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Review of Materials for pH Sensing for Nuclear Waste Containment

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

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Review of Materials for pH sensing for Nuclear Waste Containment

I. INTRODUCTION

The continuing investigation by the Nuclear Regulatory Commision into the encapsulation and disposal of high level radioactive waste requires an availability of sensors for long term, insitu, high temperature, corrosive environment pH measurements. pH sensors are also needed for laboratory measurement applications and for monitoring deep geologic aqueous fluids. In both cases, the most immediate need is to model accurately and predict the long term viability of the various proposed waste encapsulation schemes. Laboratory measurements of encapsulation corrosion processes and rates and the subsequent modeling efforts require accurate in-situ pH measurements. The other application is the eventual monitoring of the pH in deep geologic nuclear waste repository sites. These measurements are intended to indicate the effectiveness of the waste containment procedures. Prediction of metal container viability as a function of the accelerated pit corrosion processes is one of the key issues in the evaluation of proposed waste disposal technologies.

This report defines the performance criteria of the needed pH sensors and reviews the performance of a number of elevated temperature pH sensing technologies with respect to these criteria. The criteria of electrode performance were developed to predict the utility of various pH electrodes in these simulated environments. The classes of pH electrodes reviewed are the glass electrode, yttria stabilized zirconia, palladium hydride and a variety of metal oxides.

The latter sections of the report focus on a relatively new solid state electrode material, reactively sputter deposited iridium oxide. The performance of this thin film material is of particular interest because its low electrical resistivity and high corrosion resistance eliminate some of the shortcomings of the glass and ceramic materials. The reactive sputtering technology permits these films to be deposited and pattern defined on a wide variety of substrate materials. Low electrical resistivity, which simplifies electrical contacts, and a flexible deposition technology make this material a prime candidate for micro pH sensors. These pH sensors would be small enough to measure the corrosion chemistry in high aspect ratio corrosion pits.

II. CRITERIA FOR pH ELECTRODE EVALUATION

This report evaluates high temperature pH electrodes according to the following criteria:

1. Nernstian response (where the voltage is proportional to log of the activity) to [H+] and temperature from pH 1-14.
2. Ionic and redox interference.
3. Hysteresis and long term stability.
4. Corrosion resistance and mechanical robustness.

Four classes of electrodes will be considered: glass, ceramic, palladium hydride and metal oxides. Of particular interest is the predicted performance of these electrodes in aqueous solutions simulating expected repository site conditions.

The two types of repository sites receiving primary interest at present are the salt bed and basalt flow geologic formations. These repositories are expected to have slightly elevated pH, pH 9-10, and temperatures primarily between 90° and 160°C. More extreme conditions are possible, including temperatures up to 260°C and pH 11. However, for laboratory investigation of corrosion rates, satisfactory electrode performance in conditions less stringent and more representative of the majority of expected storage environments, was assumed to be useful.

Information on ionic concentrations that can be expected is available, but information on redox levels is not definitive for basalt flows and apparently unavailable for salt beds. As indicated by Table 1, salt beds are characterized by high dissolved solid concentrations and the basalt flows by much reduced concentrations. The salt bed data was taken from compositional analysis of fluid inclusions in the Salina Salt Bed. The data on basalt ground water was obtained from samples taken out of the Grande Ronde Formation, Columbia River Basalt Group. The two sets of data are included to indicate to what extent ionic interference effects will impinge on electrode pH selectivity.

Hysteresis and long term drift are indications of an electrode's usefulness in extended studies of corrosion and corrosion rates. Hysteresis indicates irreversible electrode processes which will almost certainly result in a gradual decrease in electrode performance or steady corrosion. These processes and others result in electrode drift, which necessitates frequent recalibration. Recalibration may not always be convenient.

The corrosion resistance and mechanical robustness of an electrode are particularly relevant if the device is to be used in the field or for corrosion studies over extended periods of time. Often, even fragile or awkward mechanical designs can be implemented in a laboratory, if sufficient care and ingenuity are employed. However, such designs are often inconvenient and unreliable. The design of effective electrode seals for high pressure autoclave systems is made more difficult by fragile electrode materials. For the rugged demands of field testing and implementation, the robustness and corrosion resistance of electrode systems are particularly desirable.

Table 1

Approximate Molar Concentrations of the Aqueous Media Existing in the Proposed Repository Sites

Species	Salt(1)(M)	Basalt(2)(10^{-3}M)
Na^+	3.0	13.0
Cl^-	3.1	7.9
K^+	0.09	0.1
F^-	3.05×10^{-3}	1.8
Si	-	1.14
Ca^{+2}	0.34	0.07
Mg^{+2}	0.07	0.01
F_e	-	$<2 \times 10^{-4}$
As	-	$<3 \times 10^{-3}$
SO_4^{-2}	0.47	1.8
CO_3	-	1.2
pH	-	9.7

(1) Physical Properties Data for Rock Salt, L.H. Gevantman, ed. National Bureau of Standards, Dept. of Commerce, NBS Monograph 167 issued January 1981.

(2) D.L. Lane, T.E. Jones, M.H. West, "Preliminary Assessment of Oxygen Consumption and Redox Conditions in a Nuclear Waste Repository in Basalt", Geochemical Behavior of Disposal Radioactive Waste, ACS Symposium Series 246 (1984).

III. GLASS ELECTRODE

The combination glass electrode has, for many years, been the preferred method for measurement of pH in aqueous solutions. The glass electrode responds in a Nernstian manner to pH and is insensitive to the redox potential of the solution. It is not poisoned by, nor does it respond to, common electrode poisons such as cyanides, sulfides, chloroform, phenols, alkaloids, and salts of the noble metals. Dissolved gases such as O_2, H_2 and N_2 also do not affect the electrode response[1]. For most aqueous pH measurement environments at ambient and slightly elevated temperatures, the glass electrode is the electrode of choice, because of its hydrogen ion selectivity.

In extreme or harsh environments, the glass electrode technology has sometimes proved inadequate. The glass electrode is known to exhibit sodium ion error in high pH solutions, especially at higher temperatures[2]. Elevated temperatures above 150°C and particularly above 200°C have been reported to degrade electrode performance due to leaching and glass corrosion phenomena[3].

Response Mechanism

The mechanism of the glass electrode pH response is rapid hydrogen ion exchange at the hydrated silicate glass surface. The glass electrode phase boundary potential between the surface of the glass and the electrolyte solution is dominated by the hydrogen ion concentration or activity in the solution. Presumably, the high mobility and lability of the hydrogen ion is responsible for hydrogen ion exchange processes dominating all other exchange equilibria[1].

For solutions of high pH, cations other than hydrogen, affect the phase boundary potential and the potential measured is no longer Nernstian with respect to pH. As the concentration ratio of hydrogen ions to cations such as Na^+, K^+ and Li^+ decreases as the pH is increased, cation exchange begins to compete favorably with hydrogen ion exchange processes. The result is that above pH 10, glass electrodes begin to exhibit cation interference.

Lithia containing glasses have replaced sodium based glass compositions for elevated temperature pH measurements. Lithia glasses exhibit both reduced sodium ion error and increased response linearily in high pH solutions. The improved corrosion resistance of the lithia glasses is achieved by decreasing the lithia to silica ratio. The lower limit to the lithium: silica ratio is determined by the desired electrode impedance. Decreasing lithia increases the impedance of the electrode. The impedance of the lithia based glass formulations is greater than 10^9 cm at 100°C[3]. This impedance is comparable to that of yttria stabilized zirconia electrodes at 100°C. These glasses also display a sub-Nernstian pH response which becomes more severe after exposure to high temperature, high pressure measurement environments.

2. Internal Reference Electrode and Electrolyte

The internal reference electrode and electrolyte have been chosen to establish stable, well characterized potentials across the inner glass membrane surface/electrolyte-fill interface and the electrolyte-fill/solid state reference electrode interface. Ag/AgCl electrodes have been a common choice for the inner reference. AgCl has been reported stable at elevated temperatures except in alkaline solutions or solutions containing dissolved H_2S and H_2[5]. The electrolyte fill can be selected such that it is low pH and contains no dissolved, interfering gases.

Some speculation has been made concerning the long-term stability of the Ag/AgCl electrode. Hydrolysis of AgCl to AgO and gradual dissolution of AgCl into solution are possible electrode degradation mechanisms[6]. Elevated chloride concentration in the filling solution can inhibit these degradation processes.

The choice of electrolyte fill is also critical in minimizing asymmetry potentials across the glass membrane. An asymmetric potential between the internal and external membrane interfaces can occur due to[1]:

a. Unequal leaching or corrosion of the glass surfaces.

b. Mechanical or chemical damage to the external surface.

c. Disturbance of exchange capacity for hydrogen ions with the adsorption of foreign ions, grease, proteins and surface active agents. Leaching, corrosion and other damage to the internal surface of the membrane can be reduced by choosing a low pH, high concentration fill. The buffers often used for ambient temperature pH electrodes, in particular, low pH buffers generally exhibit a temperature dependent pH variation and are poorly characterized at elevated temperatures. Low pH fills are desirable because the reduced pH results in reduced glass corrosion[5]. High salt concentration fills are thought to reduce leaching of the internal glass surface[3], which results in a stable potential across the inner membrane interface.

The buffers employed as filling solutions for ambient temperature pH measurements are unsuitable for elevated temperature measurements. Low pH buffers, which minimize corrosion, are too dilute, possess insufficient buffer capacity and exhibit temperature dependent pH variations that are poorly characterized at elevated temperatures.

3. Extended Operation

The glass electrode has performed poorly during extended exposure to aqueous environments above 150°C and at pH higher than neutral. Corrosion and leaching degrade the pH response and cause long-term drift. From 1978-1980, the Department of Energy funded the development of corrosion resistant glass pH electrodes for in-situ measurement of geothermal fluids. The Division of Geothermal Energy independently funded both Owens-Illinois and Leeds and Northrop, through Pacific Northwest Laboratory. Both efforts experimented with the durability of various glass compositions containing silica, 10-30% lithia and 5-10% other oxides.

The DOE sponsored efforts produced several glass compositions that did not suffer substantial corrosion below 200°C, but between 150-200°C exhibited a gradual degradation of pH response. Most commercial pH glass compositions evidenced substantial corrosion even below 150°C. Of the few newly synthesized glass compositions that survived 200°C autoclaving for 24 hours, autoclaving for four hours at 250°C resulted in a 30% degradation of pH response.

Degradation is attributed to two separate processes, leaching and hydration. Leaching of the silica glass modifiers, Li_2O, Cs_2O, lanthanum oxide, and alkaline earth oxides, occurs in high temperature water and results in an increased electrical impedance and reduced pH response. High temperature water, particularly above neutral pH, also hydrolyzes the SiO_2 glass matrix. According to Filbert et al.[5], silica is readily attacked by alkali but rarely, if at all, by acids. Below pH 7, alkali or alkaline earth ions are replaced by H^+, but the original glass matrix of Si-O-Si bonds is unaffected. Alkali solutions differ in their mode of attack in that Si-O-Si bonds are broken to form Si-O-Na and Si-OH, whereas for acids only SiOH forms at the sites of leached alkali or alkaline earth ions. Since the impedance of the glass electrode is comparable to that of the yttria stabilized zirconia electrode at 100°C, the zirconia technology must be given strong consideration because, as explained in a subsequent section, it performs well in alkaline brines.

Due to these corrosion processes, the glass electrode which is not useful even for short periods above 200°C, is useful for several hours at temperatures between from 150 and 200°C.

It is of potential utility at 100-150°C for measurement of pH over extended periods. Above 250°C, hydrolysis of the Si-O-Si matrix occurs at substantial rates. Below 200°C, the primary mode of degrdation is leaching. Hydrolysis and leaching can both be roughly modeled by first order kinetic dependencies on temperature and pH.[2,3,5] Neither Owens-Illinois nor Leeds and Northrop report extended in-situ measurement of pH between 100-150°C. However, the results of the higher temperature survival tests and reported first order kinetic degradation processes are indications that glass electrodes are viable at 100-150°C and should be capable of accurate, stable pH measurement for extended time periods.

4. Expected Performance

The glass electrode technology can be expected to provide reliable measurement of pH from 100-150°C. However, the presence of large concentrations of alkali metal ions, such as Na^+, will interfere with the electrode response in alkaline solutions. Since the corrosion resistance also decreases with increasing pH, the glass electrode is not expected to be very useful in elevated temperature, alkaline brines. The high impedance of lithia glasses below 150°C makes calibration at ambient temperatures difficult, particularly since these glasses exhibit subNernstian responses. Calibration is only accurate in this case if done at the operating temperature. Attempts to reduce impedance by fabricating thinner glass membranes are constrained by durability and mechanical strength considerations.

IV. YTTRIA STABILIZED ZIRCONIA

Yttria stabilized zirconia sensors are the most developed and presently viable technique for pH measurement at 150°-300°C. Early prototypes designed by Niedrach at General Electric[7] resembled the mechanical construction of glass electrodes, a ceramic tube with an internal electrolyte and reference electrode. Later models developed by Niedrach[8], and MacDonald and Tsurata[9], used solid internal fills such as Cu/Cu_2O as an electronic-ionic contact to the internal surface of the insulating, ionic conducting zirconia membrane [see Table 2]. Early experiments established that these membrane electrodes exhibited nearly Nernstian response at elevated temperatures and appeared to exhibit little sensitivity to interfering ionic, redox and other easily reduced aqueous species.

Recent published efforts by D.D. MacDonald, S. Hettiarachi and P. Kedzierzawski at SRI International[10,11] and separate work done by M. Danielson, H. Kosk and J. Myers at Pacific Northwest Laboratory[6,12,13] have focused on improving the accuracy and temperature range of these sensors. They have investigated the suitability of ceramics from different vendors with varying yttria concentrations, the efficiency of various internal electrode schemes and sealing procedures, the effects of extended exposure to interfering species, and the mechanisms of the long term degradation of sensor performance. This section on zirconia pH sensors will discuss the state-of-the-art, briefly mention some intimately related questions regarding internal reference electrodes and indicate the limitations experienced by these electrodes at present. This discussion is intended to indicate the present utility of these electrodes and which aspects of electrode design might merit further development.

1. pH Electrode Performance

The electrode performance reported by the groups at GE, SRI,and PNL is summarized in Table 2. All three groups report a linear open circuit potential response as a function of log [H^+], with little, if any, observed interference from O_2, H_2, Na^+, Cl^- and H_2S. The slope of the response is generally observed to be approximately 10% less at 100°C than the theoretical Nernst figure of 2.303 RT/F, but the disparity generally decreases as the temperature approaches 300°C[6,11]. The improved performance of the zirconia membrane above 250°C has been attributed to ion conduction which increases with increasing temperature[7,11,13]

2. Mechanism of pH Response

The mechanism for the pH response of ceramic zirconia membranes is oxide ion conduction. The indirect relationship of oxygen concentration in the aqueous phase and pH, establish the pH dependent potential drop across the solid ion conductor, zirconia, and the aqueous solution interface. Calculation of activation energies from membrane impedance vs. temperature plots show the activation energies to be very close to those of high temperature oxygen sensors[12,13,14]. The correspondence of activation energies implies an oxide ion conduction mechanism for the zirconia pH sensor.

The low temperature (<200°C) pH response has been correlated with the electronic impedance. Various stabilizing oxides have been added to zirconia to reduce the impedance, but 8-10% yttria is apparently close to the optimum composition[73]. Impedances around 10^9 at 100°C cause several problems. Noise and spurious charging are serious problems; Faraday cages are often required to provide electromagnetic shielding. Electrode response time and the observed open circuit potential are affected by resistive shunts intrinsic to the ceramic, the hermetic sealing and/or the input impedance of the electrometer. The

Table 2

Comparison of Yttria Stabilized Zirconia pH Electrodes

General Electric	SRI International	Pacific Northwest Lab
8% Yttria, Corning Glass Works	9% Yttria, Coors Ceramics	8% Yttria, Corning Glass Works
Cu/Cu_2O internal reference	Cu/Cu_2O, Ag/HgO internal reference	(Cu/Cu_2O), Pt internal reference
Linear response to pH 95-285°C, pH 3-9	1:1 pH response relative to the standard hydrogen electrode, 125°-275°C, pH 2.5-9.0; >90% theoretical Nernst slope	Linear response to pH 85°-300°C, pH 3-9.5; >90% theoretical Nernst slope
An initial calibration spread of 0.5 pH units amongst the three sensors tested		E_0 for a number of tubes falls within ±0.5% of a pH unit
Insensitivity to 100 ppm sulfide, free from sodium ion error	Insensitivity to O_2, H_2, Cl-, 780 ppm S^{-2}; insensitive to pressure variation of 200-1000 psi	Insensitive to the redox potential
Sensors responded poorly at 95°C after operation at 285°C	Report sluggish performance below 150°C; results of thermal cycling not reported	Thermal cycling (T>250°C) results in sub-Nernstian response at lower temp.
Stress cracking of the ceramic at the sealing collar; corrosion resistance to 20% NaCl and 100 ppm H_2S	Report sealing difficulties	Report sealing difficulties

resistance of the ceramic to the formation of small cracks, the effectiveness of the high pressure seal around the brittle zirconia tube, and the ohmic/ionic intimacy of the internal electrode determine the accuracy of low temperature pH measurements.

3. Internal Electrode Schemes

The first internal electrode used by Niedrach was a Ag/AgCl type inserted into the zirconia tube filled with a potassium chloride solution[7]. Difficulties with long-term drift due to changes in the concentration of the internal electrolyte, deterioration of the Ag/AgCl electrode and sealing difficulties posed by the vapor pressure of the hot internal electrolyte solution led to the consideration of several solid fill internal electrodes. Solid fill electrodes were hoped to possess long-term stability, thermodynamic reversibility and physical characteristics permitting simple, effective sealing at high temperature and pressures. If the internal electrode is not reversible, space charge or other polarization phenomena will cause unreproducible open circuit potential readings. An electrochemical equilibrium must exist to connect reversibly the pure electronic conduction of the internal metal electrode with the ionic conduction of the zirconia ceramic[13].

Cu/Cu_2O[7,8,9], Hg/HgO[11], Ag/Ag_2O,[11], Ag[13] and Pt[13] have been tested as internal electrodes. Hettiarachi; et al.[11] found the Cu/Cu_2O filled tubes to exhibit unreproducible responses. X-ray diffraction indicates an irreversible decomposition of Cu_2O; this decomposition results in the expansion of the internal electrode material, placing the ceramic tubes under mechanical tension[11,13]. The Ag/Ag_2O fill was also shown by x-ray analysis to degrade[11] as the Ag_2O thermally decomposes to Ag.

Hettiarachi, et al. demonstrated stable electrode performance with a Hg/HgO internal electrode[11]. They assert the stability of the Hg/HgO internal reference electrode[11] at their operating temperature (<275°C) was "beyond any doubt". As communicated by M. Danielson, operating stability is not necessarily evidence of reversibility[14]. Further evaluation of the reversibility of the Hg/HgO half cell appears to be indicated if it is to be used in experiments involving extended periods of time. The Hg/HgO must also be used with discretion, because mercury has a high vapor pressure and boils at 356°C. Mercury is also very toxic.

M. Danielson[13], et al. reports the application of metallic paint to the internal surface of the zirconia tube. The authors suggest that the loss of pH response after the sensor was at ambient temperature for several days was due to the adsorption of water at the metal-zirconia interface. Water at the interface may interfere with the electrochemical conversion of oxygen into the oxide ion, resulting in a net polarization.

Recent work at PNL has resulted in a platinum internal electrode which, from thermodynamic evidence, appears to be reversible[6]. The bottom two cm of the zirconia tube is coated with a platinum ink and fired at 400°C for 18 hours. Electrical contact to the platinum film is made with a metal spring contact. The advantages of the platinum internal electrode are:

a. It appears to be reversible, which should result in long term stability.

b. Contact of metal to ceramic is intimate, resulting in an order of magnitude reduction in total impedence of the electrode over the powder fills.

c. The electrode is poised after the 400°C firing and does not need to be "seasoned" at high temperature in the autoclave.

d. The E_0 (the pH=0 intercept) appears to be within a range of 10 mV for all the sensors tested, consequently simplifying calibration procedures.

4. Calibration and Associated Reference Electrode Questions

Some of the most difficult and important problems associated with high temperature pH sensing are calibrating the pH electrodes and implementing well characterized buffer solutions and reference electrodes. The performance of reference electrodes and buffer solutions with increasing temperature, particularly above 200°C, has been addressed, but there is certainly a need for further investigation. The development of the pH zirconia sensor is hoped to provide a tool for making direct measurements of hydrogen ion concentrations. "The lack of a simple and reliable pH electrode for environments above 100°C has been a great impediment to assembling the thermodynamic data base to make aqueous chemistry at elevated temperatures a quantitative science[13]". Since the zirconia electrodes operate best at 250-300°C, it is important to understand their performance and the aqueous solution chemistry at these temperatures in order to characterize their behavior at lower temperatures. At this temperature, electrode impedence is substantially increased and slopes drop further from the theoretical Nernst response. With most other pH electrode systems, high temperature measurements are an extension of low temperature measurements; the zirconia membrane is different in this respect.

Calibration of a pH electrode requires establishing the E_0 and the slope of the open circuit potential (OCP). E_0 is generally taken to be the y-intercept of the OCP. Its temperature dependence can be calculated[11,13] using theoretical hydrogen-oxygen electrode potentials under standard conditions. The actual value of E_0 varies amongst zirconia tubes from the same supplier, from different internal electrode systems and different preconditioning histories. Differences amongst internal electrode systems emphasizes the necessity of a reversible system. An irreversible system is far more likely to accentuate preconditioning history differences.

The PNL group investigated the effect of preconditioning on electrode performance and report reduced preconditioning sensitivity and improved low temperature performance for a platinum internal electrode. They report that sensors with Cu/Cu_2O, Ag/Ag_2O, Ag and graphite filled electrodes require "seasoning" in the autoclave at temperatures exceeding 250°C. Between 250° and 300°C, newly made Cu/Cu_2O or silver fill sensors suddenly jump several hundred millivolts (several pH units) in the oxidizing direction and become poised by oxygen. Once the electrodes are poised (preconditioned), returning them to 100°C does not reverse the poising. However, if the sensor is allowed to sit at ambient temperatures for more than a few days, it is no longer *poised* to oxygen and suffers significant loss of pH response. Returning the electrodes to 250°C results again in oxygen *poised* electrodes[13]. Not only is the necessity for "seasoning" inconvenient, and an indication of non-equilibrium processes, but the high temperature seasoning degrades the long-term stability of the sensor for low temperature measurements. Some apparently irreversible phase or structural change[11,13] occurs at 250300°C which does not affect the high temperature performance of the sensor, but does result in reduced sensor longevity for low temperature pH sensing. Changes in the ceramic during extended autoclaving periods is discussed in more detail in the subsequent section on long-term stability.

The platinum fill electrodes developed by PNL[6] give immediate thermodynamic potentials without the need for a 300°C autoclaving and have a greater than 90% Nernstian pH response at 100°C. After 30 days at 100°C, this sensor retained a greater than 90% response. Presumably sensor performance improves as the temperature increases. The authors claim that if the pH accuracy required is only a few tenths of a pH unit, then calibration is not necessary[6]. This implies that both E_0 and the slope of the response are reprodicible from electrode to electrode to within a few percent.

Recent work at SRI which compared the pH response of 9% yttria tubes to that of a standard hydrogen electrode placed in the same autoclave establishes a pure Nernstian response for the zirconia electrodes. Earlier measurements were not as definitive, because of uncertainties in buffer behavior of elevated temperatures, particularly at low pHs[11], and uncertainties in the accuracy of several reference electrode schemes[15,16,17] Hettiarachchi and coworkers measured the OCP of a Hg/HgO zirconia sensor and an internal reference hydrogen electrode against an external Ag/AgCl reference electrode. They report a 1:1 correlation of the potentials of each electrode against the common Ag/AgCl reference from 125°-275°C. The experimental slopes of the potential (E_{sensor}/pH) plots were calculated by linear regression analysis; the linearity was shown by the regression coefficients obtained near unity. The experimental slopes are less than the theoretical Nernst values by approximately 11% at 125°C and gradually decrease to a less than a 5% deficit as the temperature is increased to 225°C. These results unequivocably establish that yttria stabilized zirconia can be an accurate, linear pH sensor. However, the less than theoretical slope value raises interesting questions about high temperature solution chemistry and the standard platinum-hydrogen electrode.

5. Long Term Stability

Experimental work has shown the zirconia sensor can provide reasonably accurate and stable pH measurement for periods greater than 30 days at both low (100°C) and high (250°C) temperatures[6,7,9] However, problems with mechanical pressure seals, fine cracking of the sensor ceramic, and corrosion of the ceramic at the grain boundaries results in either premature sensor failure or degradation. Further effort directed at optimizing the ceramic for both its mechanical and electrochemical properties seems appropriate.

The composition and density of the ceramic have been related to the electrochemical properties at elevated temperatures. Scanning electron microscope (SEM) micrographs of the surface of a sensor after extended exposure to 300°C autoclaving, revealed a significant widening of grain boundaries. Apparently, a second phase is present which contains segregated Ca, Al, and Si. These elements may have been added to aid the sintering process during manufacturing. SEM studies of higher purity materials showed no significant widening of grain boundaries[6]. It has been suggested that second phase materials may have been responsible in part for the very high impedance at low temperatures which result in a sluggish pH response[11].

A.C. impedence studies done at PNL[6] indicate a shunt resistance is responsible for both the less than theoretical Nernst slope at low temperatures and for further reduction of the slope at low temperatures after extended autoclaving at higher temperatures. As temperature decreases, ion-conduction also decreases, increasing the electrical impedence of the membrane. Thus, any shunting conductance due to whatever mechanism would result in a resistive loading of the open circuit potential. This would be observed as a lower millivolt output and an apparent degradation of pH sensitivity. At higher temperatures, membrane impedence is low enough that the effect of resistive shunting is negligible and even sensors with seriously degraded performance at low temperature, perform acceptably at high temperature.

Gaining further insight into the degradation processes, as indicated above, will enable an improvement of the low temperature, long term pH sensing capability of these sensors. Components of an electrical equivalent circuit model have not yet been correlated with the physical and electrochemical degradation mechanisms of the ceramics. Once these mechanisms are understood, modifications for optimization may be made intelligently. Changes in density, composition and membrane thickness are suggestions that have been made to improve the low temperature pH response and long term stability.

6. Applicability to the 100°-200°C Regime

The insensitivity to ion and redox interference makes this sensor very attractive for corrosion studies in hot brines. However, there is no question that the sensor performs best between 250°-300°C. Implementation at 100°-200°C will require careful selection of the ceramic vendor and internal electrode. GE, SRI, and PNL all report variability from vendor to vendor. Elimination of resistive shunting due to microcracking is very important. Other considerations concerning membrane thickness, composition and density apparently require further research. The internal electrode is directly related to the total impedance of the electrode. The two lowest impedance, reproducible, internal electrodes to appear in the literature are the Hg/HgO fill[11] and Pt ink[6]. The Pt ink electrode has been used successfully down to 85°C, the Hg/HgO to 125°C. At these low temperatures, as mentioned previously, the very high impedence (10^9) of the electrodes results in long response times and necessitates Faraday shielding from electromagnetic interference.

V. PALLADIUM HYDRIDE

Palladium hydride may be useful for high temperature reference electrode applications, but is generally considered of limited utility for high temperature pH measurement. The electrode potential is usually measured in the $\alpha+\beta$ region of the palladium hydride phase diagram. Difficulty in maintaining the $\alpha+\beta$ phase region long enough to record potentials, potential dependence on H_2 and O_2 partial pressures and evidence of irreversible electrode processes limit the potential usefulness of this material for pH measurement.

Palladium hydride exists in two forms, α and β. The α phase contains the smaller percentage of hydrogen and the phase contains the greatest. The $\alpha+\beta$ mixture is of particular interest because its electrochemical potential in aqueous solution is insensitive to the actual Pd:H ratio. As long as the palladium hydride electrode remains in the $\alpha+\beta$ region of the phase diagram, its potential with respect to the solution will not change.

The open circuit electrode potential can be used to monitor the progress of hydrogen diffusion out of the electrode. If the electrode begins in the hydrogen rich phase and hydrogen is permitted to diffuse out of the metal into the solution, then the potential will increase as the palladium is depleted. As the electrode enters the + phase, the potential remains nearly constant until enough hydrogen has escaped to place the electrode into the α region of the phase diagram. Once into the α region, the potential continues to increase as the depletion of hydrogen continues. The potential of the $\alpha+\beta$ plateau has been reported to exhibit a Nernstian relation to pH up to 195°C[18-21].

In a more recent study, D.D. MacDonald and coworkers reported their investigation into pH measurement with palladium hydride from 25°-275°C.[22,23] The mode of electrode operation was to discharge hydrogen cathodically onto the surface of the metal, pushing the palladium into the β region of the phase diagram. A brief anodization pulse was applied to oxidize and remove any metal impurities resident due to cathodization; the current was interrupted and the electrode desorbed hydrogen into the solution (as long as the fugacity of H_2 in the solution was less than that of the metal). As the metal entered the $\alpha+\beta$ region, hydrogen continued to desorb, but the potential reached a plateau. D.D. MacDonald and coworkers found that plateau potentials were reproducible to better than ±10mV up to 275°C or to better than ±0.1 pH units.

Unfortunately, the electrodes exhibited a non-Nernstian temperature dependence, irreversibility, and very short residence times at the plateau potential. The non-Nernstian temperature dependence was clearly observed above 200°C. Irreversibility was indicated by the lack of Nernstian temperature dependence and hysteresis between the absorption and desorption isotherms of the $\alpha+\beta$ mixture. Deviation from the Nernst response of a one electron exchange process ($H^+ + e^- = H(pd)$) is also an indication of either a mixed potential electrode process or simply that the adsorption-desorption of hydrogen from the palladium lattice is an irreversible or at best a quasi-reversible process. Above 200°C, the plateau residence times are too short to discern plateau potentials. Even at 150°C, the plateaus are short enough that accurate determination of plateau potentials is difficult. Apparently, above 200°C, the hydrogen escapes so rapidly from the surface that the $\alpha+\beta$ phase cannot be maintained at the interface.

The plateau potential is strongly dependent upon the partial pressure of both H_2 and O_2 in solution. The O_2 dependence appears to be almost linear for certain regions of O_2 partial pressure and temperature. The electrodes were insensitive to large amounts of carbonate ions and carbon dioxide.

VI. METAL OXIDES

1. General Comments

The literature indicates extensive use of metal oxide electrodes to measure pH. The mechanism of pH response for these electrodes is generally quite different from the simple ion exchange processes thought to dominate the response of glass and ceramic electrodes. The increased electronic conductivity of metal oxides relative to glasses and ceramics is responsible for the substantially different electrode characteristics. Most of the studies reported in the literature were done at temperatures below 100°C. The literature is fragmented in its discussion of metal oxide materials and electrode characteristics above 100°C. Problems with electrode stability and strong redox interferences have probably discouraged systematic investigation into using metal oxides for high temperature pH sensing.

Recent work at SRI[24] and the University of Pennsylvania[25] are indications of a continuing interest in metal oxides for high temperature pH sensing. SRI, in a recent study of suitable pH measurement techniques for power water reactors supported by the Electric Power Research Institute (EPRI), considered oxides of Zr, Pt, Ti, Ir and Ti-Nb. The results of the University of Pennsylvania investigation into iridium oxide prepared by reactive ion sputtering are particularly encouraging. They report a Nernstian pH response at both ambient and elevated temperature and their measurements indicate redox in sensitivity at ambient temperatures. This redox insensitivity is the primary characteristic that distinguishes the sputtered iridium oxide from all other reported metal oxides and identifies this material as a candidate for pH sensing in aqueous environments with uncontrolled redox potentials. Redox sensitive electrodes are of limited value for high temperature pH sensing, because of the difficulty of controlling the redox potential or dissolved gas concentrations in high temperature, aqueous solutions.

M.J. Madou et al. at SRI[26] have suggested the use of flatband potential measurements as an alternative to the standard open circuit potential measurements. This capacitance measurement technique is not expected to be sensitive, for appropriately doped semiconducting metal oxides, to the redox potential of the solution, because the Helmolz potential drop at the electrode-electrolyte interface is dominated by adsorption/desorption phenomena of protons rather than electron exchange. Unfortunately, this technique requires low impedance solutions and substantially more sophisticatd measurement instrumentation than open circuit potential measurements.

2. Advantages and Disadvantages of Metal Oxides

The metal oxide electrodes have a number of advantages with respect to the glass and ceramic electrode materials. The relatively low electrical impedance of some of them is at least partially responsible for the primary advantages. Reduced resistance reduces thermally generated electrical noise and shielding requirements. Open circuit measurement techniques require inexpensive electrometer instrumentation and place no special requirements on the conductivity of the solution being measured.

The incorporation of these materials into electrode structures is often greatly simplified due to convenient thin film deposition techniques and the elimination of the need for including internal electrode structures. The more highly conductive oxides have been implemented as electrically free standing thin films. The film can be deposited on any convenient substrate such as Al_2O_3 and electrical contact can be made remote from the region of the film exposed to the solution. Deposition technlogies such as evaporation, reactive sputtering, and chemical vapor deposition are compatible with most microelectronic planar fabrication techniques and facilitate the development of microsensor structures. The availability of micro pH sensors would be of particular utility to present efforts to understand and model pit corrosion processes. Sufficiently small pH sensors could probe the aqueous chemistry inside pit corrosion structures.

The two primary problems generally associated with metal oxide pH probes are an almost universal response to solution redox potential and instability in the oxide-hydroxide stoichiometry. The problem of redox interference appears to be inseparably linked to the property of high electrical conductivity which is also directly responsible for the advantages these electrodes possess over the insulating glass and ceramic materials. High conductivity is generally thought to dictate a dominance of electron exchange over proton exchange processes.[1] The paradox of sputtered iridium oxide, which appears to possess both relatively high conductivity and redox insensitivity, suggests that a high temperature, metal oxide, pH electrode does not necessarily respond to redox potentials. The possible origin of the paradox and suggestions for further research are discussed in some detail in a subsequent section on iridium oxide. Many metal oxide electrodes have been observed to "age" and drift in potential over periods of days at ambient temperatures. This "aging" phenomena has been associated with hydration. Katsube, et al.[27] report acceleration of hydration times by autoclaving. Madou suggests[28] that anomolies in the temperature dependence of Pt electrode at 25-300°C may be due to the poorly understood formation of mixed oxides and hydrates.

3. Electrode Mechanisms

A. Fog and R.P. Buck in a recent paper formulated five different explanations of oxide electrode mechanisms [p. 142, A. Fog, R.P. Buck, Sensors and Actuators, 1984)].

i. Simple ion exchange processes occurring in a hydrated surface layer at electrode-electrolyte interface. This ion exchange phenomena is responsible for the glass electrode pH response.

ii. A redox equilibrium between two different solid phases, e.g., a lower and higher valence oxide, or an oxide and pure metal phase, such as the antimony electrode:

$$Sb_2O_3 + 6H^+ + 6e^- \text{ ---- } 2Sb + 3H_2O$$

iii. A redox equilibrium involving only one solid phase, whose hydrogen content can be varied continuously by passing current through the electrode:

$$H_xMO_n + yH^+ + ye^- \text{ ---- } H_{x-y} + yH_2O$$

iv. Or similarly a single phase oxygen intercalation:

$$MO_x + 2yH^+ + 2ye^- \text{ ---- } MO_{x-y} + yH_2O$$

v. A steady-state corrosion of the electrode material may, in some cases, cause a pH dependent potential. No verified example of such pH electrodes has been reported.

The mechanism of oxygen intercalation can be rewritten to include hydration effects:

$$M(OH)_x + yH^+ + ye^- \text{ ---- } M(OH)_{x-y} + yH_2O$$

$$MO_n(OH)_x + yH^+ + ye^- \text{ ---- } MO_n(OH)_{x-y} + yH_2O$$

or some combination of these reactions to account for the hydrate nature of some of the oxide materials in aqueous solution.

Each of these equations can be used to calculate an electrode potential from standard reference data. Comparison of calculated and experimental values is sometimes instructive in determining possible reaction mechanisms and evaluating likely electrode performance at elevated temperatures. Poor performance at low temperatures, as evidenced by mixed or unstable electrode potentials, oxide solubility or vulnerability to common complexing species, or a strong temperature dependence for E_0, are not necessarily proof of poor elevated temperature performance, but do indicate possible problems.

4. Metal Oxide Suitability for pH Sensing

In the sections that follow, some of the most promising oxides are discussed individually. Some results from the literature on their performance as pH electrode materials are indicated. Standard reference data and other published literature sources are used to discuss metal and oxide stability, and probable electrode reaction mechanisms. Minor emphasis is placed on the method of oxide preparation, although this generally has a pronounced effect on the composition morphology and electrochemistry of the material. Emphasis was placed on determining whether any form of the oxide might be suitable for further investigation as to its suitability for high temperature pH sensing. A significant portion of such an investigation would indeed focus on developing and optimizing preparative techniques. Suggestions as to how such an investigation might be done are indicated in the discussion of iridium oxide.

5. Transition Metal Oxides

A. Antimony

The antimony metal-metal oxide electrode has been used extensively to measure pH.[29] The equilibrium controlling the response of this electrode is[29]:

$$Sb_2O_3 + 6H^+ + 6e^- = 2Sb + 3H_2O$$

The antimony electrode is not a good choice for high temperature pH sensing because of drift, non-Nernstian temperature dependence and significant oxide solubility even at room temperature. Instability observed as drift is likely to be due to the formation of intermediate valence oxides.[30] Like most other metal oxides, this electrode is sensitive to redox interference.

B. Molybdenum

Molybdenum is a reactive metal that readily passivates forming non-stoichiometric, intermediate oxide phases[1]. The E_0 reported by I.M. Issa, et al.[31] is indicative of the redox couple

$$MoO_2 + H_2O \text{----} MoO_3 + 2H^+ \; 2e^-$$

rather than a metal-oxide redox couple. They also report a slope of 51 mV/pH at 35°C, pH2-11, which is substantially lower than the theoretical Nernst value of 61.6 mV/pH. The color of the electrode used was reported to be black which cannot be the white, anhydrous, MoO_2, but rather must be a hydroxide.[32] The MoO_2 anhydrous and hydrous form is not stable at pH 9 and above. MnO_3 is relatively soluble even at room temperatures.[32] The poor stability of the oxide and non-Nernstian pH response are augmented by a third unfavorable feature, sensitivity to solution redox potential.[31]

C. Manganese

MnO_2 is reported to respond in a Nernstian manner between pH 1-5, 25°C, for both the stoichiometric β form and the MnOOH form.[33] The potential determining reaction is thought to be

$$MnO_2 + H^+ + e^- \text{----} MnOOH$$

J. Caudle, et al.[33] also report the electrode process to be reversible and thus they observed no hysteresis. The potential-pH diagram[32] indicates that both MnO_2 and MnOOH are stable oxides, particularly for pH 4 and above. The paper by J. Caudle, et al. did not discuss the hydrogen ion response above pH 5, because their interest was in acid batteries.

Unfortunately, the real problem with this material is its known cation exchange properties. It favors exchange with cations in the order:

$$K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$$

Interference potentials are of the order of 50-100 mV for 0.001 M concentrations of these cations.[33] This level of interference would not permit accurate pH determination in even weak electrolyte solutions.

D. Tungsten

Tungsten does not have a stable oxide form for pH values higher than four according to Pourbaix's pH-potential diagram.[32]

E. Titanium

According to thermodynamic data on titanium, the TiO_2 oxide should be a stable oxide for pH sensing in most severe environments. The tetravalent native TiO_2 oxide is stable with respect to corrosion in nearly all non-complexing aqueous solutions up to 150°C. Above 150°C, the TiO_2 phase begins to experience corrosion in strongly alkaline solutions. The two other reduced oxide forms, TiO and Ti_2O_3 are not thermodynamically stable in water.[34]

TiO_2 electrodes have been reported with nearly Nernstian OCP response to pH. A. Fog[30] reports 55 mV/decade at ambient from pH 2-12, with increasing electrode error from pH 10-14[35]. K. Kinoshita, et al. [24] report similar results, but observe better responses for thermally oxidized electrodes. However, K. Kinoshita and M.J. Madou[35] also report the probable existence of a mixed potential for the anodically prepared film according to E_0 data. They also express uncertainty as to whether the high temperature pH response observed, was due to access to the titanium substrate via pinholes or due to a membrane potential established by proton conduction in the oxide[28].

The observed mixed potential-like behavior and alkaline pH error may be due to instability in the hydration character of the oxide.[29] The 30 mV of hysteresis observed by A. Fog[30] and the superior performance of thermal oxides over anodically formed oxides are also indications that the nature of the oxide hydration is correlated with OCP pH response.

For TiO_2 to become a useful pH sensing material for high temperature measurements further development is necessary. OCP measurement techniques remain attractive for this oxide, because ionic interference is reported lower than the platinum group oxides, except of course in reducing and oxidizing solutions.[30] However, work done by M.J. Madou, shows that voltage flatband techniques on Nb-doped TiO_2 may hold more promise[26].

F. Tantalum

Tantalum pentoxide, Ta_2O_5, is an insulating oxide exhibiting a Nernstian potential response to pH. It does not possess the benefits of electrical conductivity, but is noteworthy for its Nernstian response and exceptional chemical stability. The mechanism of pH response is thought to be hydroxyl ion exchange; other anions do not interfere with the observed potential[36]. Potential-pH diagrams for tantalum indicate a single phase passive layer of Ta_2O_5 that is stable in ambient, aqueous solutions[32]. It is not attacked by HCl, HNO_3, aqua regia, H_2SO_4, or caustic alkali solutions. HF etchants require a platinum catalyst for substantial etch rates to be achieved. 250°C autoclave testing in water showed Ta_2O_5 dissolution rates an order of magnitude below those of yttria stabilized zirconia and 1/3 that of Al_2O_3[28]. A doped form of Ta_2O_5 might be useful for OCP or flatband pH measurements.

G. Zirconium

ZrO_2 stabilized with yttria has already been discussed in this report as a material for measuring pH between 150-300°C. It is an insulator and possesses none of the advantages of the electrically conductive metal oxides.

In a systematic study of high temperature pH monitoring techniques done for EPRI, K. Kinoshita and M.J. Madou of SRI[37] found that thick films of ZrO_2 were insensitive to pH and thin anodic and thermal oxide films on zirconium metal exhibited nearly Nernstian behavior. The low impedance and long pH response time constants for the thin films were attributed to electron exchange reactions occurring at pinholes in the films. They suggest that at pinholes, electronic conductivity is high enough to sustain an electrochemical reaction involving protons and oxide species. They conclude that OCP measurement of pH with Zr-ZrO_2 electrodes does not show much promise, because the pH response is dependent upon defects in the oxide film.

Experiments on flatband potential response to pH were equally discouraging. They suggest doping of single crystal ZrO_2 as an alternative. This technique differs from OCP yttria-zirconia electrode, in that it does not have an internal reference electrode structure.

6. Platinum Metal Oxides

A. Osmium

Osmium is the most chemically reactive of the platinum metals. There are only two stable forms of osmium oxide, OsO_4 and OsO_2. The existence of any other forms is dubious even in the gaseous phase[29] except for gaseous OsO and Os_3O_4. The OsO_2 ---- OsO_4 redox couple is of little utility because OsO_4 is very soluble, reactive and volatile (mp. 40.6°C, bp 131.2°C). Furthermore, OsO_2 is not stable in strongly alkaline solutions[38] or in the presence of complexing species such as Cl^-, I^-, Br^-, NO_2^-, NO, $C_2O_4^{-2}$, etc.[32] The susceptibility of the binary oxide to corrosion and complexing make osmium a poor candidate for high temperature pH sensing.

B. Palladium

Palladium is a noble metal whose PdO oxide has been used by W.T. Grubb[39] at General Electric for ambient temperature pH sensing, pH 3-11. The electrode reaction from x-ray diffraction data and the E_0 value is assumed to be:

$$Pd + H_2O \text{ ---- } PdO + 2H^+ + 2e^-$$

Grubb reports very stable electrode slopes even after aging the electrodes for several years in neutral H_2O. The potential-pH diagram predicts the stable formation of several hydroxides which probably is a good indication of electrode drift due to mixed oxide-hydroxide equilibria. PdO and all of the oxides are reported to be reasonably soluble at ambient temperatures[32]; presumably at elevated temperature increased solubilities would greatly reduce the utility of the PdO electrode.

The PdO electrode responds strongly to interference from 0.05M potassium ferri and ferrocyanide, and oxygen[39].

C. Platinum

Platinum has been extensively used in high temperature studies in aqueous solution studies. The nobility and stability of platinum in aqueous solution up to at least 300°C, as well as its catalytic properties have resulted in the extensive use of this metal as a counter electrode in electrochemical studies of other corroding metals. Potential-pH diagrams show platinum and its oxides to be stable in most aqueous solutions with little variation in the diagram with increasing temperature. Platinum corrodes only in strongly oxidizing solutions at pH less than three.[34]

PtO, PtO_2 and mixed PtO-PtO_2 oxide have been utilized for pH sensing. J.V. Dobson, et al.[40] report a Nernstian response at room temperature with the E_0 reflecting the electrode equilibrium:

$$Pt + 2H_2O = PtO_2 + 4H^+ + 4e^- \quad E_0 = 0.837V$$

However, their measurements done to 250°C showed both the E_0 to be temperature dependent and the temperature dependence of the slope to be non-Nernstian. A. Fog reports different OCP slopes for PtO_2 electrodes above and below pH 5.[30] He used a pure, powdered form of PtO_2 on a Ruzicka electrode, unlike other efforts mentioned in this section which oxidized base metal electrodes of platinum. They also report 100 mV of hysteresis and strong interference from O_2, I^-, Fe $(CN)_6^{-3}$, and Fe $(CN)_6^{-4}$.

Certain oxidation techniques coat the platinum base metal with predominantly PtO rather than PtO_2[24,35,41]. K. Kinoshita, et al. report a Nernstian response at ambient temperature with an E_0 very close to the equation[10]:

$$Pt + H_2O \text{ ---- } PtO + 2H^+ + 2e^- \quad E_0 = 0.980V$$

However, they also observe a more rapid drop in potential with increasing temperature than allowed for by a simple Pt/PtO couple. They suggest temperature dependent hydration phenomena may be involved[24]. The stability of the oxide, its hydrate and exchange equilibrium with higher oxides and hydroxides should also be considered. Potential-pH diagrams show a narrow band of PtO stability. A. and M. Hecq report reactively sputtering pure PtO[42]; an electrochemical study of the elevated temperature response and stability of this single oxide sputtered thin film material would be very instructive.

At present, platinum metal oxide electrodes are of limited utility at elevated temperatures because they are difficult to calibrate, possess unknown stability and hydration characteristics and exhibit strong redox interference. However, they may merit further attention, because platinum is such a noble metal.

D. Rhodium

From potential-pH diagrams[32] and literature on the anodic oxidation of base metal electrodes,[43,44] ruthenium oxides appear neither to be as corrosion resistant nor as reversible as ruthenium and iridium. It is not as noble as platinum. Bulk rhodium forms a passivating layer except in strong oxidizing or complexing solutions. Rhodium and its passivating oxides are more stable in alkaline than acidic solutions.

Some work on anodically prepared oxide is reported in the literature. Generally, the oxide films exhibit poor adherence to glass and high solubility in acids. Unlike iridium oxide, which is formed anodically in an acid solution, rhodium is oxidized in basic solutions and most rapidly above pH 13[44]. Voltammograms indicate the existence of an abnormal second anodic peak appearing before the main anodic peak[43]. This peak is also observed for voltammograms of iridium oxide at 70°C[45]. Decreased electrochromic activity and electrical conductivity of rhodium oxide are associated with the appearance of this peak.

A. Fog and R.P. Buck[30] report non-Nernstian pH response for crystals of RhO_2-nH_2O. The slope of the potential-pH curve was not linear, possessed super Nernstian slope at ambient temperature and did not follow the standard Nernstian temperature dependence at 35° and 45°C. They also report severe redox interference and also interference from I^- and Br^-. These results plus the other negative features such as hydrated sesquioxide solubility, susceptibility to complexing[32], and apparent relative irreversibility with respect to ruthenium and iridium, make rhodium a poor choice for pH sensing. However, its accelerated oxide growth in base, as opposed to accelerated ruthenium and iridium growth in acid, raises intriguing questions about the properties of mixed platinum metal oxides.

E. Ruthenium

RuO_2, the most stable of the oxides of ruthenium[29], is stable in acid solutions, but according to potential-pH data, unstable above pH 10[32]. This information by itself, discourages further interest, because repository pH is expected to exceed pH 10. However, of the platinum metal oxides tested by Fog and Buck[30], only the RuO_2 electrode showed a reproducible, Nernstian pH-potential over part of the pH scale in the presence of oxidizing or reducing species such as ferricyanide, ferrocyanide and hydrogen peroxide. Others also report an easily established reversible potential for the redox couples Fe^{+2}/Fe^{+3}, Ce^{+3}/Ce^{+4}, I^{-}/I_2 and Cl^{-}/Cl_2[46].

Ruthenium may be useful in a mixed platinum metal oxide, pH sensitive thin film. At low pH, RuO_x films exhibit reversible behavior during cyclic voltammetry measurements. It is thought that like IrO_x, the thick oxide film undergoes internal electrochemical changes rather than metal/metal-oxide redox at the metal/metal-oxide interface[46]. XPS results show the joint existence of ruthenium Ru (IV) and Ru (VI), whereas Ir (IV) does not appear to go to a higher redox state in thick oxide films during potential cycling.[47,48]

F. Iridium

The tetravalent oxide of iridium has been used for a number of widely varying pH sensing applications. S. Bordi and co-workers used Ir/IrO_2 electrodes for rapid pH sensing in < 0°C hydro-organic solutions[49]. I. Lauks, et al. have used sputtered films for measurements in concentrated HF solutions and for elevated temperature, acid titration experiments[25]. R. Ianiello and A. Yacynych used urease enzyme immobilized on an iridium oxide substrate to monitor urea concentration; changes in pH, caused by the enzyme-catalyzed hydrolysis of urea near the electrode surface, yield a linear potentiometric response with logarithmic variation of urea concentration[50].

Iridium oxide electrodes are generally reported to respond in a linear, Nernstian manner to pH. Super and sub-Nernstian responses are reported, indicating that preparative technique is important[51,52]. Fog and Buck report a Nernst slope at 25°C, pH 2-10 for a pressed powder electrode. They also report 2 mV accuracy, 25 mV of hysteresis (pH 2 - pH 12 - pH 2), the smallest redox interference of all the platinum oxides and ionic interference from Cl^{-}, Br^{-} and I^{-}-[30]. Lauks, Katsube, Yuen and Zemel report similar results for reactively sputtered films[27], except that they report recent improvements in deposition technology have produced films with no response to bubbling O_2 gas. This apparent insensitivity to redox interference is discussed in more depth in the final section on sputtered IrO_x.

The mechanism of the electrode response is unresolved in the current literature. The majority of the most recent literature on thick (>500°A) oxide films agrees that some sort of internal processes in the oxide film and on the surface are responsible for the characteristics observed by OCP, voltammogram, and impedance measurements. The Ir/IrO_2 couple is apparently only dominant for either thin layers or large electrode poetential excursions. Most of the conjecture centers around the nature of the hydration, identification of aqueous species involved in exchange currents across the electrode solution interface, and the importance of oxide morphology and stoichiometry.

The response mechanism is unresolved because: the electrode potential has not been assigned to a known reaction; the nature of the hydration is poorly characterized; and the species responsible for the exchange currents across the electrode-electrolyte interface have not been positively identified. The measured OCP may not be due to one particular reaction, but may in fact represent a mixed potential. The thermally prepared oxide according to K. Kinoshita, et al.[24] and Ardizzone et al.[53] has an E_0 (vs. SHE) very close to either of the three reactions:

$$2IrO_2 + 2H^+ + 2e^- = Ir_2O_3 + H_2O$$

$$IrO_2 + 4H^+ + 4e^- = Ir + H_2O$$

$$Ir_2O_3 + 6H^+ = 2Ir + 3H_2O$$

At elevated temperatures, Kinoshita, et al.[24] report the absolute value of the OCP to decrease faster than can be accounted for by either a Nernstian temperature dependence or calculated solution pH temperature dependence. They tentatively suggest a change in the degree of oxide hydration with increasing temperature as a possible explanation for the presumed shift in E_0. The stability or degree of instability of the hydrated oxide will determine whether a stable, reproducible electrode potential is possible.

The hydrous nature of iridium oxide thin films is largely responsible for the unusual electrochemical characteristics and extraordinary corrosion stability of iridium electrodes. The unusually large charging capacity of iridium oxide during voltage cycling is well documented[54]. The porous structure of the hydrous film provides a large surface area for ionic exchange. Thick films (> 50 nm) exhibit a charge capacity enhancement of two orders of magnitude above bare iridium metal. The porosity of the films is confirmed by scanning electron microscope micrographs.

Several models of the hydrous structure have been proposed to account for the observed, intimately related, electronic and electrochemical film characteristics. Each model defines the amorphousness of the hydrated film differently. S. Gottesfeld[55] used electronic band diagram levels to model the five orders of magnitude electronic conductivity shift between the electrochromic bleached and colored states. The conductive, colored film is predominantly Ir(IV) and the insulating bleached state is predominantly the reduced Ir(III).[58] Electronic band models must be used with care in the discussion on non-crystalline materials, but may be useful for elucidating equilibrium rate constants for electron exchange processes across the oxide-electrolyte interface. To identify the band structure, several optical and surface spectroscopic techniques might be utilized. Ultraviolet photoelectron spectroscopy (UPS) is particularly useful for identifying the electronic structure close to the Fermi level involved in exchange rates. No substantive data using UPS is available, so it is difficult to assess whether the broad density of states functions are resolvable by and whether it will help to model electronic resistivity and exchange processes at the solution interface.

Burke and Whelan[56,57] proposed a cross-linked polymer skeleton as an alternative to the implied extended electronic band strucutre of Gottefeld's band model. They propose a mixture of linear and branched chains of hydrated oxyhydroxides. Conductivity is modeled from one dimensional solids theory, where the ability of electrons to hop from site to site in the reduced chain, Ir(III), is much less than for Ir(IV) sites. This polymer structure has also been proposed for metal oxides of molybdenum and iron.[67,68]

The third model assumes a polycrystalline structure with very small grain size[53,59]. Hydration character is proposed to be different for grain boundary and intra-grain regions. This model is more fully developed for ruthenium oxide films and is most plausible for thermally decomposed iridium cloride or reactively sputtered iridium oxide films. Rispon and Gottesfeld using a.c. impedance measurement techniques were able to resolve fast and slow charging processes[59]. They hypothesize that the fast charging process occurs in the double layer at the outer surface sites along the grain boundaries of the microcrystalline structure. The slower process is associated with the charging of bulk grains. The rate of the slow charging can be enhanced by applied cathodic potential and is thus likely related to a slower, more radical form of oxide reduction.

The equilibrium of Ir(IV) and Ir(III) valence states is widely accepted,[65,66] but the mode or precise species involved in ion insertion into the oxide film is not. Conflicting evidence for cation vs. anion insertion is reported in the literature[60,61]. Li^+ ions have been inserted using nonaqueous electrolytes, but primary ionic interference during OCP pH measurement is reported due to anions, Cl^-, Br^- and I^-[27,30]. Other work by

Mozota and Conway[62,64] indicates that a preferential adsorption of Cl^- during anodic cycling reduces oxide growth rates. The importance of understanding the insertion mechanism is to quantify a minimum expected ionic interference and identify the dominant process of electrode pH response. If the insertion mechanism involves cations, then observed cation interference is easily explicable.

Rispon and Gottesfeld[59] propose a double injection process for ruthenium oxide which is equally valid for iridium:

$$IrO_x - n(H_2O) + ye^- + yH^+ = IrO_{x-y}(OH)_y - n(H_2O)$$

This particular form of the equation represents injection of a proton from solution and an electron from the ohmic contact. The equation does not represent a redox process. The ion exchange at the electrolyte interface consists only of either single or hydrated hydrogen ions. The double injection equation also indicates how high concentrations of small cations would compete with hydrogen ion injection. A similar equation can be written to model hydroxyl and anion insertion. The equations of Fog and Buck discussed previously, indicate how this can be done. Gilarum and Marshall[63] report fast kinetics for both acid and alkaline solutions but not for neutral pH. This observation suggests the existence of two different injection mechanisms and perhaps a pH dependent oxide structure as well. Further investigation is necessary to determine whether a particular form of the oxide may prove useful for very high pH sensing. The double injection model describes a possible injection/exchange process and also includes the interaction of hydrous structure of the oxide with these processes and solution pH.

Even though the complex electrode processes are not fully understood or controllable, iridium oxide has provided accurate, stable pH measurement at room temperature. It does have the characteristic redox interference behavior of conductive metal oxides, but the sputter deposition technology may reduce redox interference even at elevated temperatures. A more significant limitation is interference from anions, particularly Cl^-. Significant anion interference above 0.01 molal concentrations limit the utility of this oxide. The key unanswered question which impinges directly on the high temperature performance is the stability of the hydration structure. Preliminary indications are that the oxide changes with temperature, resulting in a nonNernstian temperature dependence[24]. It is not known whether the sputtering technology which can be utilized to deposit well-characterized, uniform oxide films of known stoichiometry, valence state, morphology, and density will lead to a stable, homogeneous, hydrated oxide in elevated temperature aqueous solutions.

VII. REACTIVELY SPUTTER-DEPOSITED IRIDIUM OXIDE

The method of oxide preparation strongly influences the observed electrochemical properties. The difference in reported properties of iridium oxides obtained from different preparative techniques raises several interesting questions. The questions of prime technological importance are why does the d.c. reactively sputtered film exhibit such apparently superior performance and what preparative procedures produce superior films? One answer might be that anodic, thermal and chemically deposited oxides of iridium are polycrystalline phases whereas sputtered iridium oxide can be amorphous. Reactive sputtering is an ideal preparation technique for an investigation to answer these two questions because reactive sputtering offers substantial flexibility in tailoring film characteristics by process parameter variation[70]. The other techniques of thermal and anodic preparation are not so flexible. The anodic technique is further limited because samples so prepared are already hydrated. The electrochemical properties of reactively sputtered oxide films can be measured by traditional electrochemical techniques in solution but must be correlated with the atomic and molecular structural information obtained in high vacuum by surface science techniques. Information gained about the nature of the interaction of the solution with the atomic structure of the oxide and its hydrated form will indicate how sputtering conditions can be tailored to produce optimum thin films for a variety of different situations. For example, the optimum film for high pH sensing might be different than one developed for strong acid solutions. Film optimization might entail variation in IrO_x stoichiometry, film morphology or even doping with other platinum group metal oxides.

1. Present Status of Sputtered IrO pH Sensing

Results published by I. Lauks and co-workers at the University of Pennsylvania establish reactively sputtered IrO_x as a candidate material for pH sensing according to the criteria of Nernstian response, small or acceptable ionic and redox interference, corrosion resistant and possible incorporation into mechanically robust electrode structures. At room temperature to 100°C, the following electrode characteristics were observed.[27,69]

1. Nernstian response as described by the equation:

$$E = E_O - [2.303\ kT/q]\ pH$$

At 100°C, the measured slope is approximately 3% less than predicted by this Nernst equation. Linearity was measured from pH3-12. E_O is independent of temperature.

2. Cloride ion interference less than +10mV for sodium concentrations below 0.1M. The effect of dissolved Pb^{+2}, Fe^{+3}, Fe^{+2}, Cu^{+2}, and Ag^{+} are less than 8 mV for concentrations less than 0.01 M.

3. Excellent reproducibility of the open circuit potential slope (OCP - pH vs. E). However, the E_O exhibits drift apparently due to hydration. The E_O is reported stable after hydration is complete. Autoclaving the electrodes in high temperature, aqueous solutions results in stable E_O values; autoclaving is thought to accelerate the hydration of anhydrous as-prepared sputter deposited films.

4. The reactive sputtering technology permits thin films to be deposited onto a number of different substrates including metals, glasses and ceramics such as Al_2O_3. This technology leads to the design of relatively simple electrode structures that are robust, corrosion resistant and easily installed through autoclave seals.

IrO_x exhibits strong utility for <100°C aqueous pH measurements in dilute aqueous solutions.

The performance of IrO_x at higher temperatures has not been extensively documented. Early studies[25] subjected thin film samples to autoclaving in deionized water at 160°C and 200°C for two hours. No degradation of room temperature pH response resulted later, from an in-situ, 156°C pH measurement. 800°A thick IrO_x anodic films on ceramic alumina substrates accurately monitored the acid titration of 0.01 M KCl from pH 9 to pH 3 with 0.01 M HCl. The slope of OCP vs. $[H^+]$ at 156°C agreed well with the Nernst slope at 156°C, 2.303 k(156°C/q = 85 mV/pH). The measurement of ionic and redox interference, long term stability and hysteresis at elevated temperatures was not addressed by Lauks and co-workers. Madou's investigation of sputtered films[28] indicated that they responded to the solution redox potential above 150°C. He also experienced problems with film adhesion, due perhaps to the bubbling molecular oxygen. No such adhesion difficulties are reported by Lauks, et al. Either the presence of high concentrations of bubbling oxygen is responsible for the adhesion/corrosion instability or the two groups sputtered different thin films of iridium oxide. Film morphology and stoichiometry are sensitive to the deposition parameters.

The remainder of this report proposes a research approach to develop well-characterized, reactively sputter-deposited iridium oxide thin films for pH sensing. The approach can be segmented into three progressive sections:

i. Establish a well controlled technology for reactively sputtering iridium oxide.

ii. Establish a relationship between sputtering conditions, film morphology and electrochemical properties in solution.

iii. Analyze and understand the mechanisms responsible for elecrochemical behavior so that these films may be intelligently optimized for high pH, elevated temperature, non-dilute, aqueous solutions.

A systematic investigation such as this is expected to provide a metal oxide alternative to other materials such as the yttria stabilized zirconia.

2. Reactive Deposition of Iridium Oxide

The method of depositing the iridium oxide by reactive sputtering provides substantial flexibility to tailor film morphology and composition. The characteristics of deposited films are very sensitive to process parameters during deposition[70,77]. Characteristics vary with partial gas plasma pressures, reactive to inert gas ratio, system configuration, substrate temperature, power, target to substrate distance, target composition, and several variables of lesser importance such as power frequency in an a.c. plasma.[73] The ability to reproducibly deposit well controlled films with identical characteristics is very important to ensure consistency in the analysis. The analysis is a comparison of properties as measured by a number of different techniques, each often requiring a different sample form.

Since the deposition of iridium oxide is done reactively, the chemistry of the reactive gas, O_2, on the substrate, the target, and in the plasma largely determines the characteristics of the deposited film. The critical process control parameters determining the chemistry are the partial pressures of O_2, the temperature, and rate of deposition. The relationships between adsorption and reaction kinetics on the surface are certainly complex and do not need to be directly addressed (others have approached this by attempting to sample the plasma at the substrate surface[74]). However, the kinetics can be empirically controlled by regulating substrate temperature, substrate positioning, power, and gas flow into the sputtering chamber.

The pH sensing iridium oxide films prepared by Lauks and coworkers at the University of Pennsylvania were sputtered at low power densities and for periods of time measured in hours to produce films of 100 nm thickness[25]. Other workers report similar sputtering times[75]. They also report significant sample variation with 10% changes in gas mixtures and power densities. The proposed work will fabricate films in a wide range of sputtering conditions using a planar magnetron in both d.c. and a.c. modes. Morphological, electrochemical and surface analysis measurements are expected to provide information detailing why certain sputtering conditions produce electrochemically useful films and other conditions do not. Such information will prove useful to others involved in reactively sputtering other platinum group, metal oxides as well as iridium oxide. At present, very little published work exists on reactively sputtered platinum group metal oxides which are potentially important not only for numerous types of solid state sensors but also in the production of catalytic films and solid state electronic structures.

3. Film Characterization

The purpose of these measurements is to establish the relationship between materials properties and electrochemical properties, particularly as they relate to pH sensing. The measurements proposed for the iridium oxide thin films fall into two distinct classes. The first set of measurements is designed to characterize the materials properties of the films: density (specific gravity), resistivity, morphology and stoichiometry. The second set of measurements is aimed at defining the electrochemical and surface chemical properties.

An index of each as-prepared sputtered film will be obtained by measurement of resistivity, density, degree of crystallinity, stoichiometry and morphology. Resistivity is calculated from four point probe and film thickness measurements. Resistivity of an unhydrated, dry film indicates the electronic characteristics. Thickness, along with area and weight, define density; a discussion on the expansion and porosity of hydrated films has been published[75]. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and optical microscopy are standard tools for defining morphology and will be used in this study. X-ray diffraction results are expected to indicate both the degree of crystallinity and stoichiometry. If the films are amorphous and x-ray diffraction results are not very informative about either stoichiometry or molecular composition, then a combination of XPS, SIMS, and SEM microprobe measurements might yield the desired quantitative information. Implementation of XPS and SIMS techniques is discussed further below.

Once a film has been properly characterized according to its density, resistivity, morphology and stoichiometry, conclusions concerning sensing mechanisms might be drawn with more confidence from electrochemical and surface measurements. The proposed set of measurements are designed to clearly identify the electrochemical mechanisms defining the response of the films to pH and to other interfering redox or ionic species. The measurements fall into two traditionally separate disciplines, those of the electrochemist and those of the surface scientist. The correlation of the results of these two different approaches is expected to be far more definitive with respect to mechanism than either measurement approach by itself. Recommendation for this sort of correlation has been expressed in several papers[65,76] and measurements have been initiated on the IrO_2 system by two research groups based in Switzerland[71,78].

The three electrochemical measurements proposed are open circuit potential (OCP), voltammograms and complex plane impedance plots of the electrode in solution. OCP is most likely the mode in which these films will ultimately be used to measure pH. Measurements of electrochemical potential versus temperature indicate the range of Nernstian operation. OCP as a function of different solution compositions shows the extent of ionic interferences. Voltammograms and impedance plots are intended primarily to elucidate electrode mechanisms, kinetics at the interface and bulk transport through the film. The impedance plots are a new technique as applied to iridium oxide. However, substantial voltammogram studies of iridium oxide, formed primarily by anodic techniques, have already been done. Results have been interpreted to define ion insertion-extraction[61], redox state changes[71], and electronic band structure[69]. It has been postulated that the superior pH performance of sputtered films over anodically deposited films is due to valence band structure differences associated with the amorphous nature of the sputtered films[69,77].

No published work explores the pH response or electrochemical characteristics of iridium oxide films as a function of reactive sputtering conditions. Efforts have been directed at the electrocatalytic[48] and electrochromic[28] behavior of iridium oxide. Films prepared anodically have been reported to have poor characteristics for pH sensing[35,52]. Anodic preparative techniques fall short of the flexibility inherent in reactive sputtering. The sputtered films can be prepared in an anhydrous or hydrated form depending on whether water vapor is introduced into the sputtering chamber. Also, as detailed in a previous section, morphology, stoichiometry, etc. are very sensitive to sputtering process parameters. If small changes in physical characteristics can be correlated to changes in surface electrochemistry and molecular-electronic structure, then the sputtering technology itself becomes an incisive tool in deconvoluting the simultaneous processes determining iridium oxide electrochemistry.

The three high vacuum spectroscopy measurements proposed are x-ray photoemission spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and ultraviolet photoemission spectroscopy (UPS). The nature of the high vacuum measurement environment makes these techniques static measurements of a chemical state. Kinetic information must be obtained from already described electrochemical methods which are carried out in solution. However, knowledge of the bonding configurations, extent and character of hydration, complexing and diffusion of interfering species such as ionic iron, and adsorption of water and molecular oxygen are valuable in understanding the chemistry of an iridium oxide surface in solution.

XPS and SIMS are complementary measurements. Identification of fragments observed by SIMS provides confidence for deconvoluting XPS results. SIMS provides identification according to mass number of different species, e.g. H_2O, OH, IrO, etc; but strong matrix effects have made quantitative efforts of dubious value. However, knowledge of existing species makes deconvolution of XPS data much more reliable and increases confidence in the quantitative analysis of bonding in hydrous and anhydrous sputtered films. Also, since the methods differ both in excitation source and detected emission, measurement distortions inherent in each technique due to sensitivity variation, matrix effects and surface vs. bulk property variations, should be quantified more confidently with a comparison of measurement results.

The ultrahigh vacuum measurement system that possesses both SIMS and XPS capabilities contains two chambers. One is for sample preparation at atmospheric to 10^{-10} torr pressures and the second chamber is reserved for ultrahigh vacuum surface measurements. The system is also equipped for thermal desorption experiments which are used for studying the adsorption sites and interaction energy of gases onto surfaces. Sorption-desorption measurements of gases and water vapor onto iridium and iridium oxide should well be very informative. Fortunately, some clean metal surface science work on iridium has already been reported in the literature[79,80,81]. This serves to simplify and shorten the proposed task, since these results will aid in the interpretation of measurements made on the more complex, intrinsically disordered amorphous materials. The primary thrust of the proposed research is the study of the alteration of the amorphous oxide surface by the solution. The alteration of bulk properties is harder to access with these techniques because any attempt to remove surface layers, by for instance, ion bombardment during SIMS, is almost certain to alter bulk characteristics.

XPS has very recently been used to study oxidation state changes and hydration of anodically prepared iridium oxide films as a function of solution pH[23]. Samples were prepared by anodically oxidizing iridium electrodes in different pH solutions. The authors then used XPS to study oxygen bonding to iridium. They correlated oxygen's core level energy shifts with voltammogram structure to propose a reaction pathway for oxide valence changes and hydration. Their results answered only the questions of surface properties and could not address bulk valence changes or bulk hydration. In particular, the bulk OH insertion mechanism proposed by Beni et. al.[61] could not be addressed. Depth profiling measurements, such as those possible using SIMS, would be particularly germaine for investigating differences in surface and bulk composition. As already mentioned, any conclusion about bulk properties using this technique must be reached cautiously.

SIMS may also be a very useful approach for studying ion and redox interference. SIMS could be better suited than XPS for identifying trace metals that may have diffused into the iridium oxide matrix. The types of fragments observed by SIMS or alternately the bonding character indicated by XPS would help to define the nature of ionic and redox interference. It may prove possible to optimize the film morphology or stoichiometry to minimize ionic and redox interference.

Of the three UHV spectroscopic techniques, UPS will probably provide the most definitive information towards identifying reasons for differences in sputtered oxide film electrochemical performance. XPS measurements provide information about oxidation states, molecular coordination and atomic bonding through core level electronic shifts. The UPS technique directly probes the valence electrons and electronic density of states near the Fermi level. The density of states near the Fermi level determnes the nature of the electronic exchange currents and ionic adsorption phenomena at electrode surfaces[82]. Metals, semiconductors, and insulators exhibit characteristically different behavior as a result. The two primary questions of iridium oxide are: "What is the relationship of electronic structure to surface aqueous electrochemistry"; and "What is the origin of surface electronic structure with respect to surface and bulk solid state structure, e.g. surface states, oxygen vacancies, hydration, etc...". Fortunately, recent data on rutile iridium oxide band structure using high resolution synchrotron radiation techniques[83] will provide a reference point for the proposed UPS measurements on amorphous films.

Once the three phases of measurement - physical, electrochemical, and surface are completed, the connection between the physical characteristics of the sputtered film and its electrochemical performance should be evident. The knowledge of how structure, composition, and electronic band structure relate to performance will enable these films to be tailored for different pH measuring environments. This tailoring may only involve iridium oxide, but more than likely mixed platinum group metal oxides will be used to produce pH sensors and pH based sensors for a wide range of measurement needs and environments.

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This report defines the performance criteria of the needed pH sensors and reviews the performance of a number of elevated temperature pH sensing technologies with respect to these criteria. The criteria of electrode performance were developed to predict the utility of various pH electrodes in these simulated environments. The classes of pH electrodes reviewed are the glass electrode, yttria stabilized zirconia, palladium hydride and a variety of metal oxides. The report focus on a relatively new solid state electrode material, reactively sputter deposited iridium oxide. The performance of this thin film material is of particular interest because its low electrical resistivity and high corrosion resistance eliminate some of the shortcomings of the glass and ceramic materials. The reactive sputtering technology permits these films to be deposited and pattern defined on a wide variety of substrate materials. Low electrical resistivity, which simplifies electrical contacts, and a flexible deposition technology make this material a prime candidate for micro pH sensors.

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