEC research are presently in various stages of preparation for publication:

1. "Hydrogen Ion (Proton) Conduction in Thoria-Base Solid Electrolytes," by D. A. Shores and R. A. Rapp. This paper is essentially complete and ready for submission (to Journal of the Electrochemical Society) with the succeeding paper (as a pair). A copy of this paper is attached separately as report number COO-1440-22.
2. "Mixed Conduction in Pure ThO_2 , $\text{ThO}_2\text{-Sm}_2\text{O}_3$, and $\text{ThO}_2\text{-La}_2\text{O}_3$ Solid Solutions," by D. H. Primas, D. A. Shores, and R. A. Rapp. The initial draft of this paper is essentially complete.

3. "Mixed Conduction in Pure and Doped Dy_2O_3 and Gd_2O_3 ," by J. M. Macki and R. A. Rapp. This paper is being reduced in size from an initial rough draft. The paper is intended for publication in the Journal of the American Ceramic Society.

During the past year a paper entitled, "Proton Conduction in Solid Oxide Electrolytes" was presented by D. A. Shores at the 99th annual meeting of the AIME in Denver, Colorado. Dr. Rapp presented one-hour seminars on "Solid Electrolyte Studies" at the General Motor Research Laboratories in Detroit, at the Department of Metallurgical Engineering of the University of Pittsburgh, and at the Department of Nuclear Engineering of The Ohio State University.

Dr. David Shores, a post-doctoral Research Associate on this contract concluded his work at Ohio State University in March 1970. Dr. Shores has joined the Materials and Process Laboratory of the General Electric Laboratories in Schenectady, N.Y. The intended replacement for Dr. Shores was Dr. Shlomo Zelouf from Pennsylvania State and Israel. However, Dr. Zelouf was unable to initiate his research in March because of hospitalization in Israel with a serious lung infection. Because of an extended waiting period for the convalescence of Dr. Zelouf which would extend through the winter 1971, it was finally decided to withdraw the intended appointment of Dr. Zelouf. Doctorate candidate Trikur Ramanarayanan passed his general written and oral examinations during the year with the highest marks of his group of eight candidates. During the summer months, Dr. Kyril Wylie worked on this contract with the purpose of establishing

the feasibility of determining experimentally the solubility of hydrogen in solid oxide electrolytes by the use of tritium or deuterium. (A report of this study is included.) Dr. Wylie is presently an Assistant Professor in the Department of Mechanical Engineering, University of Mississippi, University, Mississippi.

The principal research studies during the past year have been concerned with (a) the investigation of partial proton conductivity in mixed conducting oxides by D. Shores and R. A. Rapp (see the attached report COO-1440-22), (b) the investigation of hydrogen diffusion in ThO₂-base solid electrolytes by the measurement of transient electrical conduction upon sudden changes in hydrogen activity (a paper by D. A. Shores may be forthcoming), (c) use of the dual-temperature stainless steel apparatus to determine $\Delta G^{\circ}_{\text{UO}_2}$ (but the initial experimental runs were not successful), (d) consideration of a tracer method to determine the solubility of hydrogen in solid oxide electrolytes, and (e) use of the beta-alumina and pyrex electrolytes to study mixed conduction in fused salts. Details of the progress on the last two topics follow directly.

MIXED CONDUCTION IN FUSED SALTS

T. Ramanarayanan

Since the previous annual report of August 1969, progress has been made in the equilibrium and electrical conduction studies of the NaCl-TiCl_x fused salt system. Two important aims were indicated in the previous report:

(a) Chemical analysis of the NaCl-TiCl_x system for Ti^{2+} , Ti^{3+} and Ti^{4+} ions for an electrochemically-fixed thermodynamic activity of sodium and fixed total content of titanium in solution. An interpretation of the composition change of the fused salt with variation in the activity of sodium was also indicated.

(b) Investigation of the electrical conductivities in the NaCl-TiCl_x system at various fixed sodium activities and fixed total titanium contents. The possibility of finding electronic conduction over a certain sodium activity range was indicated.

EXPERIMENTAL

It was mentioned in the previous annual report that the following cell would be used to fix the activity of sodium in the fused salt.

$\text{Pt, Sn-10at\%Na} \mid \beta\text{-alumina} \mid \text{Pt, NaCl, Ti}^{2+}, \text{Ti}^{3+}$. In order to test whether β -alumina was reversible to sodium ions, the following cell was tested: chromel B, Sn- 10at%Na $\mid \beta\text{-alumina} \mid$ Na, chromel B. The β -alumina was in the form of a crude (large grained with porosity) crucible with two bored holes $\frac{1}{4}$ " in diameter, $\frac{1}{2}$ " in depth and $\frac{1}{4}$ " apart. One bored hole contained the Sn-Na alloy, and the other pure sodium.

Chromel B wire with a thin layer of oxidized surface was used for electrical contact. The bores were closed with boron-nitride lids and sealed tight with high temperature alumina cement. The cell was heated to 850° in an argon atmosphere having a very low oxygen pressure. (De-oxidation of commercial argon was carried out by first passing the gas through a Cu-Cu₂O mixture at 150°C and then through Ti turnings at 800°C.) A steady voltage was not obtained for this cell even at the end of two days. This resulted possibly from the fact that the β -alumina used was not dense enough so that sodium vapor could escape through it. Also, the high temperature alumina cement was probably not sufficiently dense.

It was decided, then, to determine whether pyrex could be used instead of β -alumina as an electrolyte for the transport of sodium ions. Glass containing sodium had already been used successfully by Hauffe and Vierk as an electrolyte which conducts sodium ions. The following electrochemical cell was therefore constructed:

The sodium was contained in a closed Pyrex tube attached to a capillary tube. Cut pieces of sodium were transferred into the tube under an argon atmosphere. A chromel wire with a thin oxidized coating was introduced through the capillary into the sodium and the capillary was sealed around the chromel wire under vacuum. The pyrex tube containing sodium was surrounded on the outside with the sodium-tin alloy contained in an alumina crucible. Chromel wire was used as the electrode on the alloy side also. The cell was heated under a low oxygen pressure to a temperature

of 500°C. A steady E.M.F. of about 500 m.v. was attained after about 12 hours. An attempt was made to transfer electrochemically sodium to the alloy by short circuiting the cell. It was observed that Pyrex could transport sodium ions.

The next step was to design an electrochemical cell with Pyrex as the electrolyte for sodium and with the sodium-tin alloy on one side and molten NaCl on the other. The Sn-Na alloy was contained in a quartz tube. Over the alloy, a 1 cm thick layer of powdered Pyrex was placed. Over this was placed a $\frac{1}{2}$ " layer of sodium chloride. A Pt gauze placed at the Pyrex-NaCl interface served as one electrode. The other electrode was a Pt- wire attached to a little piece of chromel wire connected to the alloy. The Pt- wire was sheathed in an alumina thermocouple tube to prevent short circuiting. The cell was heated to 850°C under an argon atmosphere low in oxygen. At this temperature the alloy, NaCl and Pyrex were all in a molten condition. It was observed that at 850°C the alloy attacked the quartz tube and therefore a steady open-circuit voltage was not attained.

It was decided, therefore, to contain the alloy, Pyrex and sodium chloride in an alumina crucible. The same experimental arrangement as just described was used with the alloy forming the lower-most layer, Pyrex the layer above it, and sodium chloride the top layer. Again a Pt gauze electrode was used at the Pyrex-sodium chloride interface and a piece of chromel attached to Pt served as the electrode dipping into the alloy. The cell was heated to 850°C under an argon atmosphere low in oxygen pressure. The open-circuit E.M.F. gradually decreased

from a value of 700 M.V. to a value of 150 m.v. over a period of 5 days and still decreased at a slow rate. This indicated that the sodium was diffusing from the alloy through Pyrex to the sodium chloride under the action of a chemical potential gradient. An external voltage of 600 m.v. was then applied in a direction opposed to the cell voltage. It was observed that within about half an hour the cell voltage reached a value close to the applied voltage. This indicated that sodium ions travelled through molten Pyrex quite fast under an applied potential and that a predetermined value of sodium activity in sodium chloride could be obtained by applying a proper potential.

FUTURE EXPERIMENTAL PROGRAM

The (Sn-10at%Na) alloy would be contained in an alumina crucible. A layer of powdered Pyrex would be placed above this and a layer of sodium chloride above the Pyrex. A Pt gauze at the NaCl-Pyrex interface would serve as one electrode with a small length of chromel wire attached to Pt- and dipping into the Sn-Na alloy as the other electrode. The alumina crucible would be contained in an outer closed-end alumina tube, closed at the top with a water-cooled brass cap. Two Pt conductivity probes will be introduced into the fused sodium chloride. The cell will be maintained at a temperature of 850°C in an atmosphere of purified argon having a low oxygen pressure.

At the start of a run, a measured amount of TiCl_4 will be dropped into the fused sodium chloride. A predetermined E.M.F. will be applied across the cell to fix the relative amounts of Ti^{3+} and Ti^{3+} in solution in the fused salt. (The amount of Ti^{4+} present will be negligibly small.)

A conductivity measurement will be made and a sample of the fused salt will be withdrawn for chemical analysis of Ti^{2+} and Ti^{3+} . An apparatus for the analysis has already been designed, built and tested. The E.M.F. will be adjusted to cover the sodium activity range from predominance of $TiCl_2$ to predominance of $TiCl_3$. For each sodium activity, a conductivity measurement and chemical analysis will be carried out. The experiment will then be repeated by adding more $TiCl_4$.

THEORY

The theory to be outlined here is quite similar to the one given in the previous report. The electrochemical cell involved may be represented as:

If ' refers to the right-hand electrode and " to the left-hand electrode, then the open-circuit E.M.F. of the above cell is related to the sodium activities at either electrode through the relation:

$$E = - \frac{RT}{F} \ln \frac{a'_{Na}}{a''_{Na}}$$

where R is the gas constant, T the temperature in $^{\circ}K$, F the Faraday constant and a_{Na} the activity of sodium. When an external voltage is applied with polarity opposite to the cell voltage, sodium ions get transported through pyrex from one side to the other until the open-circuit voltage becomes equal to the applied voltage. Under these conditions,

$$E_{app} \cong - \frac{RT}{F} \ln \frac{a'_{Na}}{a''_{Na}}$$

Solving for the unknown sodium activity in sodium chloride,

$$a'_{\text{Na}} = a''_{\text{Na}} \exp\left(-\frac{E_{\text{app}} F}{RT}\right)$$

Upon addition of TiCl_4 , the following equilibria would be set up:

The amount of TiCl_4 present in solution in NaCl at 850°C will be negligible. So, it is sufficient to consider only the second equilibrium. The equilibrium constant for this reaction may be represented as:

$$K = \frac{a_{\text{TiCl}_2} a_{\text{NaCl}}}{a_{\text{TiCl}_3} a'_{\text{Na}}} ;$$

$$\frac{a_{\text{TiCl}_2}}{a_{\text{TiCl}_3}} = K \frac{a_{\text{Na}}}{a_{\text{NaCl}}} = K \frac{a''_{\text{Na}}}{a_{\text{NaCl}}} \exp\left(\frac{-EF}{RT}\right) ;$$

$$\frac{N_{\text{TiCl}_2}}{N_{\text{TiCl}}} = \frac{\gamma'_{\text{TiCl}_3}}{\gamma'_{\text{TiCl}_2}} \frac{K a''_{\text{Na}}}{a_{\text{NaCl}}} \exp\left(\frac{-E_{\text{app}} F}{RT}\right)$$

The above expression shows that by varying E_{app} , one may vary the ratio

$$\frac{N_{\text{TiCl}_2}}{N_{\text{TiCl}_3}}$$

When this ratio is about equal to unity, one may expect a significant amount of electronic conduction in view of the electron exchange reaction:

The measured total conductivity may be plotted as a function of the ratio

$$\frac{N_{\text{TiCl}_2}}{N_{\text{TiCl}_2} + N_{\text{TiCl}_3}}$$

Since the ionic part of the measured conductivity is a linear function of the concentrations of the species involved, this part may be subtracted from the measured total conductivity in order to yield the electronic conductivity. From the form of the curve obtained, it may be possible to deduce an equation for the behavior of the electronic conduction.

Electronic conduction has been studied in the $\text{CaO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$

system as a function of the ratio $\frac{N_{\text{Fe}^{2+}}}{N_{\text{Fe}^{2+}} + N_{\text{Fe}^{3+}}}$.

SOLUBILITY OF HYDROGEN IN SOLID OXIDE ELECTROLYTES

Dr. Kyril Wylie

INTRODUCTION

The purpose of this study is to ascertain the feasibility of using a tracer technique to determine experimentally the solubility of hydrogen in several different solid oxide electrolytes in the temperature range of 800 to 1400°C.

In this study, it is assumed that tritium or deuterium can be used as the tracer which would enter the electrolytes through an equilibration with a H_2 - H_2O gas containing the tracer either in the H_2 or in the H_2O . The validity of such an assumption depends upon whether the tracer behaves in the same manner as protium and whether measurable quantities of the tracer would be soluble in the electrolytes.

USE OF TAGGED HYDROGEN

Consider the experimental system shown in Figure 1 where the hydrogen-water gas mixture is prepared by passing an accurately metered flow of tagged hydrogen gas (denoted by X) through a nontagged water saturator (which is maintained at a carefully controlled temperature). The solid oxide electrolyte pellet located in the furnace as well as the experimental

atmosphere in the furnace tube are maintained at some constant temperature, and equilibrium is attained by diffusion. At equilibrium, within the gas phase, the concentration of each species present in the gas is established by equilibrium

constants and therefore, thermodynamics. The equilibrium gas mixture resulting from the passage of tracer X_2 through H_2O at an elevated temperature would contain all gaseous species X_2 , H_2O , H_2 , HX , and HXO .

The diffusion of tracer X into the pellet requires a dissociation of the constituent tagged constituent and

Constant Equilibrium gas IF a Control Volume. "Experimental Atmosphere" Pellet

equal amounts, the ability to ascertain the origin of the tracer in the pellet is lost. The molecular mechanism of dissolution could not be established.

An indication of the relative amounts of the three possible combinations

from equilibrium constants such as

Fig. 1. Experimental Apparatus for Determination of Solubility of Hydrogen in Solid Oxide Electrolytes.

have provided values which are approximately 4% lower than those shown in the figures. However,

Fig. 2. Equilibrium Constants for Reactions Involving Protium, Deuterium and Tritium.

Fig. 3. Equilibrium Constants for Reactions Involving Protium, Deuterium and Tritium.

the recent studies are confined to lower temperatures while this experimental work would be conducted in the temperature range of 800 to 1400°C. Furthermore, as Weston¹¹ pointed out in 1965, the work still seems to be passing through a period of experimental uncertainty.

The tabulated bond energies for 800°C of V. I. Vedeneyev et al. (12) or Herzberg (13) show that the HT and HOT molecules, or HD and HOD molecules dominate the equilibrium gas when tritium or deuterium is used as the tracer. Furthermore, T₂, H₂O, H₂ and T₂O molecules, or D₂, H₂O, H₂ and D₂O molecules must be considered to exist in lesser quantities.

DETECTION OF TAGGED HYDROGEN

Consider that approximately 10^{-7} g-mole of hydrogen is present in a given solid oxide electrolyte pellet (0.2 cc) and that the hydrogen consists of equal amounts of tracer nuclei and protons. With the mass-spectrometric technique, a 100-fold increase in the sample size would be required to render a border-line detection of deuterium gas. Thus, the detection of deuterium as a tracer in a 0.2 cc solid oxide electrolyte pellet is not experimentally feasible.

Under the same assumptions mentioned above, calculations indicate that the use of approximately 50 mCi of tritium feed

gas per experimental study would result in 4.5×10^{-3} μCi per pellet. The maximum counting efficiency with liquid scintillation techniques is 50%. An easily detected counting rate of 3×10^3 cpm is realized with only a 30% counting efficiency. These calculated results tend to imply that it is experimentally feasible to detect dissolved tritium in solid oxide electrolytes. Whether the solubility of tritium is identical to that of hydrogen is, however, doubtful.

A disadvantage of the use of tritium or deuterium as a tracer for protium in this particular type of solubility experiment is their relative sizes which should be an important factor in the limit of solubility.

TRITIUM SAMPLE PREPARATION AND COUNTING

To determine the tritium in a sample saturated with tritium plus hydrogen, the pellet would be crushed and then dissolved in H_2SO_4 . At present, a technique is not known which would allow the direct use of this solution or its conversion into a form to permit the employment of a liquid scintillation counting reagent such as PPO, butyl PBD, POPOP, etc. However, a technique for the liquid scintillation measurement of low energy beta emitters might provide adequate counting rates for this particular solution.

This technique employs approximately fifty (0.5 mm diameter and 25 mm long) scintillation "B" filaments¹⁴ packed and heat-fused at the ends to provide a plastic scintillation dumb-bell. The dumb-bell is then placed into a low potassium glass vial,¹⁵ which is sealed after the introduction of the solution to be counted.

Standard liquid scintillation counting techniques are calibrated by first counting the sample of unknown specific activity, and then, after adding a known amount of a tritium standard¹⁵ to the sample, recounting the combined sample and "spike". This technique provides two activity determinations; the first is the "raw" counting rate of the unknown, while the second is the sum of the unknown and standard. Thus, it is possible to determine the specific activity of the unknown sample.

DISCUSSION

Use of the tracer technique to determine experimentally the content of tritium in solid oxide electrolyte pellets is feasible. An advantage of the tritium tracer is that studies conducted with 0.2 cc volume pellets provide sufficient radioactivity for liquid scintillation counting. Larger pellets are required for deuterium in order to increase the

sample size so that it can be detected by mass spectrometric techniques. Disadvantages to the tritium tracer method are numerous and, in fact, seem to prohibit the determination of hydrogen solubility by this method:

1. Owing to the variety of species in hydrogen-water-tritium gas, it is not possible to determine experimentally the sources or the relative proportions of the tracer and hydrogen in the pellet; only the tritium can be detected.
2. Owing to the size differences between the tritium and protium nuclei, the determination of tritium content could not be used to infer hydrogen solubility.

Further consideration of the experimental determination of hydrogen solubility in solid oxide electrolytes is not anticipated.

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