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Assessment of Uncertainties in Measurement of pH in Hostile Environments Characteristic of Nuclear Repositories

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Prepared for
U.S. Nuclear Regulatory Commission

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Assessment of Uncertainties in Measurement of pH in Hostile Environments Characteristic of Nuclear Repositories

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ABSTRACT

This report focuses on evaluation and characteristics of sputtered thin film pH electrodes which can be used to assess the corrosivity of hot (100 °C) aqueous solutions present in nuclear repositories. Sputtered thin films have the advantages of high temperature capability, ruggedness, and low cost.

The iridium oxide films were found to have a linear, 58 mV/pH, response to changes in pH. They had little hysteresis but drifted approximately 0.2 V over a period of two days exposure to pH 2-12 solutions. The films were found to be insensitive to interference from most ions such as alkali ions but had redox sensitivity to ferri-/ferrocyanide ions. Although special surface treatments were needed for the films for good adherence at 200 °C the films were not degraded after 20 hours exposure at pH 4, 7, and 10 at 200 °C. Ruthenium oxide sputtered films performed equally well to the iridium oxide films in parallel tests.

The report also contains information on electrochemistry and testing of thin film electrodes and the characterization of the thin films by x-ray photoemission spectroscopy, ultraviolet photoemission spectroscopy, and ion scattering spectroscopy.

CONTENTS

	Page
Executive Summary.....	1
I. Introduction.....	4
A. Background.....	4
B. Outline.....	5
C. Fabrication Development of the SIROF.....	5
II. Electrochemistry and Testing of Sputtered Iridium Oxide Films.....	10
A. Introduction.....	10
B. Theoretical Models of the Oxide-Liquid Interfaces....	12
1. The Electrical Double Layer.....	12
2. Modification of Double Layer Model.....	15
C. Electrochemistry of IrO ₂ Films.....	17
1. Formation and Properties of Anodic IrO ₂ Films....	17
2. Electrochemical Behavior.....	19
D. Methodology of pH Testing of Sputtered Iridium Oxide Films (SIROF).....	21
1. Ionic Sensor Principles.....	21
2. pH and its Measurements.....	22
3. Testing to Insure Suitability for Geochemical Metrology.....	23
4. AC Impedance Measurements of SIROF Electro-Solution Interface.....	24
E. Summary.....	26
F. Applications to Regulations.....	31
G. References.....	34
III. Evaluation and Characterization of Sputtered Iridium Oxide pH Electrodes.....	38
A. Introduction.....	38
B. Experimental Section.....	39
C. Results and Discussion.....	39
1. Iridium Oxide Potential-pH Response.....	39
2. Model IrO ₂ Sensor Surfaces.....	48

D.	Conclusion.....	53
E.	References.....	54
IV.	Stability of Iridium Oxide Films in High Temperature, 200-250 °C, Solutions.....	55
A.	Abstract.....	55
B.	Introduction.....	55
C.	Experimental.....	55
D.	Results.....	56
E.	Conclusions.....	61
F.	References.....	66
V.	Sputtered Thin Film pH Electrodes of Platinum, Palladium, Ruthenium, and Iridium Oxides.....	67
A.	Introduction.....	67
B.	Experimental.....	68
C.	Results.....	68
1.	Platinum Oxide.....	68
2.	Palladium Oxide.....	71
3.	Ruthenium Oxide.....	75
4.	Iridium Oxide.....	75
D.	Thin Film Surface Analysis.....	78
E.	Conclusions.....	83
F.	References.....	84
VI.	Conclusions.....	85
VII.	Recommendations for Future Projects	87
A.	Iridium Oxide pH Sensing Microelectrodes.....	87
B.	Reference Microelectrodes.....	87
C.	Ruthenium Oxide (RuO ₂) pH Sensors.....	87
D.	Further Refinement of Iridium Oxide pH Sensors.....	88

List of Figures

Page

CHAPTER II

- Fig. 1. Complex plane impedance data for SIROF electrodes after exposure to a pH 4 buffer solution at 22 °C.....28
- Fig. 2. Complex plane impedance data for SIROF electrodes after exposure to a pH 7 buffer solution at 22 °C.....29
- Fig. 3. Complex plane impedance data for SIROF electrodes after exposure to a pH 10 buffer solution at 22 °C.....30

CHAPTER III

- Fig. 1. Potential-pH response curves of a sputter deposited iridium oxide film electrode in a buffer solution generated by increasing pH (o) and decreasing pH ().....40
- Fig. 2. Potential transients of three identically prepared sputter-deposited iridium oxide film electrodes in a pH 2 buffer solution.....42
- Fig. 3. Potential-pH response curves of a sputter deposited iridium oxide film electrode (sample 69A6) in buffer solution at temperatures of 3, 15, 25, 40, 50, 55, and 72 C.....43
- Fig. 4. E_{int} (extrapolated potential at pH = 0) determined from potential pH response curves as a function of temperature for samples 69A6, 69A7, and 69A8.....45
- Fig. 5. Potential-pH response slopes of samples 69A6, 69A7, and 69A8 as a function of temperature.....46
- Fig. 6. Titration of 0.1M H_3PO_4 with 0.1M NaOH as monitored by a calibrated sputter deposited iridium oxide film electrode.....47
- Fig. 7. Potential-pH response curves of a sputter deposited iridium oxide film electrode in a pure buffer solution and buffer solutions containing $10^{-6}M$, $10^{-5}M$, and $10^{-4}M$ $Fe(CN)_6^{-3/-4}$49
- Fig. 8. 0 1s XPS spectra of a sputter deposited iridium oxide film that was 2 KeV Ar^+ bombarded and annealed at 900 K in 1.3×10^4 Pa O_2 before and after H_2O plasma treatment.....51
- Fig. 9. ISS spectra of an iridium oxide film following sequential: a) 2 KeV Ar^+ bombardment b) annealing at 900 K in 1.3×10^4 Pa O_2 , and c) H_2O plasma treatment.....52

CHAPTER IV

Page

Fig. 1.	Electrode potential versus pH for SIROF after 1400 hr in deionized water. Open squares are for increasing pH.....	58
Fig. 2.	Electrode potential versus pH for SIROF after 20 hr at 200 °C (15.5 bar) pH 4, plus 20 hrs at pH 7, plus 20 hrs at pH 10. Open squares are for increasing pH.....	59
Fig. 3.	Electrode potential vs pH for SIROF after 20 hrs at pH 10, 240 °C (40 bar).....	62
Fig. 4.	Electrode potential vs pH for SIROF before (a) and after (b) 20 hrs at 250 °C in 3x J13 water.....	63
Fig. 5.	Electrode potential vs pH for crystalline SIROF (deposited at 240 °C) after 20 hrs pH 4, 7 at 200 °C (15.5 bar).....	64

CHAPTER V

Fig. 1.	X-ray diffraction pattern of platinum oxide films as sputtered (below) and after anneal at 420 °C in air.....	70
Fig. 2.	X-ray diffraction patterns of palladium oxide films as sputtered (below) and after anneal at 420 °C in air.....	72
Fig. 3.	pH response of palladium oxide sputtered films: initial response and after 20 hours at pH 10.....	73
Fig. 4.	X-ray diffraction patterns of ruthenium oxide films as sputtered (below) and after anneal at 420 °C in air.....	76
Fig. 5.	pH response of ruthenium oxide film as sputtered and after 20 hours at pH 2.....	77
Fig. 6.	pH response of iridium oxide film as sputtered and after 24 hours at pH 2.....	79
Fig. 7.	Wide scan XPS spectra acquired from sputter deposited RuO _x , PdO _x , PtO _x thinfilms.....	80
Fig. 8.	High resolution XPS spectrum of the Ru 3d region obtained from a sputter deposited RuO _x film.....	82
Fig. 9.	High resolution XPS spectrum of the Pd 3d region obtained from a sputter deposited PdO _x film.....	83
Fig. 10.	High resolution XPS spectrum of the Pt 4f region obtained from a sputter deposited PtO _x film.....	84

Fig. 11. XPS valence band spectra acquired from sputter deposited RuO_x , PtO_x , and PdO_x thin films.....	85
Fig. 12. High resolution spectra of the O 1s region obtained from sputter deposited RuO_x , PtO_x , and PdO_x thin film.....	86

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Executive Summary

This report focusses on evaluation and characterization of sputtered thin film pH electrodes which can be used to assess the corrosivity of hot (greater than 100 °C) aqueous solutions present in nuclear repositories. A more complete statement of the goals and objectives is presented in the first chapter INTRODUCTION. Sputtered thin film electrodes have the advantages of high temperature capability, ruggedness, and low cost and the chosen material iridium oxide had already demonstrated pH measurements at 150 °C. Our goals included evaluation of the sputtered iridium oxide films up to 250 °C and evaluation of their usefulness and stability. In the course of the project we found it necessary to investigate fabrication parameters to improve the film stability and substrate adherence and to investigate the causes of instability in the films as well as the evaluation of the sensor material under a variety of conditions representative of the nuclear waste repository.

ELECTROCHEMISTRY AND TESTING OF SPUTTERED IRIIDIUM OXIDE FILMS

This report contains a literature review for electrochemical evaluation of solid state pH sensors. The requirements of pH electrode for geochemical fluids in a nuclear waste repository site are rather difficult to fulfill, that is, the electrode must have stability at temperatures up to 250 °C, low ionic and redox interferences, corrosion resistance, and robustness. Among the potential electrode materials, the IrO₂ emerges as the most promising because of its consistent near Nernstian response and its electrochemical behavior at the IrO₂-solution interface is essential in order to optimize the performance of IrO₂ electrodes for pH sensing at high temperatures and pressures. This report reviews theoretical models of the oxide-solution interfaces based on the theory of the electric double layer. Electrochemistry of IrO₂ films with emphasis on the properties of anodic films is summarized. A plan for pH testing of sputtered iridium oxide films (SIROF) for geochemical measurements at a Tuff Repository is described.

EVALUATION AND CHARACTERIZATION OF SPUTTERED IRIIDIUM OXIDE pH ELECTRODES

The suitability of thin film iridium oxide (IrO₂) as a pH sensing material has been examined. The iridium oxide thin films (~7500 Å) were deposited on aluminum oxide and single crystal silicon substrates by d.c. magnetron reactive sputter deposition. The potential of the iridium oxide thin film electrodes was measured against a Ag/AgCl reference electrode while the pH of a buffer solution was varied from 2 to 12 by drop-wise addition of concentrated acid or base. A calibrated glass electrode was used to measure the buffer pH. The iridium oxide thin film electrodes exhibited very predictable, linear, near Nernstian (~55 to 60 mV/unit pH) potential-pH responses between 0 and 75 °C with essentially no hysteresis upon cycling between low and high pH. Substantial variations in the calculated standard potential (E°) with electrode history were observed. Freshly deposited thin film electrodes exhibited E° values of approximately 0.8 V (vs Ag/AgCl). When the electrodes were immersed in a pH 2, 7, or 10 buffer the E° values decreased by approximately 0.2 V over a period of several days. The potential drift problem is not fully understood; however, a slow hydroxylation reaction occurring on the electrode surface may be responsible for the observed potential instability. Although the potential drift of the sensor makes it

unsuitable for long term applications, frequent calibration (0 to 4 hours) allows the iridium oxide electrode to measure pH to ± 0.1 pH units. A calibrated iridium oxide electrode generated a titration curve almost identical to that of a glass electrode when monitoring the titration of phosphoric acid with sodium hydroxide.

Other criteria used to evaluate the iridium oxide films as pH sensors were sensitivity to ionic and redox interferences, and response time. The response time of the iridium oxide electrode to both small (0-1) and large (>2) changes in solution pH was comparable to that of the glass electrode. The iridium oxide films showed very little sensitivity (<2 mV change) to the alkali metal cations of Li^+ , Na^+ , and K^+ up to concentrations of 0.1 M over a pH range of 3 to 12. Also, little (<10 mV) response to the divalent cations of Mg^{2+} , Ca^{2+} , Cu^{2+} , and Ni^{2+} at concentrations up to 0.01 M was measured. The iridium oxide films exhibited a strong redox sensitivity to solutions containing iodide (I^-) and ferri-/ferrocyanide [$\text{Fe}(\text{CN})_6^{3-/4-}$].

To elucidate the fundamental mechanism of iridium oxide pH sensing, model IrO_2 sensor surfaces were prepared in ultrahigh vacuum (UHV) and examined with the surface sensitive techniques of X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and ion scattering spectroscopy (ISS). Clean IrO_2 -like surfaces could be prepared by ion bombardment and annealing in oxygen. It was found that the IrO_2 -like surfaces prepared by this method were inert to gas phase water. This is somewhat surprising considering that surface hydroxylation reactions are thought to occur readily on iridium oxide. It was found that adsorption of water on the IrO_2 -like surface could be activated by radio frequency excitation.

STABILITY OF IRIIDIUM OXIDE FILMS IN HIGH TEMPERATURE, 200-250 °, SOLUTIONS

Iridium oxide films have been investigated as pH sensing electrodes. They have a Nernstian response, of approximately 58 mV per pH unit at room temperature, under a wide range of solution conditions. The advantages of these solid state electrodes include their ruggedness, small size, high voltage/low impedance output, and the low cost of fabrication. They also have high temperature capability and have been considered for geothermal sensing applications.

This study investigated the stability of reactively sputtered iridium oxide films on alumina substrates on exposure to pH 4, 7, 10 and in concentrated J13 solutions at 200 °C (15 bar) and 250 °C (40 bar). The exposures were made in a teflon lined bomb. The results of over 50 tests, cycling pH between 2 to 10 before and after exposure, are discussed. Changes of E° , the formal potential, and the slope were most severe under acidic conditions at 250 °C. The most severe conditions also caused film breakdown and loss of adhesion to the substrate. The incorporation of ion assisted deposition in the fabrication of the films lead to improved adherence under the most severe conditions of the exposure. The results indicated similar behavior with films deposited at 500 K (crystalline) and those deposited at room temperature (amorphous).

SPUTTERED THIN FILM pH ELECTRODES OF PLATINUM, PALLADIUM, RUTHENIUM, AND IRIIDIUM OXIDES

Thin films of platinum, ruthenium, and palladium oxides were reactively sputtered and compared with sputtered iridium oxide films. X-ray analysis confirmed the rutile structure of RuO_2 and the monoclinic PdO structures. The PtO_x structure appeared amorphous until an air anneal at 420°C generated a fine grained PtO_2 structure. Electrical conductivity of the films corresponded to expected results for those structures with RuO_2 having resistivities in the 200-400 $\mu\text{ohm cm}$.

The pH response of the films indicated that neither PtO_x or PdO would be stable enough for use for the NRC intended applications. However, RuO_2 performed very well, in fact, in our tests it out performed the SIROF and should be considered a candidate for high temperature pH measurements.

The surface chemical state of the as-deposited PtO_x , RuO_x , and PdO_x films was investigated using XPS. The results can be compared to our previous reports on thin film IrO_x pH sensors. The XPS binding energy of the $\text{Pd } 3d_{5/2}$ line and valence band lineshape obtained from the PdO_x film indicate that the surface stoichiometry is predominately PdO . The XPS binding energy of the $\text{Ru } 3d_{5/2}$ line and valence band lineshape obtained from the RuO_x film indicate that the surface stoichiometry is predominately RuO_2 . Valence band and $\text{Pt } 4f$ data from the PtO_x film are more complex and suggest that the surface regions contains Pt in at least two different oxidation states. In addition it is likely that all the films are hydrated to some extent at the surface.

I. INTRODUCTION

This report relates to the Interagency Agreement No. 87-08 "Assessment of Metrological Uncertainties for Waste Package Testing". Previous reports under this agreement have included quarterly progress reports and the NRC reports NUREG/CR-5166 "Electrochemical Evaluation of Solid State pH Sensors for Nuclear Waste Containment" and NUREG/CR-5484 "pH Sensors Based on Iridium Oxide". This final report is intended to be complete and includes all of the findings of the project.

A. Background

High-level nuclear waste overpacks in the proposed repository in tuff will be (over the lifetime of the repository) in contact with air/steam/water over a range of elevated temperatures. DoE's conclusions as to overpack performance will be based in part on their assessment of local conditions, and this assessment will in turn be based on measurements of the chemical and the electrochemical properties of the fluids (liquid and/or vapor) surrounding the waste package. Hence, specific regulatory issues relevant to waste that need to be addressed are the precision and accuracy of the techniques used to measure these properties (e.g. pH and Eh (redox potential) or a similar measurement of redox potential under very severe experimental conditions).

The characterization of the geochemical environment of the laboratory experiments is important to ensure that the laboratory results do, in fact, reproduce what was observed and/or will be expected in the natural systems. Eh and pH are the two important parameters affecting the degradation of the waste packages. The use of geochemical models such as EQ3/EQ6 requires input values for Eh and pH, making these measurements critical to the satisfactory use of codes based on these models.

The most common method of measuring pH and Eh is the use of a probe with consists of an electrode at which some electrochemical reaction can take place. The electrochemical potential in the electrolyte being measured is compared to that of another electrode in some known state.

There are, however, a number of areas of uncertainty associated with the use of common electrodes. These include:

- (1) errors in measurement at elevated temperatures
- (2) errors in measurement at elevated ionic strengths
- (3) the instability of electrode measurements (e.g. drifting)
- (4) the long-term stability of the electrodes themselves (i.e. degradations)
- (5) the response of different probes in different environments
- (6) instrument sensitivity and accuracy

The purpose of this experimental research program is to develop the NRC's ability to judge the metrologic uncertainties inherent in determinations of the chemistry of the waste package environment in tuff and especially the determinations of pH and Eh.

The primary goal of this project is to provide improved technology for the fabrication of pH sensing electrodes to more accurately characterize the electrochemical properties of the fluids surrounding nuclear waste packages in the repository. Specifically, the measurement of the pH of the fluids is of prime concern. A probe has been selected which includes an electrode for measuring pH to characterize the electrochemical activity of the fluid surrounding the containment. The approach selected has been to focus on the IrO₂ thin film electrode for electrochemical measurements. IrO₂ has indicated promise of stability at the harsh, high temperature conditions of the repository and in the harsher conditions present in corrosion testing. Other advantages of the IrO₂ films include the rugged nature of the electrode, ease of miniaturization, high voltage/low impedance output, and low cost of fabrication. A review of the suitability for candidate materials for this purpose was prepared for the Office of Research, Nuclear Regulatory Commission: NBSIR 85-3237 "Review of Materials for pH Sensing for Nuclear Waste Containment" September 1985.

B. Outline

This report is divided into six sections which are relatively independent. The sections represent phases of the research project and are presented in somewhat independent fashion for clarity. The INTRODUCTION includes the purpose, goal, and objectives followed by this outline and technical discussion about the fabrication optimization of the probe. The second part, "ELECTROCHEMISTRY AND TESTING OF SPUTTERED IRIIDIUM OXIDE FILMS", includes theoretical models of the sensor-solution interface, a review of the electrochemistry of IrO₂ films, a discussion of pH testing of the films, and the results of an investigation of the a.c. response of the IrO₂ films.

The third section, "EVALUATION AND CHARACTERIZATION OF IRIIDIUM OXIDE FILMS", contains a summary of our findings on the response and characteristics of the sputtered iridium oxide films which the results of the surface analysis studies used to uncover the mechanisms of the behavior of the films. The fourth section, "STABILITY OF IRIIDIUM OXIDE FILMS IN HIGH TEMPERATURE, 200-250 °C SOLUTIONS", reports the results of the testing at high pressures and high temperatures (200-250 °C) in acid, base, and concentrated synthetic "tuff" water (J13). This investigation of the stability of the sensor at the high temperatures helps to establish the limits of performance of the measurement system and describes the iridium oxide sensor performance under conditions too harsh for applications of glass electrodes.

Section five, "SPUTTERED THIN FILM pH ELECTRODES OF PLATINUM, PALLADIUM, RUTHENIUM AND IRIIDIUM OXIDES", pertains to studies made of alternate sputtered thin film electrodes. The ruthenium oxide electrode gave the most promising results. Finally, an executive summary is included as section six.

C. Fabrication Development of the SIROF

The advantages of sputtered iridium oxide films (SIROF) as stable electrodes have been reported by Hackwood et al. (1), Katsube et al. (2), and Lauks et al. (3). Although early applications related to charge injection electrodes, the chemical stability of the SIROF led to its application pH measurement under hostile chemical conditions. The chemical stability of iridium

oxide in hot acid and base solutions was a primary reason for its choice in this project (4). Early results at NIST, however, indicated that electrode potential drift in acid and base solutions (5) was the limiting factor in its use. A continuing effort was made to optimize the fabrication parameters to minimize that problem.

In addition to the drift problem, there is a problem in physical stability of a film/substrate sensor assembly in caustic or acid solutions at 40 bar and 250 °C. This problem was encountered in the form of film loss of the substrate and it was recognized that only a limited number of substrate materials was useful. A solution to the physical stability problem was pursued by careful materials selection of the substrate, Al_2O_3 , and enhancing the film adhesion using techniques developed at NIST.

Previous studies of sputtered iridium oxide films (5,6) established the maximum deposition rates of iridium at specific partial oxygen pressures that insured a metal free oxide. Crystalline iridium oxide has been confirmed only in the IrO_2 rutile form. In addition, we had found that although the rutile form was clearly evident in x-rays with deposits formed at substrate temperatures of 100 °C and above an amorphous structure could be formed at room temperature. In a study by Hackwood et al. (1) this amorphous structure was related to the presence of hydrogen or hydration by and affected the electrochemical behavior of the film. Their studies related the change in crystal structure on heating (amorphous to crystalline) to H_2O evolution by differential thermal analysis (DTA) and evolved gas analysis (EGA). Our work to confirm these structural aspects is reported in section III.

We believe that the source of the water in the reactively sputtered films is the residual gas in the deposition chamber or through additions of H_2O to the sputter gas. The incorporation of H_2O or OH^- in the film during deposition should exhibit a strong dependence on the sputter rate, partial pressure of H_2O , and the sticking coefficient of H_2O (or plasma species such as OH and OH^-) on the growing oxide film. Note that for a sticking coefficient of unity, a sputtering rate of 2 Å per second, and a background H_2O pressure of 10^{-6} torr, one H_2O molecule would impact the film for each Ir atom. Although the qualitative arguments can be made convincingly, it is still not clear exactly how much H_2O is incorporated in the film, or exactly how this affects the electrochemical properties since an accurate measurement of the H_2O content cannot be made. It is also apparent from our surface analysis reported below that the sticking coefficient of H_2O is far from unity, if significant at all. It is possible, however, that incorporation of hydrogen, originates from much more reactive species such as OH , H , or ions. Whatever the source, it is logical that higher H_2O partial pressures, lower substrate temperatures, and lower deposition rates would lead to more hydrogen in the deposit.

We reported earlier (6) that the H_2O could be incorporated by the films during steam or water immersion, thereby lowering the potential of the films versus a Ag/Ag Cl electrode. As we reported in NUREG/CR 5484, the sputtered iridium oxide sensors we have been preparing have a drift of -0.2 V of E° during the first few days of immersion in buffer solutions at pH 4, 7, and 10. Because there are indications in our previous work, and others, that this might relate to the water content of the films, we have attempted to prepare films under

conditions more likely to produce the incorporation of H_2O . This can be accomplished in two ways: either increase the H_2O content of the sputtering gas or decrease the deposition rate of the film. The films produced and tested earlier were deposited at approximately $2\text{ \AA}/\text{sec}$ or 1.5 sec per monolayer using partial pressures of (0.15 Pa) 1 mTorr of oxygen (O_2) and $(1.5 \times 10^{-4}\text{ Pa})$ $1 \times 10^{-6}\text{ Torr}$ of H_2O . This combination leads to a primarily anhydrous IrO_2 deposit. The rutile (anhydrous) deposit is well confirmed by x-ray diffraction for coatings deposited at 100°C or higher substrate temperatures. Two conditions were investigated: lowering the deposition rate by a factor of five to $0.1\text{ \AA}/\text{sec}$ and increasing the partial pressure of H_2O to approximately $(3 \times 10^{-3}\text{ Pa})$ $2 \times 10^{-5}\text{ Torr}$ by saturating the argon with H_2O vapor using a bubbler. This should effectively increase the H_2O content of the sputtering atmosphere by a factor of twenty. At this H_2O partial pressure there should be more than one H_2O molecule impacting the growing film for each iridium atom deposited and the incorporation of hydrogen in the film should be promoted. To accomplish these growth rates, the RF power on the 50 mm target was decreased to 15 watts and the target to substrate distance was increased to 12 cm . A deposition time of 130 minutes led to a thickness of $0.3\text{ }\mu\text{m}$ for both deposits (with and without the bubbler).

The results of testing these electrodes is presented in Table 1. Each of the 24 test results was obtained, as previously reported, by measuring the electrochemical potential versus a $Ag/AgCl$ reference electrode at the low pH (2-3) buffered solution followed by a stepwise addition of KOH up to a pH 11 and a stepwise addition of HNO_3 to return to the pH 2-3. Thus the linearity and hysteresis of each electrode could be checked after immersion in both the long term (2-50 hr) exposure to pH 3 and 2-4 hr exposure to pH 10. The sample with the highest H_2O exposure (Ar bubbled through H_2O) is I59-1 and it remained very stable throughout the acid exposure. At a pH of 10, however, a drop of 0.2 V in E° and 10% decrease in slope indicated drift similar to the earlier results with the $2\text{ \AA}/\text{sec}$ "dry" gases which have been reported. I58-2 and I58-1 which had a 24 hr soak in H_2O after deposition were made at the slow deposition rate but with no added H_2O to the sputter gases yielded results indicating more drift.

Table I
Stability of SIROF
Deposited at $0.4\text{ \AA}/\text{sec}$

<u>hr</u> <u>pH</u>		0	<u>$\frac{2}{3}$</u>	<u>$\frac{10}{3}$</u>	<u>$\frac{50}{3}$</u>	<u>$\frac{2}{10}$</u>	<u>$\frac{16}{10}$</u>	<u>$\frac{24}{10}$</u>	<u>$\frac{40}{10}$</u>
I58-1	y	<u>57.6</u>	<u>56.5</u>	<u>56.9</u>	<u>55.1</u>	<u>56.5</u>	<u>50.7</u>	<u>48.1</u>	<u>38.4</u>
(H_2O soak)	E°	1041	1029	1004	995	960	866	835	758
I58-2	y	<u>57.6</u>	<u>56.5</u>	<u>56.9</u>	<u>51.8</u>	<u>54.0</u>	<u>41.1</u>	<u>36.9</u>	<u>26.8</u>
	E°	1060	1040	901	664	680	622	604	567
I59-1	y	<u>57.7</u>	<u>56.7</u>	<u>57.0</u>	<u>55.7</u>	<u>56.1</u>	<u>52.2</u>	<u>50.0</u>	<u>49.4</u>
(H_2O)	E°	1022	985	985	976	976	906	901	800

y = mV/pH

E° = mV

The second problem of the iridium oxide film sensors relates to their physical durability. Early tests at high temperature had uncovered an adhesion problem of the film to the alumina substrate. The alumina substrates were electronic circuit boards of the highest quality 99.9% Al_2O_3 finished to a 3 μm or 0.1 μm surface which yielded better results than silicon wafers, glass slides, or polyimide films for adhesion and durability.

These results prompted a more systematic consideration of film durability and adhesion. First, a film adhesion test was added which included an epoxy bonded pull tab. This test directly measures film adhesion up to (70 MPa) 10,000 psi. In addition, a 4 point probe electrical resistivity test was added to evaluate chemical or physical film damage. Finally, a pH titration test before and after high temperature exposure was performed. Because we were experiencing film adhesion problems, especially in the pH 4 solution at 200 °C several film adhesion enhancement approaches were tried. Standard cleaning of both Al_2O_3 and Si substrates had included an acetone and rinse followed by an HF etch and water rinse to remove contaminants and activate the surface for the sputtered iridium and reacted oxygen.

Adhesion enhancement techniques have been used previously at NIST to improve adhesion to oxide substrates. The first technique adds a three minute exposure to 180 nm ultraviolet (UV) radiation which generates considerable ozone. This technique is especially useful in removing hydrocarbons and water. The second technique is to ion beam sputter the substrate immediately before and during the first few minutes of IrO_2 deposition. This technique is used commercially to assist in the adherence of Ti_3N_4 layers to steel in cutting tools. The third technique tried is to form an ultrathin 3-5 nm thick bonding layer between the oxide and the sputtered layer. This process is the subject of a patent application from this laboratory arising from work in another project. The most successful bonding layer was found to be Cr - Cr_xO_y . A thin layer of chromium is applied after gettering the chamber with Cr vapor, then Ir and Cr are applied simultaneously; then oxygen is introduced to react with the metallic films and the oxygen deficient substrate. The final Cr content of the film is less than 0.3% of the Ir and buried between the substrate and the IrO_2 . A question of raw edges (fractured after deposition) might be raised especially since these locations were the sites of the film adhesion problem with earlier samples.

Film adhesion tests of the IrO_2 (sample I50) after high temperature exposure indicated adhesion strengths of (4-8 MPa) 700-1500 psi after 20 hr at 200 °C and pH of 10, and (1-15 MPa) 400-2800 psi after 20 hr at 200 °C and pH 7. Similarly poor adhesion 2-15 MPa was measured after 20 hr at 200 °C and pH 4. These tests were performed on samples deposited after standard cleaning procedures.

The results of tests performed on the films deposited with the enhanced adhesion techniques are presented in Table I. Both the ion beam assisted deposition and the Cr-Bond approaches exhibited good film adhesion after 240 °C exposure. The films fell off the other two sensors as indicated in the table. The adhesion tests do not work well on the 0.04 in. thick Si wafers because the wafers shatter if the film is adherent (>10 MPa). However, the films fell off the Si after 240 °C at pH 4 for 20 hr with the standard surface preparation and

with the Cr-bond on the Si.

Table II
Enhanced Adhesion of IrO_2 to Al_2O_3

	Surface Preparation	Film Adhesion (MPa)	After 240 °C pH 4 (MPa)
I50	STD (HF)		
I52	UV Ozone	>70	0
I53	Ion Beam	>70	70
I54	Cr Bond	>70	50

Electrical resistivity tests indicated slight increases in resistivity in the I50 series films: 10% after 20 hr-200 °C-pH 7, 2% at pH 10, and 6% at pH 4. These data indicate the primary adhesion problem must be at the interface since the film integrity is virtually unaffected and little film thickness loss (if any) is observed. The resistivities of the films I53 and I54, which still had good adherence after 20 hr at 240 °C and pH 4 were significantly increased. I53 (0.5 μm) of IrO_2 (with ion beam surface preparation) had a resistance more than 10 times as great and I54 (0.6 μm of IrO_2 with Cr bond) had a resistance more than twice as great. Observation at 500x in the light microscope indicated some new porosity in the exposed films. It may be inferred that exposure at 240 °C and a pH of 4 is too severe a corrosion medium for these films. It may be necessary to define those limits carefully.

II. ELECTROCHEMISTRY AND TESTING OF SPUTTERED IRIIDIUM OXIDE FILMS

A. Introduction

The National Institute of Standards and Technology (NIST) has reviewed technical reports on the high level waste package for nuclear waste storage. The Department of Energy (DOE) waste package test data have been evaluated and compiled by the NIST for the Nuclear Regulatory Commission (NRC) (1). It is clear from these reports that pH is one of the most important parameters affecting the degradation of the waste packages. Accurate and reliable pH measurement is critical to the satisfactory use of a geochemical code to model the path of reaction between nuclear waste materials, alteration products, and various aqueous solutions. The information obtained for the reaction of nuclear waste materials with aqueous solutions is essential for understanding and predicting the behavior of these materials under repository conditions. The NIST has also reviewed the performance of a number of elevated temperature pH sensing technologies for the NRC (2). Measurement of pH in a geologic repository requires the use of pH sensor in high pressure and elevated temperature corrosive brines. Recent work of Hodges and Pederson (3) at Pacific Northwest Laboratory (PNL) indicated the chemical composition of brines interacting with a high-level nuclear waste package in salt can affect brine pH produced at high temperatures. However, the hydrogen ion activity of the brine is difficult to measure directly, especially at high temperatures and pressures. The hydrogen ion activity is related to the hydrogen ion concentration through the activity coefficient, the value of which depends on the temperature, the pressure and the composition of the solution of interest. The value of the hydrogen ion activity, therefore the pH, can be determined by the direct measurement of the hydrogen ion concentration in brines, provided the activity coefficient is known.

The instability of the conventional reference electrodes such as calomel or silver/silver chloride electrode is also a problem when measuring pH at temperatures above 100 °C. The contamination of the internal reference solution is also a problem if the back pressure becomes greater than the internal pressure. Danielson reported (4) a flowing type of reference electrode, which may be used at high temperatures and pressures.

In a recent report to the Office of Research, Nuclear Regulatory Commission the National Institute of Standards and Technology (formerly National Bureau of Standards) presented a "Review of Materials for pH Sensing for Nuclear Waste Containment" (2) (NISTIR 85-3237). The review was based on the assumption that higher temperature pH sensors would be needed to evaluate the corrosion potential of containment vessels. The authors described the criteria for pH electrode evaluation, the performance of glass pH electrodes, the developmental program on cubic zirconia electrodes and a summary of research studies of fourteen other exploratory electrode materials. A special emphasis was placed on the most promising of the high temperature electrode materials - IrO_2 .

The criteria for selection of a pH electrode for use at temperatures up to 250 °C were: linear response from pH 1-14, low ionic and redox interference, long term stability, corrosion resistance, and mechanical robustness. The review of the applicability of the glass electrode concluded that although the recent work at the Pacific Northwest Laboratories (PNL) has indicated useful corrosion

resistance in the 150-200 °C range, the glass electrode has serious stability problems above 150 °C. Other problems with the glass electrode relate to its high impedance, SiO_2 hydrolysis at high pH levels, and lack of mechanical robustness.

Yttria stabilized zirconia pH sensors have been studied by Niedrach (5), at General Electric, Tsuruta and Macdonald (6) at SRI, and Danielson at PNL. Generally these $\text{ZrO}_2(\text{Y})$ sensors are linear between pH 3-9 and at temperatures above 150 °C to 300 °C, and exhibit few interference problems if any. The inconvenience of poor room temperature performance, however, complicates the calibration and flexibility of the sensor. The results of research on palladium hydride and numerous metal oxide films for use as pH electrodes are also discussed in the NIST/NRC review including Sb_2O_3 , MoO_2 , MnO_2 , TiO_2 , Ta_2O_5 , ZrO_2 , OsO_2 , PdO , PtO_2 , RhO_2 , RuO_2 , and IrO_2 . Of these, the IrO_2 emerges as the most promising primarily because of its wide range of stability (both pH and T), its low impedance in thin films and its consistent Nernstian-linear response.

The remainder of the review by Dietz and Kreider outlines the research findings in IrO_2 pH sensor studies, the key questions to be answered and a suggested approach for developing the reactively sputtered IrO_2 film as a high temperature, harsh environment sensor.

In order to develop the pH electrode for use at high temperatures and pressures and to understand the interaction between the electrode and the solution, quantitative information about the electrochemical behavior at the oxide-solution interface is essential. One of the fundamental factors determining all electrochemical phenomena occurring at the solid-liquid interfaces is the electric charge and potential distribution in these regions. The simplest model reflecting the real electrical structure of the interface region is the electrical double layer (e.d.l) model. An electrical double layer occurs at all interfaces and its structure depends on the properties of the contacting phases. Knowledge of the structure of the electrical double layer and the charge and potential distribution in the layer is very important because it will greatly influence or determine such pH electrode phenomena as hydrogen ion sensitivity and selectivity, open circuit potentials, electrode stability and others.

Therefore, improved understanding of the electrochemical behavior at the IrO_2 -solution interface is needed to optimize the performance of IrO_2 electrodes for pH sensing at high temperatures and pressures.

Several workers have attempted to quantitatively describe the charge and potential distribution at the oxide-liquid interface using various theoretical models. These models are described in Section B.

Hydrous oxides are of major interest in the areas of technology such as aqueous battery systems, colloid chemistry, electrochromic display systems and pH sensing. Hydrous iridium oxide films are of special interest since iridium oxide has been shown to have good chemical stability in aqueous solutions at temperatures up to 200 °C (7). In Section C of this report, the electrochemical preparation, redox behavior, and some important properties of hydrous iridium oxide films are described.

Section D describes pH testing of sputtered iridium oxide films (SIROF). The general principles of ionic sensing are briefly described, followed by a discussion of pH measurement methods. The scope of testing for geochemical metrology is then described for geochemical measurements.

A summary of this report is presented in Section E.

B. Theoretical Models of the Oxide-Liquid Interfaces

This section reviews theoretical models used to describe the e.d.l for colloidal metal oxide systems. The surface charge and potential of an insoluble metal oxide is determined in large part by the pH of the solution in which it is immersed. For such systems the OH^- and H^+ ions are potential-determining ions as a result of the following reactions

where M represents metal. The presence of hydroxyl groups on metal oxide surfaces has been amply demonstrated by infrared spectroscopy. Theoretical models useful for describing the electrochemical behavior of a colloidal system may not be strictly applicable to iridium oxide, which has a metal-like conductivity. Based on the more recent studies of metal-liquid and semiconductor-liquid interfaces, however, useful information may be obtained to characterize electrochemical properties of iridium oxide-liquid systems within the framework of the theoretical models described in this section.

1. The Electrical Double Layer

In this section, no attempt is made to cover all studies of the oxide-liquid interface. Recent work is reviewed to obtain the important facts that are relevant to the nature of the interface. A considerable amount of work in this area has also been reviewed by Lyklema (8,9), Ahmed (10), Hunter (11), and Parsons (12).

The double layer model is the classical approach to describe the electrical structure of the solid-liquid interface and is usually referred as the Gouy-Chapman-Stern-Grahame (GCSG) model. In this model, the electrical double layer consists of two regions: an outer diffuse region and an inner Helmholtz region. In the outer diffuse region, the ions undergo thermal Brownian motion and are distributed according to the Boltzmann statistics. The inner Helmholtz region has two planes. The inner Helmholtz plane (IHP) is the plane of the centers of adsorbed ions near the solid surface. The outer Helmholtz plan (OHP) is the plane of the centers of hydrated ions near the diffuse region.

The mean electrical potential at any point in the diffuse layer satisfies the well-known Poisson-Boltzmann equation

$$\nabla^2 \phi = -(e/\epsilon\epsilon_0) \sum z_i n_i \exp(-z_i e \phi / kT) \quad (2)$$

where ϕ is the mean potential, n_i is the number of ions of type i per unit volume

in the liquid phase, z_i is their valency with sign, e is the unit of electric charge, ϵ is the dielectric constant of the medium, ϵ_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ Fm}^{-1}$), k is the Boltzmann's constant and T is the absolute temperature. For a flat interface, Eq. (2) is solved with the boundary conditions $\phi = \phi_d$ at $x=0$, where ϕ_d and x are the potential and the coordinate, respectively, at the OHP and $\phi = d\phi/dx = 0$ at $x = \infty$. The solution is given by

$$\phi = (2kT/ze) \ln [1 + \gamma \exp(-\alpha x)] / [1 - \gamma \exp(-\alpha x)] \quad (3)$$

where $\gamma = \exp [(ze\phi_d/kT) - 1] / \exp [(ze\phi_d/kT) + 1]$, and $\alpha = 2z^2e^2n_i / \epsilon\epsilon_0kT)^{1/2} = 3.29 \times 10^9 z(c)^{1/2} \text{ m}^{-1}$ at 298 K, and c is the bulk electrolyte concentration in mol dm^{-3} .

The diffuse layer charge density, σ_d , contained in a cylinder of unit cross-sectional area extending from $x=0$ to $x=\infty$ is given by

$$\begin{aligned} \sigma_d &= -(8n_i\epsilon\epsilon_0kT)^{1/2} \sinh (ze\phi_d/2kT) \\ &= -11.74 (c)^{1/2} \sinh (19.46 z\phi_d) \mu\text{C cm}^{-2} \end{aligned} \quad (4)$$

at 298 K, where ϕ_d is in volts.

The surface charge density of adsorbed ions at IHP is given by the Stern adsorption isotherm

$$\begin{aligned} \sigma_\beta &= \frac{z_+eN_a}{1 + (A_0/n_+M)\exp[(z_+e\phi_\beta + \Phi_+)/kT]} + \\ &\quad \frac{z_-eN_a}{1 + (A_0/n_-M)\exp[(z_-e\phi_\beta + \Phi_-)/kT]} \end{aligned} \quad (5)$$

where $z_\pm$ is the valency of cations or anions with sign, N_a is the number of available adsorption sites, A_0 is Avogadro's number, $n_\pm$ is the bulk concentration of the ionic species in ions/cm^3 , and M is the relative molecular mass of the solvent. $\Phi_\pm$ are specific adsorption potentials that account for non-Coulombic interactions, such as changes in the state of solvation of the adsorbed ions, van der Waals interactions, or hydrogen bonding between the adsorbate and the surface. When these non-Coulombic interactions contribute significantly to the free energy of adsorption of ions, the adsorption is said to be specific (13). A specifically adsorbed ion can therefore adsorb against electrostatic repulsion such that σ_β in Eq. (5) is greater than σ_0 , the surface charge density at the solid surface. This leads to a reversal of the signs of the diffuse layer charge and potential. This possibility is of great importance for the case of adsorption of H^+ or OH^- ions which are chemically bound.

Because of electroneutrality, the charge densities at the surface, the IHP and the OHP are related by

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \quad (6)$$

If the potential drop between each plane is assumed to be linear, the integral capacity per unit area, C_1 , of the zone between the surface and the IHP is given by

$$C_1 = \sigma_o / (\phi_o - \phi_\beta) = \epsilon_1 \epsilon_o / \beta \quad (7)$$

where ϵ_1 and β are the dielectric constant and separation between the surface and the IHP, respectively. The integral capacity per unit area between the IHP and the OHP, C_2 , is given by

$$C_2 = -\sigma_d / (\phi_\beta - \phi_d) = \epsilon_2 \epsilon_o / d \quad (8)$$

where ϵ_2 and d are the dielectric constant and separation between the IHP and the OHP, respectively. Hence the five equations (4) to (8) relate to six variables σ_o , σ_β , σ_d , ϕ_o , ϕ_β , and ϕ_d of the GCSG model of the electrical double layer. Thus, if one of these six variables is known then the others may be computed provided that the values for the parameters N_a , ϕ_z , C_1 , and C_2 are also known.

The total double layer differential capacity, $d\sigma_o/d\phi_o$, can be obtained by combining Eqs. (7) and (8) to give ϕ_o ,

$$\phi_o = \sigma_o / C_1 - \sigma_d / C_2 + \phi_d \quad (9)$$

and then differentiating with respect to σ_o

$$d\phi_o/d\sigma_o = (1/C_1) - (1/C_2)(d\sigma_d/d\sigma_o) + (d\phi_d/d\sigma_o)(d\sigma_d/d\sigma_o) \quad (10)$$

where C_1 and C_2 are assumed to be independent of σ_o . The diffuse layer capacitance, $C_d = -(d\sigma_d/d\phi_d)$, is obtained from Eq. (4) and $(d\sigma_d/d\sigma_o)$ may be expressed in terms of σ_β by using Eq. (6). Therefore the total differential capacitance, C , is given by

$$C^{-1} = d\phi_o/d\sigma_o = (1/C_1) + (1 + d\sigma_\beta/d\sigma_o)(1/C_2 + 1/C_d) \quad (11)$$

Calculated capacitance may then be compared with the experimental differential capacitance.

In the simple GCSG model described above, the surface charge densities are assumed to be uniformly distributed in each plane. The effect of discreteness of charge has been introduced by Levine, Bell and co-workers (14,15) to account

for various phenomena, e.g., adsorption at the mercury-water interface.

Blok and de Bruyn (16) were the first to describe a GCSG-based model for an oxide-liquid interface. They assumed ideal Nernstian behavior for the surface potential and compared calculated σ_0 - ϕ_0 curves for different values of the parameters with their experimental σ_0 -pH curves for ZnO electrolyte solutions. Using the following parameter values: C_1 - C_2 =100 $\mu\text{F cm}^{-2}$ for Eqs. (7) and (8); ϕ_+ = -2kT, ϕ_- = -4kT, and N_s = 10^{15} cm^{-2} for Eq. (5), good agreement between the theoretical and experimental results was obtained.

Later, Levine and Smith extended this basic model to allow for non-Nernstian behavior of the surface potential. They obtained calculated σ_0 -pH, C-pH, and ϕ_0 -pH curves in reasonable agreement with published experimental data. The double layer properties SnO_2 , SiO_2 , and quartz were investigated by Ahmed et al. (17), Tadros et al. (18), and Li et al. (19) through the use of σ -pH curves. The curves were convex for these oxides. In fact, for all oxides studied so far (20-26) including TiO_2 , $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, and MnO_2 , the slope $\partial\sigma_0/\partial\text{pH}$ increases with pH without any indication of reaching a plateau. This phenomenon has been explained by assuming that oxide surfaces are somewhat penetrable for H^+ , OH^- , and counterions (27). The consequence is that σ_0 is not a surface charge but rather a volume charge. Healy et al. (22) have noted that oxides generally exhibit very high charge density values attributed by the charge-determining H^+ or OH^- adsorbed ions.

The GCSG model in general can account for observed interfacial properties provided certain values are assigned for various parameters (e.g., specific adsorption potential, inner layer surface charge density). However, it has been pointed out that it is not at all certain that the parameter values assigned are reasonable (22).

2. Modification of Double Layer Model

In order to explain the phenomena associated with the very high surface charge densities observed at oxide-solution interfaces as mentioned before, various nonclassical models have been proposed. These models include the porous double layer model (27-29), the gel layer (30-32), the transition layer model (33,34), and the site-binding model (35-37).

(a) Porous double layer model (27-29)--This model assumes that the oxide surface is porous to charge-determining ions and counterions. This approach accounts at least qualitatively for the general trends observed in interfacial properties. The surface charge is substantially higher in solutions of certain ions that can penetrate the solid than in solutions of other ions. For example, in 10^{-1}M LiCl at pH 10, on hematite, σ_0 is almost twice as high as in 10^{-1}M KCl , apparently because Li^+ can penetrate into the solid, thereby occupying Fe^{+3} -sites. Penetration distances of less than 1 nm are usually needed to account for the observed high charges (27). The theory indicates that high valence charges require much counterion compensation, therefore the charge remaining in the diffuse double layer part is comparatively small.

(b) Gel layer model (30-32)--This model assumes that there is a homogeneous gel-like layer of definite thickness (2-5 nm) at the interface

containing metal hydroxy groups $M(OH)_n$ into which various ions can adsorb. This model accounts for the high surface charge in terms of ion penetration into subsurface regions of the oxide.

(c) Transition layer model (33,34)--This model combines the basic ideas of porous and hydrolyzed gel-like layer theories for the oxide-solution interface. The essential feature of this model is the existence of a transition layer of atomic dimensions in which an equilibrium between oxide and aqueous ionic species is established.

(d) Site-binding model (35-37)--This model assumes that the adsorbed electrolyte cations and anions are distributed in two ways: first, as interfacial ion pairs formed with oppositely charged surface groups, and second, in a diffuse layer to balance the remaining unneutralized surface charges. Potential-determining ions and counterions are considered to react or bind with the acid-base sites on the oxide surface. This model is generally adequate for accounting for the shapes of σ_0 -pH curves and specific ion effects (38). In this model the high surface charge is rationalized in terms of ion-pair formation between surface ionized groups and counterions. Yates et al. (36) assumed that a porous hydrated oxide surface layer at the interface is penetrated by supporting electrolyte ions.

The site-binding model was recently applied to study the temperature coefficient of the metal oxide-liquid interfacial potential as a function of pH for ion-sensitive field-effect transistors (ISFET's) (39). At electrochemical equilibrium, the electrochemical potentials for a metal oxide-liquid system are given by

$$\begin{aligned} & \mu_{MOH_2}^O + kT \ln v_{MOH_2}^+ + q\phi \\ & = \mu_{MOH}^O + \mu_H^O + kT \ln v_{MOH} + kT \ln a_H^+ \text{ and} \end{aligned} \quad (12)$$

$$\mu_{MOH}^O + kT \ln v_{MOH} + q\phi = \mu_{MO}^O + \mu_H^O + kT \ln v_{MO}^- + kT \ln a_H^+ \quad (13)$$

where M represents metal, μ_x^O is the standard chemical potential for the x's species, v_x is the activity of the x's species at the surface, k is the Boltzmann constant, q is the electronic charge, and ϕ is the potential difference developed at the interface and is given by

$$\phi = q(v_{MOH_2}^+ - v_{MO}^-)/C_H \quad (14)$$

where C_H is the capacitance per unit area across the electrical double layer. Eq. (14) is valid if we neglect space charges in the diffuse layer.

It can be shown that the surface potential, the number of active surface sites, the pH, and the temperature are related by the following equation

$$a_H^+ = (K_1\eta + [K_1^2\eta^2 + 4(1-\eta^2)K_1K_2]^{1/2}) \exp(q\phi/KT)/2(1-\eta) \quad (15)$$

where a_H^+ is the activity of H^+ , K_1 and K_2 are the dissociation constants given by

$$K_1 = \exp[\mu_{MOH_2}^0 - \mu_{MOH}^0 - \mu_H^0]/kT \quad (16)$$

$$K_2 = \exp[\mu_{MOH}^0 - \mu_{MO}^0 - \mu_H^0]/kT \quad (17)$$

and η is given by

$$\eta = \phi C_H / qN_s \quad (18)$$

in which N_s is the density of available active sites per unit area at the metal oxide surface. Eq. (15) was used to determine the temperature characteristics of silicon nitride pH-ISFETs for various pH values. Good agreement was obtained between theory and experiment (39).

The site-binding model has been extended to a two-site theory (40) for explaining the features of the potential-pH response of both silicon nitride and borosilicate glass ISFETs. The theory was used to interpret the behavior of chemically treated gate materials for SiO_2 and Ta_2O_5 ISFETs as pH sensing devices (41).

C. Electrochemistry of IrO_2 Films

1. Formation and Properties of Anodic IrO_2 Films

Burke and Lyons (42) have recently surveyed both the theoretical and the experimental work that have been done on hydrous oxide films on several noble metals including platinum, palladium, gold, iridium, rhodium, and ruthenium. This section is concerned only with the electrochemical formation and redox properties of the hydrous IrO_2 films.

One of the most convenient techniques used to generate hydrous oxides in a form suitable for studying their redox behavior is that of potential cycling (43-45). In this case the potential of the parent metal electrode, which may be noble or non-noble, is cycled repetitively between suitable limits in an aqueous solution of appropriate pH. A sinusoidal, square, or triangular potential wave form may be used for hydrous oxide film growth. The triangular wave is most commonly implemented because cyclic voltammetry can then be used to monitor the growth and redox behavior of the iridium oxide film.

The mechanism of hydrous oxide growth on repetitive cycling is now reasonably well understood, at least at a qualitative level. For most metals, but especially gold, platinum, iridium, and rhodium, extension of oxide growth beyond the monolayer level under conventional galvanostatic or potentiostatic conditions is usually quite slow. Under potential cycling conditions the anodic limit plays quite a crucial role for anodic oxide film formation. The early work

on the initial stages of anodic oxide formation on Ir was described by Belanger et al. (46). Thick oxide films were readily generated on cycling the potential over the normal potential range of 0-1.5 V. It is now generally accepted that cycling the potential of Ir in a wide variety of electrolytes between certain limits induces irreversible formation of a battery-type, porous, hydrous oxide layer (37) whose thickness increases with increasing number of cycles.

On the other hand, the monolayer oxide growth on Ir has been investigated by several researchers. Rand and Woods (44) used a solution of $5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$, in which the hydrous material is soluble, and observed hydrogen peaks on the anodic sweep at 0.09 and 0.25 V, with oxygen adsorption commencing above 0.4 V. Two very broad peaks were observed in the oxygen adsorption region at 0.7 and 1.0 V, respectively. Similar behavior was also reported by Mozota and Conway (47). They assumed that a monolayer of OH species was formed in the region of 1.1-1.2 V, conversion to an IrO monolayer being completed at 1.4 V.

The conditions required to produce a thick hydrous oxide layer on iridium under potential cycling conditions were investigated by Buckley et al. (48) and Conway and Mozota (49). The optimum upper and lower limits in acidic media were found to be 1.60 and 0.01 V, respectively. Oxide growth on cycling was observed with the upper limit just above 1.4 V. Significant penetration of oxygen into the second, or even the third, layer of metal atoms of the bulk lattice is probable. Increasing the upper limits above 1.6 V causes dissolution of oxide species at the interface. Critical values for both upper and lower limits required for oxide growth on cycling are influenced by a range of kinetically and thermodynamically important factors, e.g., sweep rate, solution composition, temperature, degree of oxygen penetration, and oxide stability. Among other factors which affect the hydrous oxide growth reaction are sulfuric acid concentration, pH, the presence of chloride ions and temperature (43,49-51). The presence of chloride ion in solution is assumed to inhibit the formation of an anodic oxide film on a clean iridium surface (43). This effect can be explained in terms of specific adsorption of chloride ions onto the iridium surface in aqueous solution. However, the oxide layer region of the cyclic voltammogram of iridium was unaffected by the addition of chloride (43). The rate of growth of iridium oxide films depends on the type of and concentration of supporting electrolyte. It decreases in the order $0.5 \text{ M H}_2\text{SO}_4 > 1 \text{ M HClO}_4 \gg 0.5 \text{ M Na}_2\text{CO}_3 \gg 0.5 \text{ M NaOH}$ (49). This order follows qualitatively the order of decreasing specific adsorption of the anions and presumably arises from the effects of these ions on the continuing monolayer formation and reduction that takes place on the iridium substrate beneath the growing hydrous oxide film. Cruz et al. has discussed the effect of temperature on the potentiodynamic behavior of iridium in $0.5 \text{ M H}_2\text{SO}_4$. It may be assumed that increasing the temperature modifies the structure and composition (degree of hydration) of the highly hydrated oxide layer formed under continuous potential cycling (51). This modification can then change the physical and electrochemical characteristics of the surface oxide layers on iridium.

Rand and Woods (44) postulated that cycling an iridium electrode in acid resulted in irreversible oxide formation at the metal surface. However, they assumed the material to be a porous form of the anhydrous oxide, IrO_2 , attributing the density value of 11.68 g/cm^3 of the latter to the surface layer. Buckley and Burke (43,48) claimed that the layer formed was a hydrated oxide or

oxyhydroxide, such as $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$. They used a redox transition between the Ir(III) and Ir(IV) states in the surface layer to explain the main charge storage reaction:

Mitchell et al. (52) showed that the film formed on cycling in acid was quite rough and not very adherent based on preliminary electron microscopy work. The grain size was quite small (< 50 nm). It was suggested that the film was amorphous having a hexagonal structure. Gottesfeld and Srinivasan (53) showed that potential cycling resulted in the formation of relatively thick film (250 nm after 15 hours of cycling), which they suggested was a hydrated hydroxide. By combining coulometric with optical data, McIntyre et al. (54) found that the apparent density of the hydrous material was 2.0 g cm^{-3} , i.e., one-sixth of that of an hydrous IrO_2 . They showed, using electron microscopy, that the film was porous, with microvoids on the order of 2.5 nm diameter.

Hackwood et al. (55) carried out a combined thermal and gas evolution analysis of sputtered iridium oxide films and suggested these were probably not as dispersed or hydrated as films produced by cycling. Some water was lost in heating in vacuum at 120°C and it was assumed that an amorphous to crystalline transition occurred at 300°C .

Augustynski et al. (56) studied films produced by potential cycling and it was found that the initial layer was not IrO_2 but the hydrated hydroxide. The water was assumed to be chemisorbed on the surface beneath the $\text{Ir}(\text{OH})_4$ species.

2. Electrochemical Behavior

The electrochemical behavior of acid-grown hydrous iridium oxide films are affected by: (i) the acidity of the hydrated material and the variation of this property with change in the iridium oxidation state (57); and (ii) the difference in electrical conductivity between the reduced and oxidized forms of the surface film (58,59). According to Burke et al. (60), both properties are strongly dependent on the dispersed hydrated nature of the iridium oxide layer. Both oxidized and reduced forms were assumed to be polymeric network structures. There has been considerable controversy in the literature as to whether cations (61-63) or anions (64-67) act as charge balancing ions for maintaining electroneutrality in the film in the course of electron insertion or withdrawal reactions.

The ac impedance measurements by Glarum and Marshall (58), and faradaic experiments by Gottesfeld (68), have shown that the hydrous film in the reduced state, Ir(III), has a low electronic conductivity while in the oxidized state, Ir(IV), it is highly conductive. Gottesfeld has interpreted this behavior in terms of conventional band theory. However, Burke and Whelan (60) have proposed a chemical approach involving electron hopping between neighboring Ir centers for interpretation of this behavior. The high conductivity of the oxidized state was attributed to the presence of Ir(VI) sites that behave as acceptor states in the

predominantly Ir(IV) film. The direct evidence for these Ir(VI) sites was obtained by ESCA investigation of the oxidized state (56).

In sulfuric acid media (69) a shoulder is usually observed at 0.6 V on the cathodic side of the main anodic peak. According to Burke and Whelan (57) it is probably an Ir (III/IV) transition in species containing anions other than OH⁻ within the hydrated material. Conway and Mozota (49) attributed the large currents above the main anodic peak mainly to charging of the rather extensive oxide-solution interface. However, Burke and Whelan (57) assumed that the dispersed, hydrated oxide material scarcely constituted a distinct phase, and postulated that the currents in this region were due to changes in stoichiometry in a mixed valence state, Ir(IV)/Ir(VI). A peak showing a shift of 3/2 (2.303 RT/F) V/pH can be observed (60) above the main anodic peak on transferring an acid grown film to solutions of higher pH. Such a peak was also observed (70) following transfer of a base-grown film to acid.

Although hydrous iridium oxide deposits grown in acid show little change in redox activity on transfer to base, it was demonstrated by Buckley et al. (48) that the film could not be grown on cycling a clean iridium electrode in such a medium (1.0 mol.dm⁻³ NaOH, 0.01 to 1.50 V, 30 VS⁻¹). In a detailed investigation, it was confirmed (70) that hydrous oxide formation was possible in dilute, though not in strong, base. It was also observed that after subjecting the electrode in base to preliminary cathodic pretreatment, which probably involved removal of any residual oxide film, no growth was observed. This result was explained by assuming that local pH changes within the pores of a superficial oxide layer play a crucial role in the conversion of anhydrous to hydrous oxide.

The base-grown films were found to dissolve readily in 1.0 mol.dm⁻³ H₂SO₄ or NaOH and this was attributed to their more amorphous character. On the other hand, the acid-grown films were found to be more crystalline having larger grain sizes and this was used to explain their greater stability in acidic media (70).

Yuen and Lauks (71) showed significantly different cyclic voltammograms for anodically grown and sputtering deposited iridium oxide films. An anodic iridium oxide film had a pH dependent voltammogram. The results of the voltammogram and the derived density-of-states at the Fermi level for the case of a sputtered iridium oxide film (SIROF), however, are independent of pH. It was suggested that the SIROF had a more disordered structure in acidic and alkaline electrolytes.

Reactively sputtered iridium oxide films were shown to have good chemical stability against corrosive environments even at high pressures and temperatures. An extensive series of open circuit potential measurements on d.c. reactively sputtered iridium oxide films was performed for the pH range of 3 to 10. The testing showed promising results for sputtered iridium oxide films as pH probes (7). An IrO₂ electrode was used by Fog and Buck (72) as a pH sensor and showed near-Nernstian behavior in the pH range of 2 to 12. Unfortunately, IrO₂ as a pH sensor material is subject to instability, ionic interference, and hysteresis effects (7,72). The instability was attributed to a change in the physical and electrochemical properties of the oxide with time (73). Kreider et al. also observed a shift of open circuit potential with air baking and autoclave heating

at high temperature and pressure (4.74).

D. Methodology of pH Testing of Sputtered Iridium Oxide Films (SIROF)

1. Ionic Sensor Principles

Described here is a conventional electrochemical electrode for sensing of ions. The other new chemically sensitive electronic devices can be found in reference (75). A solid membrane separating two liquids of different ionic content can develop an electrical potential difference across it. This phenomena can be expressed by the Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_1}{a_2} \quad (20)$$

where E = voltage

E^0 = reference voltage

R = universal gas constant = 8.32 J/mol.K

T = temperature, K

F = Faraday constant = 9.65×10^4 C/mol

n = ionic change

a_1 = activity of ion to be measured in solution on one side of membrane

a_2 = activity of same ion in solution of other side of membrane

The ionic activity is related to ionic concentration, c, by

$$a = \gamma c \quad (21)$$

where γ is the activity coefficient and has a value of one for highly dilute electrolytes. In Eq. (20), if a_2 of the reference solution is known, then a_1 of the measurand can be determined provided that no other ions are present which would interfere with the measurand.

For ionic sensors using a solid membrane, a basic problem is making electrical contact with the solutions. If metal electrodes were used for this purpose, then additional voltages would be generated in the electrical circuit due to the chemical reactions at the electrode surfaces. In general, a stable and reproducible ionic sensor requires half cells coupled to the electrolytes by salt bridges or buffer solutions. A half cell consists of an electrode immersed in an electrolyte with which it is in electrochemical equilibrium. Only half cells with electrochemically reversible cell reactions give reproducible results and are useful. The calomel cell (mercury in contact with mercurous

chloride/potassium chloride paste) and the silver/silver chloride cell are the most common reference cells.

The output voltage at 25 °C is given by

$$E = E^{\circ} - \frac{0.059}{n} \log (\gamma c) \text{ volts} \quad (22)$$

where E° is a constant for the particular nature of electrode materials and n is the number of ionic charge. A high-input impedance is required so that the voltage may be measured at near zero current. Traditionally this type of ionic measurement is referred to as open circuit potentiometry.

2. pH and Its Measurement

Hydrogen ion activity is usually defined by the logarithmic measure of pH, i.e.,

$$\text{pH} = \log (1/A_{\text{H}^{+}}) \quad (23)$$

At 25 °C the activity of H^{+} and OH^{-} ions in pure water is $10^{-7} \text{ mol dm}^{-3}$ each. pH values are temperature dependent because the extent of H_2O dissociation increases with temperature. At 100 °C pure water has a $C_{\text{H}^{+}}$ of $10^{-6} \text{ mol dm}^{-3}$, i.e., the pH is 6, but the water is neutral. The activity product ($A_{\text{H}^{+}}$) ($A_{\text{OH}^{-}}$) remains constant when the concentration of either ionic species in an aqueous solution is increased by addition of a solute. For our high temperature work here, we approximate the concentration same as the activity.

It has been found that the conventional glass pH electrode has a good selectivity for H^{+} . Its construction, operating principle, and the composition of the glass are discussed in detail in references 73 and 74. Its operation involves ion transport through a thin glass membrane, made from a glass containing appropriately chosen ionic constituents. The overall mechanism of pH sensing, however, is not simple. The glasses are formulated for optimum behavior under specific conditions of use. Soda glasses containing sodium ions are generally inaccurate above pH 9; lithia extends the range to about 13. Glasses incorporating tantalum, niobium, or rare earth oxides having lower electrical resistance can be used to make thicker glass membranes for electrodes.

General purpose glasses can measure pH from 0 to about 12 at temperatures from 0 to near 100 °C (and sometimes beyond). Their electrical resistances at 25 °C are in the several hundred megaohm range, the exact value depending on glass composition and membrane thickness. Resistance of the glass varies exponentially with temperature. A glass whose resistance is 100 megaohms at 25 °C may be around 1000 megaohms at 0 °C and 1 megaohm at 80 °C. General purpose glasses show an interference response to sodium ions above approximately pH 10. Glasses formulated for use at higher pH show a greatly reduced response to sodium and other alkali metal ions but also have a higher electrical resistance, five or more times that of general purpose glass.

The measurement of hydrogen ion activity uses a galvanic cell constructed by combining the glass electrode with a reference electrode, usually the saturated calomel electrode or silver/silver chloride electrode.

The emf of this cell is given by

$$E = E(\text{Cal}) - E'(\text{glass}) + E_l + (2.303 \text{ RT/F})\text{pH} \quad (24)$$

where the liquid junction potential, E_l , at the analyte and saturated KCl interface has been included. If one uses the formal definition of pH of Eq. (23), then the pH value of the analyte cannot be deduced from Eq. (24) unless the liquid junction potential is known. Therefore, the formal definition of pH has been replaced by form of Eq. (24). Consider the measurement of the cell emf for a buffer solution of known pH. If the pH value is pH_s and the emf value E_s , then Eq. (24) can be written as

$$E_s = E(\text{Cal}) - E'(\text{glass}) + E_l + (2.303 \text{ RT/F})\text{pH}_s \quad (25)$$

For an analyte solution of unknown pH, if the pH value is pH_u and the emf value E_u , then Eq. (25) becomes

$$E_u = E(\text{Cal}) - E'(\text{glass}) + E_l + (2.303 \text{ RT/F})\text{pH}_u \quad (26)$$

Assume that the liquid junction potential does not change in changing the standard buffer solution for the unknown pH analyte, then from Eqs. (25) and (26), one obtains

$$\text{pH}_u = \text{pH}_s + (E_u - E_s)/(2.303 \text{ RT/F}) \quad (27)$$

Here we have noticed that the definition of pH is based on carefully defined buffer solutions. The National Institute of Standards and Technology (NIST) has proposed a set of standard buffer solutions. Their pH values have been established from the emf of cells without a liquid junction. The operational definition of pH accepts the pH of these buffer solutions as correct (77).

For the pH range of 2 to 12 and for low ionic strength solutions ($<0.1 \text{ mol dm}^{-3}$), the measured pH using the method discussed should be within 0.02 of the correct value. Outside these ranges, errors in excess of 0.1 are possible.

3. Testing to Insure Suitability for Geochemical Metrology

To insure the applicability of SIROF pH electrodes for geochemical fluids, the SIROF electrodes will be evaluated for the environmental conditions of the particular repository site of interest. The environments of different repository sites may differ significantly in expected moisture, pH values, redox conditions, etc.

The proposed Tuff Repository in Yucca Mountain, Nevada has many features that make it attractive as a site for burial of nuclear waste material. The repository is located approximately 400 meters below the surface in a compacted, hardened volcanic ash referred to as welded tuff. This level is about 100 meters above the water table. Water influx in the welded tuff is estimated to be less than one millimeter per year and the total moisture content is six percent by weight. Chemical analysis of groundwater (1) taken from Well J-13 indicates that the pH is near neutral at 7.1 and the concentrations for all ions is low. These ions are HCO_3 (120 ppm), SiO_2 (61 ppm), Na (51 ppm), SO_4 (22 ppm), Ca (14 ppm), Cl (7.5 ppm), NO_3 (5.6 ppm), K (4.9 ppm), F (2.2 ppm), and Hg (2.1 ppm). The water also contains 5 to 6 ppm of oxygen. The estimated temperature of a spent-fuel waste-package for a Tuff Repository (1) is less than 60 °C during the operations period. However, it is estimated to be in the range 100 to 300 °C during the thermal period of the first 300 years.

The nuclear waste will affect the long-term temperatures and pressures of the containment system. The pH sensors, therefore, must be able to withstand these elevated thermal conditions without undergoing changes in sensor properties.

The measurements of long-term stability and ionic interference at elevated temperatures have not been addressed before for SIROF electrodes. Laboratory simulation will be performed for these measurements up to 250 °C and 600 psi in accordance with the environmental conditions for a Tuff Repository. The stability testing will be performed up to 30 days at various temperatures and pH levels. The selectivity of SIROFs will be investigated by studying the effect of various ionic species as previously described, on the electrode response. Special attention will be paid to the ions of HCO_3 , SiO_2 , Na, SO_4 , and Ca, because these ions have higher concentration than other type of ions in the solutions in a Tuff Repository (1).

4. AC Impedance Measurements of SIROF Electrode-Solution Interface

Since long-term stability of ion-selective electrodes is an electrochemical phenomenon, various electrochemical test has been suggested and found useful in evaluating the stability of an ion-selective electrode. In other sections of this report, open circuit potential (OCP) measurements (experiments with current $i=0$) are reported to elucidate long-term stability of SIROF electrodes. Methods (experiments at $i \neq 0$ current conditions) such as impedance methods, polarization studies, and electrode transport experiments can also be used to provide information on the electrical properties of ion-selective electrodes and the phenomena at the electrode-solution interface.

The different techniques are considered equally relevant for the interpretation of the response mechanism of SIROF electrodes for pH sensing. Accordingly, efforts have been made to study the long-term-stability of SIROF

electrodes in various pH values using the impedance technique. The impedance method permits the characterization of an electrochemical system and the analysis of electrochemical reactions. This section includes a summary of the evaluation of SIROF electrodes based on A.C. impedance methods.

A.C. impedance measurements were made using a system based on a HP 4274A multifrequency LCR meter. The meter was interfaced to the electrochemical cell with pH solutions in which two similar SIROF electrodes were immersed. The solutions used for testing had pH values of 4, 7, and 10, respectively. The SIROF electrodes had an area of 4 mm by 9 mm immersed in solution and were separated by a distance of 15 mm. Applied signal amplitude was 5 mV in the nominal frequency range of 100 Hz to 100 KHz.

Fig. 1 shows data collected from a pair of SIROF electrode samples I47-1 immersed in pH 4 solution for 36 days. There is an apparent change in the overall impedance of the system during this period of time, suggesting that the system is not stable in the long term. In this case significant resistive effects were observed after a long immersion period of one month. The approximate straight line close to 45 °C in the region above 1 KHz may be caused by rate-controlling process as a result of diffusion effects.

The 45 °C portion of the impedance curve was also observed fore the case of the electrodes immersed in pH 7 and pH 10 as shown in Figs. 2 and 3, respectively. In the case of Fig. 2, however, there is little apparent change in impedance, especially at high frequencies above 10 KHz, during 17 days immersion in pH 7. In the solution of pH 10, similar impedance responses for relatively long testing times were observed as shown in Fig. 3. The data trends are similar to those observed in Fig. 1.

An important indication of SIROF electrode stability which may be extracted from the impedance data is the information obtained from observing the changes in system impedance as a function of time. Such changes appear to be indicative of electrode instability in various pH solutions. It is suggested that the samples I47-1 SIROF electrodes are stable in pH 7 solution. However, the data produced are open to suggested mechanistic interpretation for the cases of the electrodes immersed in pH 4 and pH 10 for a long period of time.

The overall shape of the complex plane plots could be considered to indicate the type of kinetics which are rate controlling due to Faradaic processes. The Helmholtz double-layer capacitance associated with SIROF-solution discharges via a Faradaic reaction resistance. The rate of reaction decays with decreasing open-circuit potential. The Helmholtz capacitance is dependent on open-circuit potential and is related to the electric double layer of adsorbed electroactive species or reduction/oxidation state of the SIROF. The potential dependence of Helmholtz capacitance can be expressed in the following equation:

$$\ln[C_H(E)] = \ln i_o - \ln[-(dE/dt)] + E(t)/b \quad (28)$$

where C_H is the Helmholtz capacitance and the initial current bypassing the capacitive layer, i_o , the open-circuit potential, E , the time, t , and the Tafel

slope, b , are related by Eq. (29),

$$i(t) = i_0 \exp [E(t)/b] \quad (29)$$

E. Summary

The pH values and ionic contents of geochemical solutions are important characteristics of a nuclear waste repository site (1). The changes in solution chemistry conditions with time, which are likely to exist during the period of repository closure, must be taken into account if adequate containment is necessary for a long period. Therefore, the pH determination of the geochemical solution must be measured for long-term elevated thermal conditions.

Various metal oxide electrode materials have been described in a recent report and their application for measuring pH has been reviewed (2). The requirements of a pH electrode for geothermal fluids are rather difficult to fulfil, e.g., the oxide must be stable at temperatures up to 250 °C corrosion resistance, and robust, and exhibit a low sensitivity to ionic and redox interferences. Electrode materials of this type are discussed in the NIST/NRC review, of which the IrO₂ emerges as the most promising candidate because of its consistent near Nernstian response and its property of low impedance in thin films.

In order to optimize the performance of IrO₂ electrodes for pH sensing at high temperatures and pressures, improved understanding of the electrochemical behavior at the IrO₂-solution interface is essential. Electrochemical phenomena associated with the electrical charge and potential distribution in the interface have not been studied for SIROF solution systems. The quantitative information can contribute to a better understanding of the electrode response, e.g., open circuit potential, stability, sensitivity, and selectivity.

For inorganic oxides, experimental studies have revealed the important role of H⁺ and OH⁻ ions in determining the surface charge and potential. The classical GCSG model has been used by most colloid chemists in qualitatively interpreting observed phenomena at the oxide-liquid interface. Several workers have attempted to quantitatively describe the charge and potential distribution at the oxide-liquid interface using this model. Non-classical models have been proposed to account for the high surface charges observed for oxides. The porous double layer or gel layer model has been postulated in which H⁺ and OH⁻ and counter ions are thought to penetrate into the solid oxide. However, independent measurements of oxide surface permeability cannot support porosity as a general model. The site-binding model involving surface complexation of protons and counter ions does appear to account for most observed experimental results.

Progress is obviously being made in the area of oxide-liquid interfaces. The basic phenomena are better understood, but it appears that no totally satisfactory model for the oxide-solution interface has emerged to date. Hydration, hydroxylation, and acid-base properties are all factors which require special attention. As far as the iridium oxide-solution interface is concerned, two fundamental properties affecting the electrochemical behavior of hydrous iridium oxide films are (i) the acidity of the hydrated film and the variation of this property with change in the iridium oxidation state (57), and (ii) the

difference in electrical conductivity between the reduced and oxidized form of the surface film (58,59). According to Burke et al. (78,79) both properties are strongly influenced by the hydrated nature of the iridium oxide layer.

Figure 1. Complex Plane Impedance Data for SIROF Electrodes After Exposure to a pH 4 Buffer Solution at 22 °C.

Figure 2. Complex Plane Impedance Data for SIROF Electrodes After Exposure to a pH 7 Buffer Solution at 22 °C.

Figure 3. Complex Plane Impedance Data for SIROF Electrodes
After Exposure to a pH 10 Buffer Solution at 22 °C.

This report provides the general background and also some specific information regarding a number of oxide-liquid systems. However, this does not imply that the results from colloidal metal oxide studies can all be applied to the oxides used as pH electrodes. This is simply due to the lack of information presently available on the electrochemistry of the latter group of materials. Iridium oxide has a metal-like conductivity, so that there is no potential drop in the oxide. Its Fermi level is taken as the equilibrium potential of the electrode:

For these types of oxides having a metal-like conductivity the band structures are different from those of insulating oxides (band gaps greater than 3 eV) and of n-type or p-type semiconductors. Recently, theories for the metal-liquid and semiconductor-liquid systems have begun to appear, as well as models that attempt to model the interfaces realistically (80).

No attempt has been made so far to examine the GCSG theory's applicability to the IrO_2 -solution system. Interfacial phenomena for this system are presently poorly understood. A detailed study of the capacitance properties of IrO_2 in contact with electrolyte pH solutions might give extremely valuable information concerning the dielectric properties of the contacting phases. The IrO_2 -solution system may be characterized by its capacitance-potential, capacitance-pH, capacitance-charge, and capacitance-time curves within the framework of the GCSG theory. This is of importance for interpretation of adsorption phenomena for H^+ , OH^- or other ions, of double layer effects in electrode reaction kinetics and of electrode instability in pH measurements. It is proposed that these capacitance characteristics may be obtained using d.c. and a.c. voltammetry.

F. Application to Regulations

High level nuclear waste overpacks in a salt-type geologic repository are expected to be in contact with hot corrosive brines and slurries. DOE's conclusions as to overpack performance will be based in part on their assessment of local conditions, and this assessment will in turn be based on measurements of the chemical and the electrochemical properties of the brines and slurries. Hence, specific regulatory issues relevant to waste that need to be addressed are the precision and accuracy of the techniques used to measure these properties (e.g., pH and E_h or a similar measurement of redox potential) under very severe experimental conditions.

The characterization of the geochemical environment of the laboratory experiments is important to ensure that the laboratory results do, in fact, reproduce what was observed and/or will be expected in the natural systems. E_h (redox potential) and pH are the two important parameters affecting the degradation of the waste packages. The use of geochemical models such as EQ3/EQ6 requires input values for E_h and pH, making these measurements critical to the satisfactory use of codes based on these models.

The most common method of measuring pH and E_h is the use of a probe which

consists of an electrode at which some electrochemical reaction can take place. The electrochemical potential in the electrolyte being measured is compared to that of another electrode in some known state.

There are, however, a number of areas of uncertainty associated with the use of common electrodes. These include:

- (1) errors in measurement at elevated temperatures,
- (2) errors in measurement at elevated ionic strengths,
- (3) the instability of electrode measurements (e.g., drifting),
- (4) the long term stability of the electrodes themselves (i.e., degradation),
- (5) the response of different probes in different environments, and
- (6) instrument sensitivity (i.e., what are the error bars for a particular measurement.)

In addition to the areas of uncertainty listed above, questions specific to the measurement of Eh that need to be addressed include: (1) at what temperature can kinetic effects in the solution be ignored and internal equilibrium be reasonably assumed, and (2) are alternative methods of measuring redox conditions, such as oxygen fugacity or redox couples, appropriate in experiments simulating the waste package environment, and, if so, under what conditions are they more representative of redox conditions (especially as regards open circuit potential) than E_h measurements?

Surrounding the metallic canister and overpack in the high level waste engineered barrier system may be a layer of "backfill" or "packing." The purposes of this layer are to retard ground water from contacting and corroding the canister/overpack barrier, to provide a large sorptive capacity for nuclides released from the waste package, to delay the release of radionuclides from the engineered barrier system, and to act as a stress readjustment medium. Numerous materials are being considered for use as packing including bentonite, illite, and other smectite clays; quartz, crushed host rock; or a combination of these. The majority of design proposals for the packing layer include bentonite, a weathering product of volcanic ash, as the key component. Naturally occurring bentonite is composed of ash, feldspar, illite, kaolinite, and approximately 90% montmorillonite. It is because of the large montmorillonite component that bentonite is useful as a packing material.

In the presence of water, montmorillonite swells allowing the packing to fill nearby cracks in the host rock resulting from emplacement hole drilling. This infilling significantly increases the mass transfer resistance offered by the packing. Another benefit of montmorillonite is its low permeability, $K_0 = 10^{-20} \text{ m}^2$. This enables the packing to prevent flowing ground water from contacting the waste package. The swollen gel also exhibits a large degree of plasticity which makes it a good choice for a stress readjusting medium. In addition to these benefits, bentonite offers a large cationic sorptive capacity.

These investigations use the role of a bentonite-based packing in limiting the release from the engineered barrier system. These investigations will provide data needed for paralleling analyses of the release rate of a radionuclide from the engineered barrier system as required in 10 CFR Part 60, 113.

Previous research under FIN B3040 developed equipment models and data needed for predicting diffusion through montmorillonite. However, several problems were left unfinished by the investigators. These problems are: (1) the effects of the variability in the composition of bentonite-based packing material on diffusion rates; (2) the effects of corrosion products (iron) on diffusion rates and on the mineralogical stability of bentonite-based packing; and (3) the effects of packing on limiting the corrosion rate of the overpack by limiting the mass transfer of iron and oxygen. This research is intended to resolve those problems.

The purpose of this experimental research program is to develop NRC's ability to judge the metrologic uncertainties inherent in determinations of the chemistry of the waste package environment in salt and clay, and especially the determinations of pH, E_h , and mass transport rate measurements.

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III. EVALUATION AND CHARACTERIZATION OF SPUTTERED IRIIDIUM OXIDE pH ELECTRODES

A. Introduction

The glass electrode is overwhelmingly the sensor of choice for measurement of pH in industrial process control and research applications. The popularity of the glass electrode for pH determination can be attributed to its simplicity, relatively rapid and stable Nernstian response to hydrogen ion activity, and inertness to oxidizing and reducing agents. In addition, the existence of glass electrodes for nearly 70 years has allowed for extensive refinement and optimization of their performance (1). Despite these qualities, glass electrodes still possess several nonideal properties such as acid and alkaline error, sensitivity to monovalent cations, high impedance, mechanical fragility, and instability at high temperatures ($>100^{\circ}\text{C}$). These properties can seriously impair the glass electrode's ability to measure accurately pH in a wide range of applications. This has led some researchers to investigate the feasibility of using a variety of semiconducting metal oxides as pH sensing electrodes (2-4).

Among the most promising candidate materials and the one that has received the most attention is iridium oxide, IrO_2 (5-11). Iridium oxide is attractive as a pH sensing material because of: 1) its good chemical stability over a wide range of pH and temperature in aqueous solutions, 2) its low impedance, and 3) the many methods available for preparing IrO_2 that offer the potential for sensor miniaturization. IrO_2 pH sensing films have been fabricated by thermal oxidation (3-5), electrochemical potential cycling (6,7) and reactive sputter deposition (8,9). Reactive sputter deposition of IrO_2 is a particularly appealing method of fabrication because parameters that might influence pH response such as film crystallinity, thickness, and stoichiometry can be readily controlled (12). Katsube et al. were the first to report the pH response of d.c. reactively sputtered iridium oxide films. They observed a nearly Nernstian slope between 0 and 100°C over a pH range of 3 to 10. The effect of several ionic interferences was examined and deemed negligible. A drift in electrode potential was attributed to slow hydration of the surface. The properties of iridium oxide pH sensors were also previously reported to NRC in NBSIR 85-3237 (10) and NUREG/CR-5166 (11).

In the first part of this paper we report further results on the pH sensing behavior of d.c. magnetron reactively sputtered iridium oxide films. We compare their pH response with that of the glass electrode and also assess iridium oxide's sensitivity to ionic and redox interferences. Our ultimate goal in this work is to optimize the pH sensing performance of iridium oxide electrodes. Moreover, we are making an effort to elucidate the fundamental mechanism of iridium oxide pH sensing by examining model IrO_2 sensors with the surface sensitive-techniques of x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and ion scattering spectroscopy (ISS). A microscopic understanding of reactions occurring at the iridium oxide/solution interface will enable new strategies to be developed which prevent electrode instability and response to interferences. In the second part of this paper results are presented on methods for producing clean, hydroxyl-free and hydroxylated iridium oxide surfaces in an ultrahigh vacuum environment. It is shown that clean IrO_2 -like surfaces prepared by ion bombardment and annealing in oxygen are inert to large doses of gas phase water. It is also demonstrated that

in situ rf plasma excitation of water activates adsorption on these surfaces and results in a hydroxylated iridium oxide surface.

B. Experimental Section

All iridium oxide films were prepared by d.c. magnetron reactive sputtering of a 99.99%, 5 cm-diam Ir target in a 50:50 argon:oxygen atmosphere. After reaching a chamber pressure of 2.7×10^{-4} Pa or less, sputtering was initiated with the total chamber pressure held at 0.35 Pa. Typically a 600 V target bias at 0.1 amp was used, and under these conditions the deposition rate was approximately 150 Å/min. Film thicknesses were determined by a stylus technique and the results reported here are for iridium oxide films of approximately 7500 Å. No effort was made to control substrate temperature during the deposition and the temperature was observed to rise to 307 K during a 50 minute deposition. Single crystal, n-type silicon <100> was used as a substrate material for the surface analytical studies, while Al_2O_3 (0.6x2.5 cm) substrates were used for pH sensor evaluation.

Potentiometric measurements were performed by partially immersing the iridium oxide/ Al_2O_3 samples in a buffer solution and measuring their potential versus a single junction Ag/AgCl reference electrode with a digital voltmeter. The pH of a stirred buffer solution consisting of 0.01 M CH_3COOH , H_3PO_4 , H_3BO_3 , and 0.1 M KNO_3 was varied by addition of concentrated solutions of KOH or HNO_3 as in reference 2. The pH of the solution was monitored with a calibrated glass electrode and a pH meter. All solutions were prepared with analytical reagent grade chemicals and air saturated deionized water ($>17 \text{ M } \Omega\text{cm}$). All measurements were performed between 23 and 24 °C except where noted otherwise.

Surface studies were conducted in a single ultrahigh vacuum system consisting of an analysis chamber that houses all of the spectroscopic techniques and a sample preparation chamber where relatively high temperature and pressure (up to 10^5 Pa) treatments are performed. A description of this system can be found in reference (13). A long-throw manipulator was used to transport samples between the coupled chambers. Heating was accomplished by passing current through the iridium oxide film while monitoring the sample temperature with a W/Re thermocouple. Water plasma treatments were performed in the preparation chamber using a glass reactor similar to one described previously (14). A 13.56 MHz power supply and a matching network were used to sustain the discharge. A typical discharge was run at a H_2O pressure of 6.7 Pa and a net power of 15 Watts.

C. Results and Discussion

1. Iridium Oxide Potential-pH Response

A typical potential-pH response of an iridium oxide film/ Al_2O_3 electrode is plotted in Fig. 1. The data were obtained with the electrode immersed in the same buffer solution by varying the pH with addition of acid or base. The circles represent an increase in pH from 2 to 12 while the triangles a decrease from 12 to 2. A very linear potential-pH response and essentially no

Figure 1

Potential-pH response curves of a sputter deposited iridium oxide film electrode in a buffer solution generated by increasing pH (○) and decreasing pH (▲).

hysteresis are observed. A linear regression analysis of these points gives a slope of -57.9 mV/unit pH that is very close to the theoretical Nernstian value of -58.8 mV/unit pH at 23.5 °C. For all samples examined the potential varied linearly with pH and the calculated slopes were between -55.5 and -60.0 mV/unit pH with most values near -58 mV/pH unit. This was true of iridium oxide films that were freshly deposited and ones that had been aged in buffer solutions of varying pH.

Substantial variations in the calculated E_{int} (defined as the extrapolated potential intercept at pH = 0) values with electrode treatment were observed, however. This has been noted previously by Katsube et al. (8) and by our laboratory (9) and attributed to a surface hydrolysis reaction. The data in Fig. 1 were obtained from a relatively "fresh" iridium oxide film that was rinsed with deionized water and placed in buffer solution at pH=2.2 for approximately 10 minutes. The calculated E_{int} value of +0.795 V is reasonably close to the value of approximately +0.850 V (corrected for the difference in reference electrodes) reported by Katsube et al. (8) for as-deposited iridium oxide electrodes prepared by sputter deposition. Over a period of several days the E_{int} values of freshly prepared films generally drifted in a negative direction to values as low as +0.600 V. More erratic drifts of ± 0.100 V over the period of 24 hr were sometimes observed for electrodes that had been previously aged. This was true of electrodes stored either in air or in buffer solution of pH 4 to 7. Although, the reason(s) for electrode instability is not understood we believe that a change in surface composition is responsible. This topic is treated further at the end of this section.

We examined the potential drift (or aging) of sputtered iridium oxide electrodes in buffer solutions of pH 2, 7 and 12. Figure 2 shows the change in potential with time for three freshly prepared iridium oxide films in a pH 2 buffer. The potentials decrease sharply during the first 10 h of immersion and then gradually approach a value 230 mV negative of that of the original fresh electrodes. Similar negative potential shifts of approximately 200 mV were observed when fresh electrodes were aged in pH 7 and 12 buffers, although these potential transients exhibited considerably more scatter. In addition, potential-pH slopes for electrodes aged 48 h in pH 2 buffer decreased 5 to 7 mV/pH while those aged in 7 to 12 buffer exhibited a 2 to 3 mV/pH decrease. Hysteresis in the potential-pH response was also more evident after aging in buffer solutions. The magnitude of these effects could not be correlated with buffer pH. It should be noted that the aging of iridium oxide film electrodes is not completely irreversible. The E_{int} and Nernst slope of electrodes aged in buffer solutions can be restored to values close to that of freshly deposited films by removing the electrodes and storing them in the laboratory ambient.

The potential-pH response of iridium oxide thin films between temperatures of 0 and 75 °C was also examined. Three iridium oxide thin film electrodes designated 69A6, 69A7, and 69A8 were tested in these experiments. The pH-response testing at elevated temperatures was performed with the electrochemical cell immersed in a thermostatted water bath. The solution pH was measured with a glass electrode that was calibrated with standard pH buffers maintained at the same temperature as the that of the test buffer. Figure 3 shows the pH-response curves for sample 69A6 at various temperatures. The pH-response was relatively linear for all samples tested at all temperatures. Calculated correlation

Figure 2

Potential transients of three identically prepared sputter-deposited iridium oxide film electrodes in a pH 2 buffer solution.

Figure 3

Potential -pH response curves of a sputter deposited iridium oxide film electrode (sample 69A6) in buffer solution at temperatures of 3, 15, 25, 40, 50, 55, and 72 °C.

coefficients were greater than 0.95 for all pH-response curves. Potential drift was observed at all temperatures with the electrodes exhibiting greater drift at higher temperatures. The pH-response curves at each temperature were generated within 5 minutes which lessened the effects of potential instability. The calculated E_{int} values as a function of temperature are plotted in Fig. 4. No obvious trend in E_{int} with temperature is observed. It is noteworthy, however, that the E_{int} values for the samples are grouped together at each temperature. We believe this may be due to poisoning of the electrode potential by the solution redox potential. It is shown below that the iridium oxide is quite sensitive to certain dissolved redox species. It is conceivable that the redox potential of each buffer solution could vary in an erratic manner due to differing amounts of dissolved impurities or gases even though the solution composition is ostensibly the same. This is not unreasonable given that a new buffer solution was used at each temperature. The solutions used for these tests are buffered well with respect to pH, but not to redox potential. The calculated potential-pH slopes as a function of temperature are shown in Fig. 5. The experimental fit is given by the dashed line, while the solid line the theoretical Nernst slope. Although the data are somewhat scattered, it can be concluded that the experimental slopes are close to those predicted by the Nernst equation. The experimental fit indicates a slightly sub-Nernstian deviation of 1-2 millivolts.

Although, the drifting of the potential of the sensor makes it unsuitable for long term applications, it is emphasized that the iridium oxide film's response to pH is perfectly adequate for short term applications. With frequent calibration (0-4 hr) an accuracy of ± 0.1 pH unit is easily obtained over a pH range of 2-12. This is demonstrated in Fig. 6 where a calibrated iridium oxide electrode was used to monitor the titration of 0.1 M H_3PO_4 with 0.1 M NaOH. The titration was monitored simultaneously with a calibrated glass electrode and an identical titration curve was generated. This also allowed for a relative comparison of response times for the iridium oxide and glass electrodes. The iridium oxide potential-pH response was 10-15% faster for both small (0-1) and large (>2) changes in solution pH. This might be a consequence of a thicker hydration layer on the glass electrode that requires protons to diffuse over greater lengths to participate in ion exchange reactions with hydroxyl functionalities. Results to be discussed later from surface analytical studies in this laboratory indicate that the hydration layer on iridium oxide electrodes is very thin (<10 Å). Thus, equilibrium, involving exchange of protons, would be reached rapidly.

To further evaluate the pH response of the sputter deposited iridium oxide films, their selectivity to various ionic and redox species was examined. A change in response of 2 mV or less was observed over the pH range of 3 to 12 when the alkali metal cations of Li^+ , Na^+ , or K^+ were added to the buffer solution to concentrations up to 0.1 M. Clearly the iridium oxide sensor is superior to the glass electrode in this respect (1). The absence of alkaline error for iridium oxide electrodes has been noted by others (2,8).

Also, little or no response (<10 mV) to the divalent cations of Mg^{2+} , Ca^{2+} , Cu^{2+} , and Ni^{2+} at concentrations up to 0.01 M was measured. It is interesting to note that at higher pH values, precipitation of the metal hydroxide complexes did not seem to impair electrode performance and precipitate was not visible on the electrode surface.

Figure 4

E_{int} (extrapolated potential at pH = 0) determined from potential pH response curves as a function of temperature for samples 69A6, 69A7, and 69A8.

Figure 5

Potential-pH response slopes of samples 69A6, 69A7, and 69A8 as a function of temperature.

Figure 6

Titration of 0.1 M H_3PO_4 with 0.1 M NaOH as monitored by a calibrated sputter desposited iridium oxide film electrode.

The addition of the halide ions of F^- , Cl^- , and Br^- at concentrations up to 0.1 M caused response changes of less than 5 mV. On the other hand, the presence of I^- at 0.1 M caused a -0.200 V shift and a sub-Nernstian potential-pH response of 41.9 mV/unit pH. The interference of I^- with IrO_2 powder electrodes has been reported before and attributed to a complexation or reduction of the surface (2). Surface analysis results of I^- exposed samples are briefly discussed below.

Iridium oxide films exhibited a strong sensitivity to certain dissolved redox species. Figure 7 shows the potential-pH response of an iridium oxide film immersed in buffer solution and buffer solution containing equimolar concentrations of ferricyanide and ferrocyanide from 10^{-6} to 10^{-4} M. At 10^{-4} M the $Fe(CN)_6^{3-/4-}$ couple acts to pin or poise the iridium oxide electrode potential much as would occur with a Pt indicator electrode. Even at 10^{-6} M $Fe(CN)_6^{3-/4-}$ a serious error in pH measurement would result. The redox sensitivity of iridium oxide prepared by potential cycling and thermal methods has been noted by other workers (2,4,7). This precludes the use of iridium oxide pH sensors in solutions containing redox couples that exhibit facile electron transfer kinetics with iridium oxide electrodes.

Several iridium oxide electrodes that were immersed in various electrolyte solutions were examined by XPS to try to correlate the potential response with the state of the electrode surface. Three electrodes were analyzed: 1) one that had undergone extensive ionic and redox interference testing for five days, 2) one that was immersed in a pH 3.1 buffer solution containing 0.05 M KI, 3) and one immersed in a pH 3.1 buffer. The electrodes were rinsed with distilled water and allowed to dry before insertion into the surface analysis system. Surprisingly, preliminary XPS results indicate no significant differences in surface oxygen content or iridium oxidation state between the samples. These data suggest that the iridium oxide surface is not irreversibly changed by exposure to I^- or $Fe(CN)_6^{3-/4-}$. This is consistent with potentiometric results that show restoration of Nernstian behavior of I^- or $Fe(CN)_6^{3-/4-}$ treated electrodes when they are immersed in pure buffer solutions. The only difference between the electrode surfaces as observed by XPS was the extent of surface carbon contamination. The gradual adsorption/desorption of surface carbon contamination might be responsible for the day to day drift in electrode potential.

2. Model IrO_2 Sensor Surfaces

As mentioned earlier we are using UHV spectroscopies to examine the composition and structure of model iridium oxide sensor surfaces to gain a microscopic understanding of electrode behavior. In addition, results obtained from these model surfaces will greatly aid in the interpretation of data obtained from "real" iridium oxide sensor surfaces.

To study the interaction of H_2O with IrO_2 surfaces it is necessary to be able to prepare reproducibly a clean IrO_2 surface. It was discovered that the conventional UHV methods of surface cleaning fail for producing clean IrO_2 -like surfaces. Both ion bombardment and annealing in vacuo cause decomposition of the oxide surface to metallic Ir. A procedure found to produce clean, IrO_2 -like surfaces involved Ar^+ bombardment and subsequent high temperature (900 °K) annealing in an O_2 atmosphere (1.3×10^{-4} Pa) of the sputter deposited film. XPS

Figure 7

Potential-pH response curves of a sputter deposited iridium oxide film electrode in a pure buffer solution () and buffer solutions containing 10^{-6}M (), 10^{-5}M (o), and 10^{-4}M () $\text{Fe}(\text{CN})_6^{-3/-4}$.

and UPS spectra acquired from these surfaces were similar to those reported for single crystal IrO_2 (15,16).

Gas phase H_2O dosing of the IrO_2 -like surface prepared by the procedure given above was the first method investigated to produce a hydroxylated IrO_2 surface. Surprisingly, XPS, UPS, and ISS results indicate no reaction between water and the IrO_2 -like surface even with H_2O exposures up to 5×10^7 Langmuir (L). This was unexpected because hydroxylation of the surface is commonly claimed as the cause of electrochemical instability. Obviously, the adsorption and/or dissociation of water on this surface is an activated process and much higher H_2O exposures are necessary to observe a reaction. It is possible that the Ar^+ bombardment/high temperature O_2 annealing surface preparation produces a stoichiometric IrO_2 surface that is particularly inert to water. We plan on potentiometrically testing IrO_2 sensors that have been similarly prepared to determine if these surfaces exhibit enhanced electrochemical stability.

As an alternative to gas phase water dosing we used rf excitation of the gas phase water (plasma treatment) to, in effect, force the reaction between water and the IrO_2 -like surface. Plasma treatment activates the adsorption of water by creating reactive gas phase species such as OH , H , H_2O^+ , H_3O^+ , and $\text{H}(\text{H}_2\text{O})_2^+$ that can react with the surface (17). Figure 8 shows XPS spectra of the oxygen 1s region of an IrO_x film annealed at 900 °K in 1.3×10^4 Pa O_2 before and after H_2O plasma treatment. The broadening on the higher binding energy side of the plasma treated film indicates that H_2O plasma treatment introduces adsorbed hydroxyl groups and/or H_2O on the surface. Consistent with this observation is the 12% increase in the O/Ir ratio that is obtained by taking the ratio of the oxygen 1s and iridium 4f peak areas (no correction is made for the difference in the photoelectric cross sections and the photoelectron escape depths for O and Ir).

ISS was also used to examine the effects of water plasma treatment. The great advantage of this technique is that it is sensitive to only the top atomic layer. Figure 9 contains ISS spectra collected from an iridium oxide surface that was sequentially 2 KeV Ar^+ bombarded, annealed at 900 K in O_2 , and then H_2O plasma treated. As expected, the Ar^+ bombarded surface is very oxygen deficient (XPS data show the presence of metallic Ir) and the O/Ir ratio is low. After annealing at 900 K in O_2 the relative intensities of O and Ir have reversed indicating oxygen incorporation at the surface. This is consistent with XPS data that show the surface to possess Ir^{4+} stoichiometry. When this surface is water plasma treated the O/Ir ratio increases further (note the decrease in the Ir signal). The ISS results suggest that hydroxylation reactions and/or adsorption of water occur at surface Ir atoms that are not coordinately saturated by lattice oxygen (O^{2-}). The Ir atoms of the O_2 annealed surface that are not fully coordinated can be "seen" by the He^+ beam. After H_2O plasma treatment of this surface, hydroxyl groups or water bonded to Ir at these uncoordinated sites, largely shadow the exposed Ir surface atoms. Due to the large increase in the O/Ir ratio, it is believed that most of the hydroxylation of the IrO_2 -like surface is confined to the upper most atomic layer.

Figure 8

O 1s XPS spectra of a sputter deposited iridium oxide film that was 2 KeV Ar⁺ bombarded and annealed at 900 K in 1.3×10^{-4} Pa O₂ before and after H₂O plasma treatment.

Figure 9

ISS spectra of an iridium oxide film following sequential: a) 2 KeV Ar^+ bombardment, b) annealing at 900 K in 1.3×10^4 Pa O_2 , and c) H_2O plasma treatment.

D. Conclusion

The pH sensing behavior of d.c. magnetron reactively sputtered iridium oxide films was evaluated. With frequent calibration these electrodes measured solution pH to better than 0.1 of a pH unit. In addition, the iridium oxide films exhibited a near-Nernstian potential-pH response between 0 and 75 °C. Little hysteresis and response to ionic interferences (alkali, alkaline earth, and transition metals) were exhibited; however, a high sensitivity to some electroactive species ($\text{Fe(CN)}_6^{-3/-4}$, I^-) was observed.

It was demonstrated that clean IrO_2 -like surfaces prepared by Ar^+ bombardment and high temperature and O_2 pressure annealing were inert to relatively large doses of gas phase H_2O . Model hydroxylated surfaces were prepared by H_2O plasma treatment of IrO_2 -like surfaces.

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IV. STABILITY OF IRIIDIUM OXIDE FILMS IN HIGH TEMPERATURE, 200-250 °C, SOLUTIONS

A. Abstract

Iridium oxide films have been investigated as pH sensing electrodes. They have a Nernstian response, of approximately 53-58 mV per pH unit at room temperature, under a wide range of solution conditions. The advantages of these solid state electrodes include their ruggedness, small size, high voltage/low impedance output, and the low cost of fabrication. They also have high temperature capability and have been considered for geothermal sensing applications.

This study investigated the stability of reactively sputtered iridium oxide films on alumina substrates on exposure to pH 4, 7, 10 and in concentrated J13 solutions at 200 °C (15 bar) and 250 °C (40 bar). The exposures were made in a teflon lined bomb. The results of over 60 tests, cycling pH between 2 to 12 before and after exposure, are discussed. Changes of the potential intercept, and the slope were most severe under acidic conditions at 250 °C. The most severe conditions also caused film breakdown and loss of adhesion to the substrate. The incorporation of ion assisted deposition in the fabrication of the films led to improved adherence under exposure to 200 °C solutions.

B. Introduction

Iridium oxide as a thin sputtered film is being considered as a pH electrode for high temperature (above 100 °C) solutions. The desirability of the sputtered iridium oxide film (SIROF) for measurements in harsh environments has been described by Katsube, et al. (1), Lauks, et al. (2), and by Dietz, et al. (3). The glass electrode, which is the standard pH measurement instrument below 100 °C, becomes less stable at higher temperatures and the alkali interference problem is also aggravated. Iridium oxide had indicated good stability at 156 °C (2) from pH 3-7. We at NIST have reported previously on SIROF sensors (4-7) fabricated by sputter deposition and are currently investigating their use for pH measurement in nuclear repositories. These applications may require a sensor to indicate the corrosiveness of brine solutions at temperatures up to 300 °C. In this paper, we describe the results of testing the pH response of SIROF electrodes after exposure in pH 4, 7, and 10 solutions in a pressurized bomb at 200 ° and 250 °C. In addition, we exposed six test specimens to 200 and 250 °C in concentrated (3X) synthetic J13 liquid.

C. Experimental

Iridium was sputtered from a pure (99.99%) iridium 5 cm diameter target with a 13.5 MHz rf planar magnetron source using a 10 cm target to substrate distance. Argon and oxygen were mixed in a 1:1 ratio at a total pressure of ~0.40 Pa. The 0.5-0.7 µm thick depositions were made primarily on alumina circuit board at 30-40 °C and at 240 °C. To improve adherence of the IrO₂ films to the Al₂O₃ substrates ion beam cleaning and ion assisted deposition from a Kaufman ion source were investigated. The ion source was used for 10 minutes of predeposition substrate cleaning and for ion assisted iridium oxide deposition during the first 2 minutes. The argon pressure was 0.05 Pa (0.38 x 10⁻³ torr) during cleaning and 0.11 Pa (0.8 x 10⁻³ torr) during deposition.

The plan of testing was to compare the potential-pH response of the films before and after exposure to deionized water, pH 4, 7, and 10 at 200 °C (15.5 bar or 225 psi) and 250 °C (40 bar or 600 psi). High temperature exposure was made in the teflon lined bomb using potassium hydrogen phthalate (pH 4.01), disodium hydrogen phosphate-potassium dihydrogen phosphate (pH 7), sodium hydrogen carbonate-sodium carbonate (pH 10.01) and deionized water as test solutions for the iridium oxide. The J13 solution for testing was obtained from Dr. A. Fraher of NIST, who has been studying corrosion in J13 concentrated solutions. We used the synthetic solution at 3X concentration. The composition of the J13 is given in Table I.

Potential-pH response curves were generated by measuring the SIROF electrode potential versus a single junction Ag/AgCl reference electrode (+0.175 vs NHE) while monitoring the solution pH with a calibrated glass electrode. The tests were performed in a stirred, air saturated, buffer solution (21-22 °C) consisting of 0.01 M acetic, phosphoric, and boric acids and 0.1 M potassium nitrate. Adjustment of pH was performed by the addition of sodium hydroxide or nitric acid.

D. Results

The first series of tests were made after exposure at room temperature and a typical graph of output potential vs pH is given in Fig. 1. The plots also display the potential intercept (i.e., the extrapolated potential at pH=0) and the Nernst slope (x), as well as an indication of the hysteresis by the return slope (decreasing pH in solid dots). Each test was made using three electrodes from three different sputtering runs deposited under the same nominal conditions, but one group was cleaned ultrasonically in ethyl alcohol followed by a deionized water rinse, one had ion assisted deposition, and one had a 5 nm chromium bond coat. The first series of three electrodes were exposed to deionized water for 24, 500, and 1400 hr. No effect of the substrate preparation or chromium bond coat was observed. Typically a drop of 150-200 mV in E° and a drop in slope of 2 mV occurred in the first 24 hr and stabilized for the 1400 hr.

The next series of tests also included sample electrodes from the three batches. Each sample was tested for pH response from approximately 2-12 and returned to pH 2 with HNO_3 when fresh and after subsequent exposure to pH 4, 7, and 10 at 200 °C. All response curves were linear (correlation coefficient 0.999-1.000) and have little hysteresis. A typical response curve after exposure to pH 4, 7, and 10 at 200 °C for 20 hr is given in Fig. 2. A summary of the results is given in Table II. Test electrodes generally experienced a drop of 150-200 mV in E° and of 2-5 mV/pH slope when exposed to the solutions and a slight increase when exposed to air overnight. Exposure to the pH 7 solution for 70 hr did lead to results with even lower slopes and potential intercepts (i.e. 500-550 mV and 43-46 mV/pH). These values were raised to 890 mV and 55.9 mV/pH when baked in air at 500 °C for 20 hr. Both ion cleaning followed by ion assisted deposition and the chromium bond coat improved the durability of the films compared to some film loss by flaking on the unimproved samples on Al_2O_3 substrate. The iridium oxide films deposited on Si wafers were lost and flaked off with the high temperature exposure.

Table I
Composition of Simulated J13 Water Used

<u>Chemical Compound</u>	<u>Grams/4 Liters</u>
NaHCO_3	2.195
KOH	.095
$\text{SiO}_2 \cdot \text{XH}_2\text{O}$ (1.87 % H_2O)	.830
CaCl_2	.155
CaSO_4 ($\text{CaCO}_3 + \text{H}_2\text{SO}_4$)	.430
$\text{Ca}(\text{NO}_3)_2$	.030
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	.170
MgF_2 ($\text{MgO} + \text{HF} - 48\%$)	.048
LiNO_3	.009
$\text{Sr}(\text{NO}_3)_2$	.002
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	.001
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	.005
H_3PO_4 (85%)	.002
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	.009

FIG 1 Electrode potential versus pH for SIROF after 1400 hr in deionized water. Open squares are for increasing pH.

FIG 2 Electrode potential versus pH for SIROF after 20 hr at 200°C (15.5 bar) pH 4, plus 20 hrs at pH 7, plus 20 hrs at pH 10. Open squares are for increasing pH.

Table II
Response After Exposure at 200 °C

	FRESH		pH 4		pH 4, 7		pH 4, 7, 10	
	E° (mV)	N(mV/pH)	E° (mV)	N(mV/pH)	E° (mV)	N(mV/pH)	E° (mV)	N(mV/pH)
152A1	840 930	54.0 52.3	700 700	51.5 54.0	620	46.5	730	51.3
153A1			710 700	54.5 55.4	630	50.0	730	50.9
154A1	910	57.2	700	54.3	610	50.3	740	51.7

A third series of tests included exposures to pH 10 at 200 °C for 20 hr followed by exposure at 240 °C for 20 hr (Fig. 3). Although no degradation was evident at 200 °C, a significant decrease in slope (from 54 mV/pH to 45 mV/pH) was measured in all three batches. The electrodes exposed at 245 °C to pH 4, pH 7 and to deionized water were lost as the film came off the Al_2O_3 substrate as a powder and the liquid was a dark indigo blue indicating $\text{Ir}(\text{OH})_4$. These solutions may also be attacking the Al_2O_3 . Techniques for improved adherence including ion assisted deposition did not solve the problem and the use of the SIROF at 250 °C on Al_2O_3 in acidic or neutral does not look promising.

Test specimens from the same iridium oxide depositions (room temperature) were used to evaluate the effect of high temperature exposure to concentrated J13 solution. Exposures in the teflon bomb were made at 206 °C and 250 °C for 20 hr. The pH response of one of the samples after 20 hr at 250 °C is presented in Fig. 4. The sample was not severely degraded but the slope of E vs pH decreased 2-3 mV/pH and the intercept decreased approximately 100 mV. A summary of the results of the tests is presented in Table III. The decrease in intercept (E_0) was 150-180 mV after exposure at 206 °C and less than 2.0 mV/pH decrease in slope was observed for that exposure with six tests. Similarly the results after exposure for 20 hr at 250 °C were decreases of 2-5 mV/pH in slope and 100-180 mV in intercept.

To compare crystalline SIROF with the above discussed amorphous IrO_2 films electrodes were deposited at 240 °C under the same conditions. Their rutile structure was confirmed by x-ray diffraction. Exposure to 200 °C at pH 4, 7, and 10 in the pressurized bomb yielded similar results to the amorphous films; the slopes and intercepts were not changed substantially. Typical results of these tests are displayed in Fig. 5.

E. Conclusions

In summary, we have examined the sensitivity of iridium oxide thin films on alumina substrates to high temperature (200, 245 °C) and high pressure (up to 40 bar, 600 psi) acidic and basic solutions and in concentrated J13 solution. Twenty-one sample coupons were electrochemically tested through titrations (pH 2-11) before and after several exposures. Under the most severe conditions at pH 7 and below and at 245 °C the film is lost from the Al_2O_3 . This may be a substrate or a film problem but the films were less stable on a silicon wafer substrate. The electrochemical potential was generally decreased by 150-200 mV and the slope by 2-5 mV/pH by exposures of 20 hr at pH 4, 7, or 10 at 200 °C. Both the pre-exponential factor and the electrochemical-pH slope appeared to drop further after 70 hr (200 °C) at pH 7 in Na_2HPO_4 and KH_2PO_4 . Exposure to pH 4 or 7 generated more severe drops in potential and slope than exposures to concentrated J13 water (pH=8.5) or pH 10 solutions. It should be also noted that the scatter in the data for the electrochemical potential as previously reported (5) was a problem compared to a glass electrode.

FIG 3 Electrode potential versus pH for SIROF after 20 hrs at pH 10, 240°C (40 bar).

FIG 4 Electrode potential versus pH for SIROF before
(a) and after (b) 20 hr at 250°C in 3x J13 water.

FIG 5 Electrode potential versus pH for crystalline SIROF (deposited at 240°C) after 20 hrs pH 4, 7 at 200°C (15.5 bar).

Table III
Response After Exposure to J13 (3x)

	Before Exposure		20 hr at 206 °C	
	E° (mV)	N(mV/pH)	E° (mV)	N(mV/pH)
I58A+	920	57.7	770	57.4
I58A-	920	57.8	760	56.8
I59B+	930	58.0	760	57.0
I59B-	930	58.5	750	56.4
I59A+	940	58.0	780	57.6
I59A-	940	58.2	760	55.8
	Before Exposure		20 hr at 250 °C	
	E° (mV)	N(mV/pH)	E° (mV)	N(mV/pH)
I58B+	920	57.0	800	55.3
			800	54.8
I58C+	920	57.5	740	52.6
I58C-	920	57.9		
I59C+	890	58.2	800	56.4
I59C-	890	58.5	790	55.5

+ is increasing pH, - is decreasing pH

$$E = E^{\circ} + NpH$$

F. References

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V. SPUTTERED THIN FILM PH ELECTRODES OF PLATINUM, PALLADIUM, RUTHENIUM, AND IRIIDIUM OXIDES

A. Introduction

The measurement of pH as well as other ionic species in high temperature (over 100 °C) solutions has posed an interesting problem. The maximum useful temperature for glass electrodes is in the 100 °C range since higher temperatures lead to excessive drift related to sodium ion diffusion.

Several applications require better characterization of the solution at high temperatures: pH measurements of geothermal brines, corrosive liquids in contact with nuclear waste containers, pressurized steam/water lines in power generation, and various pressurized chemical reactors. Although special considerations must be made for each application, some general characteristics of an in-situ sensors are apparent. For example corrosion resistance is of paramount importance since these high temperature solutions are nearly all aggressive environments. If the sensor is to be used for an electrochemical measurement, it is necessary that no irreversible chemical reactions take place in the test environment since this would lead to measurement drift. The criteria for the selection of a high temperature pH electrode include a Nernstian or direct voltage to pH response, negligible ionic and redox interference, and minimum hysteresis and drift.

An evaluation of candidate materials for high temperature pH measurements was presented by Dietz and Kreider (1). The limitations of the glass electrode were presented together with a discussion of the merits of the $ZrO_2(Y)$ electrode. The stabilized zirconia electrode has very high impedance in the temperature range 100-200 °C and has led to further investigation of metal-oxide potentiometric electrodes. Fog and Buck (2) investigated a number of metal oxides including RuO_2 , PtO_2 , TiO_2 , OsO_2 , IrO_2 , RhO_2 , Ta_2O_5 , and SnO_2 produced from powders or oxidation of the metal. Their results indicated IrO_2 and RuO_2 held the most promise. More recently Karagounis, et al. (3) have demonstrated promise with sputtered PdO . The work of Katsube, et al. (4), Lauks, et al. (5), and our work (6,7) in-house has concentrated on sputtered films of iridium oxide (SIROF). However, problems with the stability of the SIROF (8) and its sensitivity to certain redox couples (9) have encouraged an examination of alternative sputtered oxide films.

In this study, the pH measurement electrode has been formed by reactive sputtering of a thin film of a conducting oxide on an insulating substrate. This permits the fabrication of a very small and very low cost sensor which has an electrical potential in tenths of volts versus a reference electrode, and needs only inexpensive instrumentation. In addition to the small size and low cost, the electrode can be much more rugged than a glass electrode. The oxides selected for the sputtered films described below are all good electrical conductors which further simplifies sensor design.

This study focusses on a comparison of selected sputtered metal oxides with iridium oxide which has received the most attention to date. Thin films were reactively sputtered as described below and tested for stability in harsh chemical environments, pH 2-pH 11. Also, the films have been characterized by

x-ray analysis x-ray photoelectron spectroscopy (XPS), and 4-pt electrical measurements.

B. Experimental

A planar magnetron was used in reactively sputtering the oxide from 5cm diameter metal targets. Metal purities were: Ir 99.99%, Ru 99.99%, Pt 99.99%, and Pd 99.5%. The total pressure during sputtering was 0.35 Pa after a pump down to a base pressure of $2-4 \times 10^{-4}$ Pa. Both single crystal silicon wafers [111] and high purity 99.6% Al_2O_3 substrates were used. Specific deposition parameters are given in Table I. The oxygen and argon measurements were made both with a capacitance manometer and a mass spectrometer. Temperature measurements were made in the 2.5cm thick stainless steel block heater which is used to mount the substrates during deposition. The thickness measurements were made considering the weight gain of the film and confirmed with a stylus measurement. Resistivity measurements were made with an osmium four point probe.

X-ray diffraction analysis was carried out on samples before and after annealing to determine the phases present and the nature of their crystallinity. An automated vertical goniometer was used with Cu K α radiation, theta compensating slits, and a diffracted beam monochromator.

Potentiometric measurements were performed in a stirred, air saturated, buffer solution (294-296 K) consisting of 0.02 M acetic, phosphoric, and boric acids and 0.1 M potassium nitrate (2). Potentials were measured versus a single junction Ag/AgCl reference electrode (+0.175 versus NHE).

C. Results

1. Platinum Oxide

The platinum oxide thin films were deposited on both silicon and aluminum oxide substrates as described in Table I. The film resistance drops from 20 Ω cm to 5×10^{-3} Ω cm when annealed at 420 °C for one hour which may indicate some reduction of the oxide.

The x-ray data from the platinum oxide deposition on silicon, before and after an air anneal at 420 °C, are shown in Fig. 1. The silicon (400) line at 69.2 degrees 2θ from both patterns, which extends well off scale, indicates the single crystal substrate's (h00) direction is perpendicular to the sample surface. The two peaks at 61.7 and 65.9 ° 2θ are the Cu K β and W L lines associated with the Si (400) line. The lower, as deposited, pattern consists a broad peak at 14 ° 2θ , and second broader asymmetric peak at 34 ° 2θ . These two peaks indicate d spacings of 6.3Å and 2.6Å which are approximately twice the (111) and (400) spacings of silicon. This indicates that the sputtering operation, from either a lattice strain or diffusion implantation mechanism, has induced symmetry to a doubled silicon lattice. The breadth of these peaks indicates the domain size of this doubled structure is extremely small, presumably the interface region between the deposition and the substrate. The substrate lattice itself is distorted to some depth allowing for the very sharp peak at 32.8 ° 2θ which is the (200) line of Si. The (200) is an allowed reflection but is normally extinct for the face centered cubic silicon cell.

Table 1
Sputter Deposition Parameters
for Oxide Electrodes

	Gas % O ₂	Temperature °C	Thickness	Resistivity
RuO ₂ 11	33	30	0.36	4-6
RuO ₂ 12	50	230	2	1-2
PtO _x 11	75(67)*	30	0.6	2x10 ⁵
PdO 11	50(40)*	30	0.5	200
IrO ₂ 55	50(50)*	35	0.4	4-6

*As determined by mass spectrometer.

Figure 1. X-ray diffraction patterns of platinum oxide films as sputtered (below) and after anneal at 420°C.

These features all disappear after the annealing operation indicating that the heat treatment is sufficient to return the silicon to the favored structure. The small peak at $56.3^\circ 2\theta$ is the (311) of silicon, indicating the presence of silicon crystals no longer epitaxial to the substrate.

The asymmetry of the broad peak at $34^\circ 2\theta$ is due to the amorphous hump in the region of 25 to $30^\circ 2\theta$ associated with the as deposited PtO_x , a second halo is located at $57^\circ 2\theta$. After annealing, the pattern is indicative of extremely fine grained PtO_2 , ICDD card #23-1306*, illustrated by the lines on Fig. 1.

The pH response of the platinum oxide films was 52 mV/pH when fresh but dropped to 27 mV/pH after 20 hr at a pH of 2.7 and dropped to 3-4 mV/pH when immersed in pH 7 for 70 hr. Fog and Buck had also noted problems below pH=5. The reactions of these films in the test solutions indicate they would not be useful as pH indicators in the nuclear repository.

2. Palladium Oxide

Palladium oxide films were deposited on silicon wafers and alumina circuitboard substrates as described in Table I. The x-ray data from the palladium oxide films on silicon are shown in Fig. 2. The orientation of the substrate is identical to that of the Pt films. The doubled silicon cell phenomena is also apparent. The initial height of the double cell (111) line is considerably greater than that of the Pt depositions, which the (400) reflection is less intense and narrower. This may indicate a difference in the damage induced to the Si lattice by Pd ions as opposed to Pt. None of the artifacts of the alterations silicon substrate are entirely removed by the annealing operation. The (200) line at $32.8^\circ 2\theta$ is seen to remain in the post anneal data, a small diffuse hump at $14^\circ 2\theta$ is observed. The (400) line induced at $34^\circ 2\theta$ is obscured by the 100% line of PdO . The two small peaks at 47.7 and $56.3^\circ 2\theta$ in both patterns are the silicon (220) and (311) lines respectively and indicate a small amount of silicon not epitaxial to the substrate.

The upper pattern indicates that after an air anneal at 420C the film consists of fine grained PdO , (ICDD #6-515). The lower, as deposited, pattern consists of a mixture of PdO and PdO_2 . The PdO of this film exhibits a smaller lattice parameter than that of the annealed film and the ICDD reference data. This may be due to excessive oxygen in the lattice. Two small sharp peaks at 35.6 and $54.5^\circ 2\theta$ indicate the presence of PdO_2 , ICDD #34-1101; shown by the series of lines on Fig. 3. The resistivity of the deposited film was approximately $2.0 \times 10^{-2} \Omega \text{ cm}$.

The pH response of two PdO films as deposited is given in Fig. 3. Although the initial response of the PdO film was similar to that of Karagounis et al., holding at a pH of 10.3 for 20 hr caused a severe drop in the potential-pH slope to 35-39 mV/pH (Table II). Exposure for another 50 hr at pH 9.8 caused further reduction of slope. A second series of tests including a 20 hr exposure at pH 9.0 caused a similar deterioration in the alkaline solution and indicated that our sputtered PdO would not be an appropriate electrode for the pH monitoring of the nuclear repository.

*International Center for Diffraction Data, Swathmore, PA 19081.

Figure 2. X-ray diffraction patterns of palladium oxide films as sputtered (below) and after anneal at 420°C.

Figure 3. pH Response of as Sputtered Palladium Oxide Films

pH Response after 20 Hrs at pH 10

Table 2
Response of Ruthenium, Iridium, and Palladium
Oxide Films after Exposure to Acidic and Basic Solutions

SAMPLE	FRESH mV° -mV/pH		2 Hr pH 2 mV° -mV/pH		6 Hr pH 2 mV° -mV/pH		24 Hr pH 2 mV° -mV/pH	
R12A6+	840	54.6	800	53.2	780	49.5	760	50.1
R12A6-	830	54.3	810	54.6	810	52.6	790	52.4
155A1+	850	55.0	780	54.0	730	50.7	690	47.9
155A1-	830	53.2	790	54.7	740	52.0	720	50.0
155A3+	980	54.4	860	52.4	800	52.4	730	43.8
155A3-	910	45.8	880	53.8	900	64.4	720	43.6

	FRESH		1 Hr pH 11		6 Hr pH 11		24 Hr pH 11	
R12A/+	850	46.1	820	53.8	780	47.6	680	40.2
R12A7-	830	46.0	820	50.0			690	41.4
155A4+	1000	46.9	890	49.5	830	43.4	720	35.6
155A4-	960	43.9	890	51.0	830	44.6	750	40.5
155A2+	900	57.9	790	53.4	750	49.2	610	33.5
155A2-	850	52.0	780	52.7	750	49.2	610	35.8

	FRESH		20 Hr pH 6	
Ru12A1+	890	55.6	910	53.9
Ru12A1-	930	59.5	930	55.7
Ru12A2+	900	56.6	900	53.0
Ru12A2-	930	60.4	920	55.3

	FRESH		20 Hr pH 2		20 Hr pH 10	
R11A4+	850	53.7	770	54.6	710	52.1
R11A4-	870	57.6	780	55.0	710	52.9
R11A5+	880	54.8	800	54.8	712	51.7
R11A5-	890	57.4	800	55.0	890	57.4
Pd11A3+	660	42.0			580	35.1
Pd11A3-	690	49.3			600	39.3

mV° indicates potential at pH = 0
+ increasing pH - is decreasing pH

3. Ruthenium Oxide

The most positive results were discovered with ruthenium oxide. Fog and Buck (2) have reported sensitivities of 61.8 mV/pH, plus good repeatability and little hysteresis between pH 2-12 with electrodes made from powders. It was hoped that the reactively sputtered films might demonstrate similar or better properties. Two types of films were tested: sputter depositions made at room temperature, and depositions made at 230 °C (Table I). The ruthenium oxide depositions on oriented silicon substrates are shown in Fig. 4. The as deposited, lower, pattern displays a diffuse pattern of RuO₂, ICDD card #21-1172; shown by the series of lines on Fig. 5. The upper pattern is seen to be complete and, which much sharper than the as deposited film, the breadth of the peaks indicates the fine grain size of the PdO₂ after annealing. The presence of the silicon double cell symmetry is seen to increase with the annealing operation, particularly indicated by the growth of the double cell (400) line at 34 ° 2θ. The distortion of the substrate lattice also increases. The silicon (200) line at 32.8 ° 2θ is barely discernable in the as deposited pattern, while it is significant after annealing. The appearance of the silicon (220) and (311) line again indicate the presence of non-epitaxial silicon in both RuO₂ specimens.

The high temperature deposits (R12), which have large grained crystals, had E ° values 0.89-0.93 V and slopes of 54-60 mV/pH in four tests. This performance is similar to the IrO₂. Exposure to the pH 2 solution for 20 hr caused a decrease in the potential-pH slope in the crystalline RuO₂ to 50-52 mV/pH. A typical response curve after 20 hr in pH 2 is given in Fig. 5. Modest changes in the formal potential, E °, to the range 0.76-0.79 V were also observed after the pH 2 exposure. Exposure to neutral pH solutions also caused a decrease in slope of 2-4 mV/pH. Some problems were encountered in testing sample R12A7 for pH 11 exposure; however, the tests on the room temperature deposited films R11A4 and A5 indicate little degradation of the slope after 20 hr at pH 10.

The RuO₂ formed at room temperature (R11) showed a sensitivity of 54-59 mV/pH (Table II) and an E ° of 0.85 to 0.89 V. Exposures to buffer solution at pH 2 or 3 for 20 hr did not decrease the sensitivity. Twenty hours at pH 10 caused small decreases in sensitivity 52-54 mV/pH, and E ° (0.71-0.73 V). This decrease in sensitivity was recovered by exposure to room temperature air (54-55 mV/pH) after 10 days. The pH cycling tests indicate that the RuO₂ produced and tested at room temperature by reactive sputtering performs as well or better than the iridium oxide films.

4. Iridium Oxide

The structure of sputtered iridium oxide films has been previously reported (8,9). At room temperature the films appear amorphous with x-ray diffraction and a clear rutile pattern emerges from films deposited at 200 °C and above. The most stable films are generally deposited at very slow rates (<2 nm/min) and at room temperature. The pH response of these films has also been reported (6,7,8,9) and elsewhere in this report. Generally, results to date indicate a decrease in E ° (the potential at pH=0) of about 150-200 mV developing in the first 24 hr exposure to buffered acid and basic solutions. Also a proportionately smaller decrease in slope is generally observed.

Figure 4. X-ray diffraction patterns of ruthenium oxide films as sputtered (below) and after anneal at 420°C.

Figure 5. pH Response of as Sputtered Ruthenium Oxide Films

Response after 24 Hrs at pH 2

In this study we tested the SIROF along side the RuO_2 and PdO films to ensure a useful comparison. The results of the iridium oxide film tests are given in Table II. A typical response of a SIROF after 24 hr at pH 2 is presented in Fig. 6 which indicates a 10% decrease in slope and 140 mV decrease in E° . It is interesting to note that the RuO_2 films appear more stable than the iridium oxide films in both acidic, pH 2, and basic, pH 11, solutions.

D. Thin Film Surface Analysis

Although there have been reports in the literature of the use of the PtO_x , RuO_x , and PdO_x as pH sensing materials (2,3,9), efforts have not been made to characterize the stoichiometry and structure (amorphous or polycrystalline) of the noble metal oxides. In addition, the form of the noble metal oxides used in these studies have ranged from high area bulk powders to thin films fabricated by electrochemical potential cycling or thermal decomposition of halide salts. Thus, there remain many doubts as to the compositional and structural identity of the materials used in the previous studies. We believe that full characterization of the sensing material is necessary to confirm its identity and better aid in understanding the mechanism of pH response. To this end we have used x-ray photoelectron spectroscopy (XPS) to characterize the surface and bulk composition of the sputter-deposited PtO_x , RuO_x , and PdO_x thin film pH sensors. XPS is a surface sensitive technique whereby the sample is irradiated with monochromatic x-rays which causes the ejection of photoelectrons. Kinetic energy analysis of the electrons yields the binding energy of the orbitals from which the electrons originated. The binding energy is characteristic of a given element, and, in favorable cases, the chemical state of an atom can be ascertained from small binding energy shifts. The intensity of a photoelectron peak can be used for elemental quantification with the aid of sensitivity factors. XPS is a surface sensitive technique and for the metal oxides examined here the spectra reflect information about the upper 20-30 Å of the material.

The details of the PtO_x , RuO_x , and PdO_x thin film deposition procedure are presented in Table 1. Samples RuO_x 12, PdO_x 11, and PtO_x 11 were examined with XPS. Wide energy XPS spectra of the PtO_x , RuO_x , and PdO_x thin films acquired under low energy resolution instrumental conditions are shown in Fig. 7. Photoelectron lines are designated by the orbital from which they originated, while Auger lines are designated by the Auger processes of KLL or MNN. All lines in each spectrum can be identified with an element. The expected Ru, Pd, Pt, and oxygen features are found in each spectrum. Also, the ubiquitous carbon contamination (C 1s at ~ 285 eV binding energy) from air exposure is evident in each spectrum except that of RuO_x where the Ru 3d peak overlaps the C 1s line. The spectra of the PdO_x and PtO_x samples indicate that sodium (Na 1s at ~ 100 eV) is a contaminant of these surfaces at a concentration of ca. 5% and 10% atomic concentration, respectively. The sodium contamination most likely originates from the glass substrate. It is somewhat surprising, however, that the sodium surface concentration is so high considering the fact that the depositions were performed at approximately room temperature. Apparently the sodium either diffuses through the growing film from the substrate or a sodium overlayer forms readily at the initial stage of film deposition and rides on top the growing film. The effect of the sodium on the pH response is unclear, but it is likely that some of the sodium dissolves into the solution during the measurement if it exists as an oxide, or it undergoes ion exchange reactions with cations in solution.

Figure 6. pH Response of as Sputtered Iridium Oxide Films

Response after 24 Hrs at pH 11

Figure 7

Wide scan XPS spectra acquired from sputter deposited RuO_x, PdO_x, PtO_x thin films.

More detailed chemical state information about the oxidation state of Ru, Pd, and Pt is gained from the high resolution spectra presented in Figs. 8, 9, and 10, respectively. The Ru $3d_{5/2}$ peak at 281.0 eV agrees well with binding energies reported for single crystal (10), sputter-deposited (11), and powder (12) RuO_2 indicating that Ru is in the +4 oxidation state. The broad Ru $3d_{3/2}$ line (at ~285 eV) is due to overlap with the C 1s peak that arises from surface carbon contamination.

The Pd $3d_{5/2}$ line at 336.8 eV is close to values reported for PdO in the literature when corrections are made for differences in calibration of binding energy scales (13,14,15). Together with the observation that the Pd 3d lines are relatively narrow and symmetric, we are confident that the Pd in the sputter-deposited film is in the +2 oxidation state.

The Pt 4f doublet peaks, on the other hand, exhibit relatively complex lineshapes. The broadness of the peaks and slight asymmetry on the lower binding energy side of the Pt $4f_{7/2}$ line suggest the existence of at least two chemically distinct states of Pt at the surface of the sputter deposited film. The 73.6 eV binding energy of the Pt $4f_{7/2}$ peak maximum matches well with values reported for both PtO and PtO₂ (16,17). There is no indication, however, of metallic Pt which would appear at a binding energy of 70.9 eV. It is emphasized that the XPS data is sensitive to the surface region only, thus we cannot with certainty conclude that the surface phase is characteristic of the bulk. Unfortunately, the XRD data of the as-deposited PtO_x film provides relatively little information about the stoichiometry of the bulk material, indicating only that the film is amorphous in character. To determine the surface stoichiometry more reliable XPS data is needed on platinum oxide surfaces of known stoichiometry, and we believe that this subject merits further investigation. The observation of a mixed stoichiometry surface phase leads us to theorize that the pH response of PtO_x could be fixed by the electrochemical equilibrium of two (or more) oxidation states of Pt. In support of this hypothesis, the PtO_x film electrodes exhibit substantial sub-Nernstian potential-pH responses (~30-40 mV/pH unit).

Further information about the chemical state of the oxides can be obtained from the valence band region of the XPS spectra at low binding energy. The valence band region is commonly used as a "fingerprint" of chemical state of a compound. The valence bands of the PtO_x, RuO_x, and PdO_x sputter-deposited thin films are displayed in Fig. 11. For the metal oxides examined here the valence band region is comprised of O 2p orbitals (between ~ 3 and 20 eV) and the 4d orbitals of Pd and Ru and 5d orbital of Pt (between ~0 and 4 eV). Note that there exists a significant density of states for all the oxides at the Fermi level (~ 0 eV) which is consistent with the electrically conductive nature of the oxides. The valence band of RuO_x is almost identical to that published for polycrystalline RuO_2 samples prepared by decomposition of Ru halide salts and thermal oxidation (18,19). The shape of the valence band of PdO_x resembles that in the literature for PdO which is consistent with the Pd 3d data (13). The PtO_x valence band is more complex in shape and the Pt d band component is significantly broader than that of the other oxides. The broad shape of the Pt 5d band suggests a distribution of different chemical environments for Pt. Unfortunately, the valence bands of various platinum oxides have not been reported in the literature so we are not able to make a more definitive assignment of the Pt chemical state(s).

Figure 8

High resolution XPS spectrum of the Ru 3d region obtained from a sputter deposited RuO_x film.

Figure 9

High resolution XPS spectrum of the Pd 3d region obtained from a sputter deposited PdO_x film.

Figure 10

High resolution XPS spectrum of the Pt 4f region obtained from a sputter deposited PtO_x film.

Figure 11

XPS valence band spectra acquired from sputter deposited RuO_x , PtO_x , and PdO_x thin films.

Figure 12

High resolution spectra of the O 1s region obtained from sputter deposited RuO_x , PtO_x , and PdO_x thin films.

The hydration state of the oxides can be assessed by examination of the XPS 0 1s region that are shown in Fig. 12. The 0 1s peaks of RuO_x and PtO_x are relatively broad and exhibit tailing to the higher binding side which is evidence for -OH and H_2O in the surface region. We assume that the hydroxylation of the surface and adsorption of water occur upon exposure to atmospheric humidity. Some of the tailing can be attributed to relaxation or final state effects, but cannot account for the higher binding energy features entirely. The overlap of 0 1s peak of PdO_x with the Pd 3p_{3/2} line at ~534 eV precludes a lineshape analysis for surface hydration; however, it is likely that some surface hydroxylation of the PdO_x has occurred as in the case of the other oxides.

E. Conclusions

The response of palladium oxide and platinum oxide films for pH (2-10) measurement was observed to be less stable than would be required for use in the nuclear repository. Sputtered ruthenium oxide films, however, compared favorably to sputtered iridium oxide films between pH 2 and 12. Both amorphous and crystalline RuO_2 films were comparable to the SIROF's. The room temperature sputter deposition of PdO led to a crystalline cubic structure. Both PtO_x and RuO_2 room temperature sputter deposition led to an amorphous structure similar to IrO_2 and the crystalline phase was developed during annealing at 420 °C. The surface chemical state of the as-deposited PtO_x , RuO_x , and PdO_x films has been investigated using XPS. The results can be compared to our previous report on thin film IrO_x pH sensors (20). The XPS binding energy of the Pd 3d_{5/2} line and valence band lineshape obtained from the PdO_x film indicate that the surface stoichiometry is predominately PdO. The XPS binding energy of the Ru 3d_{5/2} line and valence band lineshape obtained from the RuO_x film indicate that the surface stoichiometry is predominately RuO_2 . Valence band and Pt 4f data from the PtO_x film are more complex and suggest that the surface regions contains Pt in at least two different oxidation states. In addition it is likely that all the films are hydrated to some extent at the surface.

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VI. CONCLUSIONS

- Sputtered iridium oxide films (SIROF) were evaluated for measuring pH under conditions too severe for standard glass electrode measurements.
- A standard test sample and test method were developed and evaluated for pH testing of thin films. Reactive sputtering was used to deposit the iridium oxide film on aluminum oxide circuitboard and a simple partial submersion of the film in the analyte produced an indicative electrode potential versus a Ag/AgCl reference electrode.
- The test sample and resultant output of the pH indicative film were not sensitive to geometry of submission or room air contact with the buffer solutions.
- SIROF pH sensors were found to yield a potential output with a linear dependence on pH (approximately -57 mV/pH) between pH 2 and 12.
- The pH response of the SIROF is related to temperature as predicted by the Nernst equation.
- The most stable and consistent films were reactively deposited with 0.2 Pa of O₂ and 0.2 Pa of Argon as the sputtering gas and very low deposition rates (0.4 Å/sec) and the addition of H₂O to the sputter gas appeared to "pre-age" the films leading to less drift.
- Little hysteresis was found in the pH response cycled between 2 and 12.
- The standard potential of the SIROF was, however, sensitive to electrode history and a slow drift leads to lower (0.2 V) potential output which stabilizes after several days.
- Calibration of the sensor can permit accuracies of ± 0.1 pH units.
- The SIROF generated a titration curve almost identical to that of a glass electrode when monitoring the titration of phosphoric acid with sodium hydroxide.
- The response time of the SIROF electrode was comparable to that of the glass electrode for both small (0-1) and large (>2) changes in solution pH.
- SIROF electrodes did not show sensitivity (<2 mV) to alkali metal cations (Li⁺, Na⁺, K⁺) up to 0.1M over a pH range of 3 to 12.
- Very small response (<10 mV) was measured in response to 0.01M concentrations of Mg²⁺, Ca²⁺, Cu²⁺, and Ni²⁺.

- The SIROF sensor had strong redox sensitivity to solutions containing ferri-/ferrocyanide [$\text{Fe}(\text{CN})_6^{-3/-4}$] and iodide ions.
- SIROF electrodes exposed to buffered solutions of pH 4, 7, and 10 at 200 °C (15 bar) for 20 hr still had good, linear pH response.
- SIROF electrodes exposed to buffered solutions of 4, 7, and 10 at 250 °C (40 bar) for 20 hr were damaged, only the samples exposed at pH 10 resisted degradation.
- Both high temperature (230 °C) depositions of crystalline IrO_2 and room temperature depositions resisted degradation at 200 °C.
- Enhanced bonding procedures were needed for adherence to the Al_2O_3 substrates at 200 °C and above.
- The successful bonding procedures included ion beam cleaning and the use of a chromium bond coat for 200 °C acidic and basic solutions.
- Neither palladium oxide nor platinum oxide films had sufficient stability in pH solutions (3-11) to succeed as a sensor.
- Sputtered ruthenium oxide films performed as well as or better than the iridium oxide films in pH 2-11 solutions.
- The sputtered ruthenium oxide films had high electrical conductivity and appeared to have properties suitable for a pH sensor.

VII. RECOMMENDATIONS FOR FUTURE PROJECTS

In the course of iridium oxide pH sensing research performed at NIST, we have become aware of related research projects that could have a beneficial impact on problems of concern to the NRC and other technologically important areas. A list of these research projects directed toward improved pH sensing in hostile environments like those encountered in nuclear repositories is presented below.

A. Iridium Oxide pH Sensing Microelectrodes

The work at NIST has dealt exclusively with iridium oxide macroelectrodes with areas of approximately 1 cm^2 or greater. A question that arises is how small can an iridium oxide electrode be made and still function as a pH sensor. Such microelectrodes could provide the means to measure very local pH changes. This capability could lead to new understanding of the mechanisms involved in areas such as pitting, crevice, and crack corrosion. Application of such a new knowledge base would be beneficial for the assessment of potential materials as candidates in the area nuclear waste containment. The desired dimensions of an electrode for measurement of pH in a developing pit or crack on a corroding metal surface would be on the order of tens of microns or less. Sensors of this size would open up new areas of pH monitoring for corrosion research and also would be extremely useful in a variety of applications, e.g., in measuring pH gradients found in biological structures.

B. Reference Microelectrodes

Implementation of an iridium oxide pH microsensor would require the development of a reference microelectrode. It is desirable to locate the reference electrode in close proximity to the pH sensing element to minimize possible solution resistive potential drops in the measuring circuit.

C. Ruthenium Oxide (RuO_2) pH Sensors

Results from initial investigations performed during the research work reported here indicate that RuO_2 thin films prepared by sputter deposition exhibit pH sensing behavior that in many respects may be superior to that of iridium oxide thin films. RuO_2 thin film sensors show near nernstian potential-pH response with little hysteresis and should be as corrosion resistant as iridium oxide. A more detailed investigation of the effect of fabrication conditions on the electrochemical behavior of RuO_2 thin film electrodes is necessary to more fully ascertain their potential drift characteristics, response time, and sensitivity to ionic and redox interferences. A more detailed, systematic study of the RuO_2 sputter deposition parameters would also be desirable to optimize the RuO_2 pH sensing behavior. In addition, characterization of the RuO_2 specimens via X-ray diffraction, electron microscopy, surface analysis, and electrical measurements would be in order to correlate observed pH response with chemical and structural properties of the thin films.

D. Further Refinement of Iridium Oxide pH Sensors

Despite the extensive studies performed on iridium oxide thin film pH sensors, several issues have arisen during the course of our investigations that, if addressed in greater detail, could lead to a substantial improvement in the pH sensing capabilities of these electrodes. A still nagging issue is the role that hydrogen plays, both in the bulk and at the surface of the films, in influencing the potential-pH response of the sensors. This may be due to changing hydrogen content in the films that is in turn responsible for the observed potential drift (both the potential-pH slope and intercept) of the sensors. We suggest that correlation of the film's hydrogen content with pH response be performed. Such a rigorous study of the effect of hydrogen content has not been performed to our knowledge and could lead to a much greater understanding of potential drift in conductive metal oxide pH electrodes.

Other issues that require further attention are (1) development of methods to eliminate or to control potential drift, (2) the radiation resistance of iridium oxide thin film sensors, and (3) the examination of the radiation stability of standard pH buffers. (Results from a study could greatly impact the methodology used to calibrate pH sensors for use in nuclear repositories.)

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11. ABSTRACT (200 words or less)

This report focuses on evaluation and characteristics of sputtered thin film pH electrodes which can be used to assess the corrosivity of hot (100°C) aqueous solutions present in nuclear repositories. Sputtered thin films have the advantages of high temperature capability, ruggedness, and low cost.

The iridium oxide films were found to have a linear, 58mV/pH, response to changes in pH. They had little hysteresis but drifted approximately 0.2V over a period of two days exposure to pH 2-12 solutions. The films were found to be insensitive to interference from most ions such as alkali ions but had redox sensitivity to ferri-/ferrocyanide ions. Although special surface treatments were needed for the films for good adherence at 200°C the films were not degraded after 20 hours exposure at pH 4, 7, and 10 at 200°C. Ruthenium oxide sputtered films performed equally well to the iridium oxide films in parallel tests.

The report also contains information on electrochemistry and testing of thin film electrodes and the characterization of the thin films by x-ray photoemission spectroscopy, ultraviolet photoemission spectroscopy, and ion scattering spectroscopy.

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