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..... An Investigation of Mixed Conduction in Solid Electrolytes

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Submitted by..... Robert A. Rapp

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TECHNICAL PROGRESS REPORT

An Investigation of Mixed Conduction in Solid Electrolytes

Since the previous annual report of August 1968 further progress has been made in the theoretical and experimental investigation of mixed conduction in solid oxide electrolytes. The review paper mentioned in previous reports concerning experimental techniques, "Solid Electrolyte Galvanic Cells", has been completed and will be published shortly by Interscience Publishers in Volume IV of Techniques in Metals Research for which R. A. Rapp is the editor. Dr. David Shores, a post-doctoral Research Associate on this contract, has co-authored this paper. A copy of the manuscript is attached and should be considered as part of the body of this report.

Two papers were presented at the 98th Annual Meeting of the AIME in Washington, D.C.: "Nonstoichiometry and Defect Structures in Pure Nickel Oxide" by Y. D. Tretyakov and R. A. Rapp and "The Electrical Conductivity of Pure and Doped Dy_2O_3 and Gd_2O_3 " by J. M. Macki and R. A. Rapp. The latter work was supported on this contract from September 1965 to August 1968, and will be submitted for publication within the next six months. Also, the investigation of "Mixed Conduction in $\text{ThO}_2\text{-La}_2\text{O}_3$ and $\text{ThO}_2\text{-Sm}_2\text{O}_3$ Solid Solutions", by D. Primas and R. A. Rapp is being prepared for publication.

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The principle 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, and b) an investigation of mixed conduction and ionic equilibria in molten NaCl-TiCl_x solutions by T. A. Ramanarayanan, a doctoral candidate, and R. A. Rapp. Materials for the latter study have been purchased, the apparatus has been designed and constructed, and preliminary tests are in progress. In addition, the apparatus for the measurement of $\Delta G_{\text{UO}_2}^\circ$ has been completed, and initial experiments are underway.

A. Proton Conduction in Oxide Electrolytes

The investigation of partial proton conductivity, which was proposed last year as a study of $\text{ThO}_2\text{-La}_2\text{O}_3$, $\text{ThO}_2\text{-Sm}_2\text{O}_3$ and $\text{ThO}_2\text{-Y}_2\text{O}_3$ solid solutions, has been enlarged to include $\text{Gd}_2\text{O}_3\text{-CaO}$ and $\text{Dy}_2\text{O}_3\text{-CaO}$ solid solutions. The previous work of J. M. Macki and R. A. Rapp on Gd_2O_3 and Dy_2O_3 solid solutions indicated a possible partial proton conductivity that had a rather different temperature dependence than was observed in ThO_2 -based solutions by D. Primas and R. A. Rapp. The present investigation has verified partial proton conductivity in ThO_2 -based solutions and has established the dependence of proton conductivity on temperature, vacancy concentration, and partial pressures

of oxygen and of hydrogen. Similar experiments on $\text{Gd}_2\text{O}_3\text{-CaO}$ and $\text{Dy}_2\text{O}_3\text{-CaO}$ solid solutions are currently underway. The attached report (attachment No. 2) describes the apparatus and technique, and presents the available experimental data along with a preliminary discussion of these results. Further analysis of the data for all of the materials in terms of an appropriate point defect model and the crystal chemistry of the materials will be made before a paper is submitted for publication.

B. Mixed Conduction in Fused Salts

From a survey of the literature, the available data on the solubility and activities in molten NaCl containing titanium has been obtained. The purpose of the present investigation is to measure conductivities, equilibrium concentrations of the various ionic species, and solubilities in a fused salt of NaCl containing Ti^{2+} , Ti^{3+} and Ti^{4+} ions in solution. Titanium is introduced into the solution by dropping liquid TiCl_4 into the melt. The proportions of the various ions are varied electro-chemically and at each stage a conductivity and composition measurement is carried out. When two titanium ions of differing valence are present in comparable proportions, one might expect significant electronic conduction in the melt, in view of electron exchange between the valence states.

1. Experiment - The fused sodium chloride is contained in a crucible of sodium- β - Al_2O_3 ($\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$) which is a Na^+ -conducting solid electrolyte. The bottom of the crucible is platinized on the inside. The crucible is surrounded by an alloy of Sn-10%Na which is contained in an outer closed-end alumina tube. A low-carbon steel lid forms a tight seal on the crucible. The top of the alumina tube is closed by means of a water-cooled brass cap. The fused salt and the alloy are maintained at 850°C , in an atmosphere of purified He having a very low oxygen pressure which is maintained by passing the helium gas through hot Ti turnings.

At the start of an experimental run, a measured amount of TiCl_4 is dropped into the fused sodium chloride. A pre-determined e.m.f. is applied across the solid electrolyte cell:

which fixes the activity of Na in the fused salt. The sodium activity in turn fixes the relative proportions of Ti^{2+} and Ti^{3+} and Ti^{4+} in the melt. A conductivity measurement is then made and a sample of fused salt is withdrawn for the analysis of Ti^{2+} , Ti^{3+} and Ti^{4+} . The e.m.f. is then adjusted to a new value and the conductivity and chemical analysis measurements are repeated. The experiment progresses by the step-wise addition

of TiCl_4 followed by conductivity measurements and chemical analysis at various applied voltages until the range of sodium activity from Ti^{4+} predominance through increasing sodium activity to Ti^{2+} predominance is covered. At the present time the apparatus has been constructed and some exploratory conductivity and sodium activity measurements are in progress.

2. Theoretical Treatment - The electrochemical cell involved may be represented as

We shall designate the left-hand electrode by means of the prime superscript (') and the right-hand electrode by the double-prime superscript ("). Upon applying a voltage to this cell, Na^+ ions are coulometrically transferred from the left-hand to the right-hand electrode and electrons travel through the outer circuit. An ammeter in the circuit will measure a current which decreases with time. When steady-state conditions have been reached, the current reaches a constant and very low value. The cell reaction may be represented by

with the free energy change

$$\Delta G = RT \ln \frac{a''_{\text{Na}}}{a'_{\text{Na}}} = -F [E_{\text{app}} - I \Omega] \quad (1)$$

where I is the final value of current (at steady-state) and Ω is the ionic resistance of the solid electrolyte. At steady-state, however, the current will be essentially zero. If Eq. (1) is solved for the unknown sodium activity, a''_{Na} , in terms of the known activity at the reference electrode, we obtain:

$$a''_{\text{Na}} = a'_{\text{Na}} \exp \frac{FE}{RT} \quad (2)$$

where a''_{Na} is the activity of sodium in the fused sodium chloride melt. In view of the equilibrium

where the activity of sodium is based on pure liquid Na as the standard-state and the chlorine activity is based on the unit fugacity standard state. K_1 is the known value of the equilibrium constant at 850°C. The combination of Eqs. (2) and (3) gives:

$$P_{\text{Cl}_2}^{1/2} = \left[\frac{a_{\text{NaCl}}}{K_1 a_{\text{Na}}} \right] \cdot \exp \left(-\frac{FE}{RT} \right) \quad (4)$$

Values for a_{NaCl} are not available in the literature for the system $\text{NaCl-TiCl}_2\text{-TiCl}_3\text{-TiCl}_4$. However, if changes in the activity of sodium chloride resulting from variations in the proportions of TiCl_2 , TiCl_3 , and TiCl_4 are small, the value of P_{Cl_2} is a function of e.m.f. of Cell I only for a given temperature and for

a given total titanium content.

In view of the equilibria:

we have,

$$K_2 = \frac{a_{\text{TiCl}_3}}{a_{\text{TiCl}_2}} \cdot \frac{1}{P_{\text{Cl}_2}^{\frac{1}{2}}} \quad (5)$$

$$K_3 = \frac{a_{\text{TiCl}_4}}{a_{\text{TiCl}_3}} \cdot \frac{1}{P_{\text{Cl}_2}^{\frac{1}{2}}} \quad (6)$$

where K_2 and K_3 are the respective equilibrium constants.

If Eqs. (5) and (6) are substituted into Eq. (4), we obtain

$$\left[\frac{a_{\text{TiCl}_3}}{a_{\text{TiCl}_2}} \right] = \left[\frac{K_2}{K_1} \cdot \frac{a_{\text{NaCl}}}{a'_{\text{Na}}} \right] \cdot \exp \left(- \frac{FE}{RT} \right) \quad (7)$$

and

$$\left[\frac{a_{\text{TiCl}_4}}{a_{\text{TiCl}_3}} \right] = \left[\frac{K_3}{K_1} \cdot \frac{a_{\text{NaCl}}}{a'_{\text{Na}}} \right] \cdot \exp \left(- \frac{FE}{RT} \right) \quad (8)$$

Equations (7) and (8) show that by varying the applied voltage of cell I the activity ratios of the different valence species of Ti in solution should be varied in a very specific, predicatable way. The fused salt is expected to exhibit significant electronic conduction corresponding to the condition:

$$\frac{a_{\text{TiCl}_3}}{a_{\text{TiCl}_2}} = 1, \quad \frac{a_{\text{TiCl}_4}}{a_{\text{TiCl}_3}} = 1$$

A plot of the conductivity versus chlorine pressure is therefore expected to exhibit peaks. The maximum points should occur at chlorine pressures corresponding to $\frac{a_{\text{TiCl}_2}}{a_{\text{TiCl}_3}} = 1$, $\frac{a_{\text{TiCl}_3}}{a_{\text{TiCl}_4}} = 1$

These partial pressures are given by

$$P_{\text{Cl}_2} = \frac{1}{K_2} \quad \text{and} \quad P_{\text{Cl}_2}^* = \frac{1}{K_3}$$

as can be easily seen by combining equations (4), (7) and (8) and using the relations:

$$\frac{a_{\text{TiCl}_3}}{a_{\text{TiCl}_2}} = 1 \quad \text{and} \quad \frac{a_{\text{TiCl}_4}}{a_{\text{TiCl}_3}} = 1$$

C. The Free Energy of Formation of UO_2

The dual-temperature stainless steel apparatus and galvanic cell arrangement for the determination of $\Delta G_{\text{UO}_2}^\circ$ has been constructed, and a schematic diagram of it is attached. Preliminary experiments with this cell are being conducted by D. Shores. As noted in the previous annual report, successful measurements should yield an accurate determination of $\Delta G_{\text{UO}_2}^\circ$ as well as t_{ion} as a function of oxygen pressure for a commercially prepared $\text{ThO}_2\text{-Y}_2\text{O}_3$ electrolyte in a mixed (electronic) conduction range. In addition, the same stainless steel apparatus when used with a

commercially prepared $\text{ZrO}_2\text{-CaO}$ electrolyte will allow a convenient measurement of t_{ion} in a mixed (electronic) conduction range which could be compared with the two or three other measurements that have been reported in the literature.