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THIN FILMS FOR GEOTHERMAL SENSING

FINAL REPORT

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TABLE OF CONTENTS

I. Introduction

II. High Temperature pH Sensing

- A. Autoclave system description and suggestions for upgrading the present system
- B. Experimental Details of the High Temperature pH measurements
- C. Low to High Temperature pH Calibration
- D. "Electrically Free Standing IrO_x Thin Film Electrodes for High Temperature, Corrosive Environment pH Sensing," Sensors and Actuators 4, 375 (1983) *(removed & cycled separately)* -

III. Polyimide in High Temperature Aqueous Sensing

- A. Polyimide Based Heterogeneous Thin Film Electrodes
- B. "Polyimide Survival in High Temperature and Pressure Dilute Aqueous Solutions," Thin Solid Films, Vol 119, No. 4, p. 439. *(removed and cycled separately)*

IV. Concluding Remarks

V. Acknowledgements

I. INTRODUCTION

In this thesis an account is given of my contributions to the development of geothermal sensors at the Center for Chemical Electronics (CCE), University of Pennsylvania. The needs of the geothermal energy industry as reported by the National Academy of Sciences Board on the Downhole Monitoring of Geothermal Brines (1) in 1978 have not yet been satisfied. Sensors are needed to measure the key chemical constituents of geothermal fluids. The availability of in-situ data from a downhole sensor system would permit direct feedback control of field operation. Scale, corrosion, flashing and other factors influencing the proper management of energy extraction from the geothermal field are critically dependent on changes in the working fluid composition. The in-line monitoring of hot aqueous fluids is not limited to geothermal wells. Many other industries as diverse as nuclear energy and food processing require increasingly accurate regulation of hot aqueous environments.

We have directed our energies into three distinct components of the geothermal measurement problem: developing appropriate chemically sensitive thin films; discovering suitably rugged and effective encapsulation schemes; and finally, conducting high temperature, in-situ electrochemical measurements. Success with the first two aspects, films and encapsulation, opened the door for us to make in-situ high temperature, pH measurements.

Two types of chemically sensitive materials have received attention. Primary interest centered on solid state thin films of IrO_x for pH sensing. Initial efforts have begun to test the feasibility of polyimide based heterogeneous membranes for the sensing of other ionic species such as sulfide and chloride.

The most critical in-situ geothermal chemical measurement is pH. pH is important in predicting the extent of scaling and corrosion (1). Efforts at other laboratories to develop pH sensors have resulted in the glass electrode of Leeds and Northrop and a stabilized zirconia electrode made by General Electric. The glass electrode is reported to perform well below 200°C , but suffers from significant performance degradation above 250°C due to glass corrosion (2). A zirconia based electrode has been developed by L.W. Niedrach and W.H. Stoddard of General Electric. Problems reported in a recently published paper (3) include mechanical failure due to circumferential cracking of the ceramic sensor element at the sealing collar, poor sensor performance below 150°C , and possible drift and/or calibration difficulties. Both groups report encapsulation and sealing difficulties. The task of developing a technology for high temperature pH sensing has not been completed.

IrO_x thin films produced by d.c. reactive sputtering in the presence of oxygen show promise for both room temperature and high temperature pH sensing. Noise and spurious electrostatic charging associated with high temperature glass and ceramic electrodes are not a problem with these low resistivity, semi-metallic IrO_x films. Redox and other ionic interferences appear to be within useful limits at

room temperature. IrO_x prepared by other techniques such as electrochemical or thermal oxidation are reported to have pH sensitivity, but suffer substantial redox interference (4). The d.c. sputtered material produced here at the CCE appears to possess superior characteristics. Further work in fabrication control, materials characterization and high temperature electrochemical measurements are clearly necessary to establish the properties of these IrO_x films.

In early 1983, high temperature, in-situ pH measurements were made with IrO_x films. The IrO_x electrodes accurately recorded the progress of an acid titration carried out at 156°C . The working pH electrode was an IrO_x film sputtered onto an inert alumina ceramic rod. The reference electrode was an electrochemically chloridized Ag/AgCl electrode. Both electrodes were encapsulated with heat shrinkable TFE teflon tubing. The teflon tubing seemed to provide effective hermetic definition of the chemically active electrode region. Results of these measurements were published in Sensors and Actuators and the paper is included as a subsequent chapter.

Three other chapters detail the equipment and techniques used to make these in-situ measurements. One chapter describes the functional operation of the autoclave system and offers suggestions for improvements necessary to make further, more informative electrochemical measurements. Another chapter fills in the nitty-gritty details germane to the measurements actually made. A final chapter describes the theoretical methods used to model the high temperature autoclave solution and calibrate the in-situ pH readings. These three

chapters along with the published paper represent a fairly detailed synopsis of the present status of high temperature in-situ measurements at CCE.

Work has been initiated on chemically sensitive heterogeneous membranes to sense ions other than pH. Other key chemical constituents of geothermal wells are the ions, Na^+ , Cl^- , S^{2-} and HS^- . Accurate sensing of these ions and pH would enable accurate assessment of down-hole geothermal chemistry. Anticipated difficulties with solid state electrode solubilities led to the consideration of embedding micro-particles of solid state electrode materials into a chemically resistant matrix. Such a matrix would presumably reduce solubility difficulties and provide the additional bonus of permitting the incorporation of electrode materials otherwise unsuitable for thin film deposition.

An electronic grade polyimide polymer was investigated for its suitability as a matrix material. Polyimide was chosen for this investigation because of its high temperature stability and chemical inertness. High quality, high purity pre-polymer polyimide solutions are available through the semiconductor industry, where they are used to produce 2-100 μm thick, uniform, dielectric films. Deposition and pattern definition of these polymer films is fully compatible with standard planar integrated circuit technology. Heterogeneous membranes using a polyimide matrix are a chemically sensitive thin film candidate for integrated electronic sensors.

Several months were spent developing techniques for incorporating small particles into a prepolymer solution of polyimide. The electrode material chosen was AgCl and the polyimide used is manufactured by Hitachi Chemical, PIQ[®]. The key problem was producing microparticles, $\leq 1 \mu\text{m}$, and then suspending them in the prepolymer PIQ solution in preparation for the spin-on application. A chronicle of these efforts and the measured electrochemical response of these films is recorded in a subsequent chapter.

In early 1984 a systematic series of tests were performed to establish the durability of polyimide thin films in high temperature, dilute, aqueous solutions. The range of polyimide film utility needed to be established. Up to what temperature and what pH would they be useful as either heterogeneous membrane matrix materials or alternately as hermetic encapsulation? The results of the autoclave test and the subsequent fourier transform infrared (FTIR) characterization of the autoclaved films are reported in the subsequently included paper on polyimide survival. The results show the films to survive admirably up to 200°C, but suffer catastrophic failure for tests done at 250°C. The question of hermeticity is tantalizing because 200°C autoclaved samples show unequivocal passivation of the SiO₂ substrate, yet 250°C autoclaved sample FTIR measurements indicate catastrophic failure by chemical hydrolysis of the polyimide and substantial substrate attack. Further in-situ impedance plane plot measurements may help to indicate the hermeticity of polyimide films up to 200°C, their apparent functional limit, and perhaps also indicate the relationship between hermeticity and chemical hydrolysis.

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II. HIGH TEMPERATURE pH SENSING

A. Autoclave System Description And Suggestions For Upgrading The Present System

The autoclave system operated by the CCE was designed for making in-situ electrochemical measurements on solutions simulating downhole geothermal environments. The system consists of a large volume autoclave, high pressure water pump, fluid injection tube, mechanical controllers and various pressure valves for system control and safety blow-out. The construction uses stainless steel and titanium throughout, which minimizes corrosion problems associated with brines and non-neutral pHs. The design allows for considerable flexibility in making measurements and reduces safety risks associated with high temperature-pressure systems.

The autoclave is of relatively substantial volume, 600 ml. Both the vessel and the head are constructed of a single piece of titanium with a stainless steel sheath providing structural strength. The pressure seals of the feedthroughs mounted onto the head, seal directly onto the titanium core. An earlier head design failed due to cracking of titanium liner tubes mounted inside a stainless steel head. The new solid core head eliminates these tubes and hopefully the stress cracking at the sealing points.

The autoclave with its corrosion resistant titanium core is specified to operate to 500°C and 5000 psi. The native TiO₂ oxide passivates the titanium against a wide spectrum of corrosive solutions. However, passivation will begin to fail at pH less than

2.5. The present seal between the autoclave head and body has been effective. The seal is titanium and somewhat vulnerable to scratches and dents. Care should be taken when handling it. The prescribed torquing pattern must be adhered to if the sealing is to be effective and the seal itself is not to be damaged.

The insertion of probes into the autoclave solution must, at present, pass through a single Conax connector (TG-20-8). The connector allows for eight 20 gauge wire leads. Two leads have generally been reserved for a thermocouple, which leaves six leads for working electrodes and reference electrodes. Several electrode encapsulation structures have been proposed. Only one has been used for high temperature - pressure electrochemical measurements. Teflon shrink tubing was used to encapsulate the electrical contact to the IrO_x film and define the electrochemically active region. See Figure 1 for more details.

Temperature regulation of the autoclave is achieved by a two zone furnace and two temperature controllers. The temperature controllers are designed to ramp the furnace up to the desired final temperature via a second order temperature ramp. The damping coefficient of this second order system determines the amount of overshoot. The damping can be altered inside the controller, but the factory setting appears to correspond to a critically damped response.

The present temperature control system is inadequate and must be manipulated to achieve stable, accurate temperatures inside the autoclave. The primary problem stems from lack of temperature feedback from the autoclave itself. At present, the two temperature

controlling thermocouples are situated within the two zones of the furnace. Their placement is necessary to avoid burning out the furnace elements. However, the temperature of the furnace is not strongly coupled to the autoclave temperature. There are several clear reasons for this:

1. An air gap between the autoclave and the furnace wall.
2. The autoclave head is exposed to the ambient environment. Some efforts toward insulation have been made. However, the elongated head was designed to bridge the thermal gradient between the vessel interior and the ambient so that the seals would not undergo substantial thermal cycling.
3. The thermal mass of the autoclave is substantially greater than that of the furnace.
4. The present arrangement is not suited for either rapid sequential or large aliquot titrations. Titration does affect the temperature.

Figure 2 indicates the sort of temperature cycling that has been done. The general procedure is:

1. Bake out water from the furnace insulation 24 hours before using the furnace at high temperature to avoid element to element shorting (100-150°C).

2. Raise the temperature setting to a high value (eg. 500°C) and insert the autoclave.
3. When the internal autoclave temperature is within 10% of the desired temperature, reduce the setting to approximately 50°C above the desired temperature.
4. Adjustment of this setting may be necessary to keep the autoclave temperature from falling below the desired level.

Throughout this procedure, the pressure should be monitored to ensure that it does not exceed 5000 psi. Safety pressure seals will rupture causing a relatively non-destructive decrease in pressurization.

Pressure regulation operates in two different modes, normal operation and safety. In the normal mode of operation pressure is produced by either heating up the autoclave or externally applying pressure via a high pressure fluid pump. The pressure produced by the autoclave above saturated vapor pressure is determined by the initial fluid level in the autoclave and the final temperature. The desired level can either be determined by experience or it can be calculated using steam tables. If the level is incorrectly determined then either substantial bleeding or alternately adding fluid with the high pressure pump must be done once the vessel has reached the desired high temperature.

The pressure of the autoclave is monitored through a direct, dedicated line by a mechanical gauge. Tampering with this arrangement is not advised due to safety considerations.

Two safety seals have been installed. One is attached directly on the autoclave and will fail if autoclave pressure exceeds the seal limit. The other is attached to the input of the titration vessel to limit the total pressure that can be applied by the pump to the titration vessel. Both safety seals are manufactured to fail at 5025 psi.

Injection of titrating fluid into the autoclave is accomplished by pushing fluid out of the titration vessel into the autoclave with the high pressure pump. The speed of titration is controlled by the air pressure applied via the regulator to the pump and the valves between the titration vessel and the pump. The titration vessel separates the injection fluid from the pump fluid with a piston possessing viton o-rings. Friction ensures that a pressure differential exists across the piston. The amount of fluid titrated can be roughly (± 7 ml.) monitored by observing the fluid displacement of the pump. The displacement is drawn from a 50 ml. buret and 7 ml. aliquots are delivered into the titration vessel by the pump.

Figure 3 is an accurate sketch of the components of the autoclave system and their relationship to one another.

Recommendations

The autoclave system to date has proved eminently adequate for material survival testing and proof of concept electrochemical measurements. More refined experiments with greater environmental control will require a slightly more elaborate system. Better pressure regulation, temperature control and more elaborate titration and extraction of vessel fluid will be necessary.

Most electrochemical measurements are done under constant temperature and pressure. The present temperature control system is not automated. A thermocouple inserted either into the autoclave wall or the autoclave fluid must be incorporated into the feedback control network. The very large heat capacity of the autoclave is the dominant element in any thermal model of the system. Ultimately, the microcomputer used to sample the electrode response should also control and record the temperature.

Pressure is also controlled manually. Maintaining constant pressure at constant temperature is relatively simple to $\pm 3\%$, but it requires constant supervision. This is a handicap for extended, overnight measurement runs and rather tedious even for several hours. The situation during titration is somewhat of a juggling act and almost requires two people; extraction, titration and data recording occur simultaneously.

Titration is presently limited to one fluid. Additional titration vessels would open new measurement possibilities. In the instance of pH measurements, three separate titration vessels would be useful: acidic fluid; basic fluid; and DI wafer (the high pressure

pump adds small amounts of contaminating grease to the pressurized fluid). Hysteresis measurements would then be possible and lost vapor (due to manual bleeding or loss through less than perfect seals) could be replaced. These features are particularly valuable for extended measurement times and allow more measurements to be accomplished during each run.

Extraction at present is rather rudimentary and not very efficient. Titration and extraction employ the same tube that extends to the bottom of the autoclave. Mixture of titrant and extract are inevitable. To minimize mixing, at least 30 ml. must be extracted before the extract matches the autoclave fluid composition. If several extractions are made, the 500 ml. volume is very noticeably perturbed and the extraction process is no longer an equilibrium process. A dedicated port for extraction seems to be indicated. This requirement would increase the diameter of the autoclave cap.

B. Experimental Details of The High Temperature pH Measurements

The published paper on IrO_x pH sensing is rather succinct in its description of experimental arrangements. Therefore, further elaboration of the experimental set-up and the rationale for the chosen electrolyte system are presented. The measurements were done at saturated vapor pressure (approximately 70 psi at 150°C) with gas bottle overpressure driving the titration vessel. Since the high pressure fluid pump was down. Instead, a modified autoclave system was configured; the net result was more meaningful extractions,

because installation of separate extraction and injection lines was possible. The configuration is detailed in figure 4. The amount of each titrated aliquot was determined empirically by setting the gas bottle overpressure and timing the period of titration. The assumption was that titration time was proportional to the amount of acid titrated. The in-situ electrodes confirmed a rough proportionality.

The electrode drift that was noted could stem from a number of sources. Suspicion rests first on the rate at which the autoclave solution returns to equilibrium after titration is complete. The extraction tube contains perhaps 20 ml. of fluid and the walls of the autoclave represent a substantial surface area which must equilibrate with the solution. The efficacy of the teflon shrink tubing hermetic seal must also come under suspicion. However, after autoclaving, several electrodes were left soaking in an alcohol based dye overnight. No seepage of dye between the tubing and the electrode was noted. If these two drift sources can be considered negligible, then drift must be isolated to the working and reference electrode materials.

The reference electrode chosen was a Ag/AgCl electrode. The electrode was prepared from a 28 gauge pure silver wire:

1. Dip the wire into nitric acid for 15 seconds as an initial cleaning step to remove any carbonaceous impurities.

2. Place in concentrated NH_4OH for 1 hour to remove residual oxides and chlorides.
3. Store in DI water.
4. Chloridize the wire in 0.1 M HCl with a current density of 1 mA cm^{-2} . It is good practice to reverse the potential initially to remove a thin layer of Ag before beginning the chloridization.

(Ag is the anode).

5. Allow the chloridized electrode to equilibrate in DI water overnight. It will turn a dark plum color.

The shrink tubing can be applied before or after chloridization. AgCl has a melting point in excess of 425°C , whereas the tubing shrinks at 330°C .

The autoclave solution was designed to maintain a constant chloride ion concentration. The potential of the reference Ag/AgCl electrode should not have changed with respect to the solution. The initial 0.01 M KCl solution was adjusted to pH 9 with concentrated KOH . High temperature titrations were done with 0.01 M HCl ; these titrations will not alter $[\text{Cl}^-]$. $[\text{Cl}^-]$ changed only if vapor escaped through high pressure seals. The autoclave and seals were correctly assembled and tightened, thus vapor loss was negligible.

The Ag/AgCl electrode was assumed to have provided an accurate reference voltage. However, care must be taken in the implementation of Ag/AgCl electrodes which are in direct contact with hot solutions. "The Ag/AgCl electrode shows some undesirable characteristics at high temperature; one is its sensitivity to hydrogen. Bubbling H₂ gas over the electrode can produce potentials intermediate between those of the hydrogen electrode and those of the Ag/AgCl electrode. Hydrogen sulfide also affects the behavior of the electrode because of the formation of the less soluble silver sulfide. This salt exhibits, in part, electronic conductivity, causing deviations from calculated values. Also, there are indications that AgCl may not be stable in dilute NaHCO₃ solutions at temperatures above 150°C, since metallic Ag is found in suspension. The Ag/AgCl electrode, however, behaves well in hydroxide solutions up to ratios of 10:1 NaOH:NaCl."¹

The autoclave solution chosen models a typical geothermal well with respect to Cl⁻ and H⁺ concentrations. The probable median range for NaCl is 0.003-0.03 M NaCl. The pH in the autoclave was titrated from pH 9 to pH 2.5. The extreme values reported for geothermal wells are pH 4 and pH 9, but vast majority fall between pH 5-7.5 .²

¹ P. 37, "Assessment of the Characterization of Geothermal Brines," U.S. Dept. of Commerce, No. PB-276 399, Final Report.

² p. 10, Ibid

C. LOW TO HIGH TEMPERATURE pH CALIBRATION

The graph of the room temperature extraction pH versus the in-situ, high temperature electrode potentials must be recalibrated. The room temperature pH must be calibrated up to the high temperature pH. For any given sample, the pH, $-\log [H^+]$, varies with temperature. The ionic activity varies with temperature, but pH dependence on temperature is dominated by variations in the dissociation constant of water, K_w . As an indication of the substantial shifts possible, the pK_w shifts from 14 to 11.5 as the temperature is increased from 20°C to 150°C.

The electrolyte system employed can be modeled by the following seven equations:

Mass Action - Equilibrium

$$\text{or} \quad K_w = [H^+] [OH^-]$$

$a(I)$ represents ionic activity. In most circumstances the activity can be equated with ionic concentration.

Mass Balance

$$[KCl] + [KOH] + [K^+] = C_{OK} = \text{total conc. of K} \quad (5)$$

$$[KCl] + [HCl] + [Cl^-] = C_{OCl} = \text{total conc. of Cl} \quad (6)$$

Charge Balance

$$[K^+] + [H^+] = [Cl^-] + [OH^-] \quad (7)$$

The system can be presented by the matrix

$a(Cl^-)$	0	$-K_s$	0	0	0	0	$a(K^+)$	0
0	0	0	$-K_B$	0	0	$a(K^+)$	$a(Cl^-)$	0
0	$a(H^+)$	0	0	$-K_A$	0	0	$a(KCl)$	0
0	0	0	0	0	$a(OH^-)$	0	$a(KOH)$	$= K_w$
1	0	1	1	0	0	0	$a(HCl)$	C_{OK}
1	-1	0	0	0	1	-1	$a(H^+)$	0
0	1	1	0	1	0	0	$a(OH^-)$	C_{OA}

For temperatures comfortably below the critical point of water, 374°C, the above equation set can be simplified by the following approximations:

i. Ionic activities equal ionic concentrations

$$\text{eg. } a(\text{H}^+) = [\text{H}^+] \quad (9)$$

ii. Complete dissociation of the various salts into their solvated ions

$$[\text{HCl}] = 0$$

$$[\text{KCl}] = 0$$

$$[\text{KOH}] = 0$$

These approximations reduce the equation set to only two non-trivial equations:

$$[\text{K}^+] + [\text{OH}^-] = [\text{Cl}^-] + [\text{OH}^-] \quad \text{charge balance} \quad (10)$$

$$[\text{H}^+] [\text{OH}^-] = K_w(T) \quad \text{water dissociation constant} \quad (11)$$

combining these two equations, a quadratic equation with respect to $[\text{H}^+]$ results:

$$[\text{H}^+]^2 + ([\text{K}^+] - [\text{Cl}^-]) [\text{H}^+] - K_w(T) = 0$$

The value of ultimate interest in this calculation is $[\text{H}^+]$ as a function of temperature. $K_w(T)$ is known; published tables of international standardized reference values have now been published.³ $[\text{Cl}^-]$ is known and held constant throughout the experiment. $[\text{K}^+]$ is not carefully controlled. It is dependent upon the initial concentration of KOH used for pH adjustment and the

3

W.L. Marshall, E.U. Franck, J. Phys. Chem. Ref. Data 10, 295 (1981).

β	pH(25°C)	pH(156°C)
-10^{-5}	9.00	6.51
-10^{-6}	8.00	5.87
-10^{-7}	7.21	5.75
$+10^{-5}$	5.00	4.99
$+10^{-6}$	5.99	5.63
$+10^{-7}$	7.79	5.74

These calculations boil down to simply correlating the change in measured pH with respect to a temperature dependent dissociation equilibrium for water.

pH CALIBRATION CURVE

pH 156°C

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(pp 23 → 27 removed and cycled separately)

III POLYIMIDES IN HIGH TEMPERATURE AQUEOUS SENSING

A. Polyimide Based Heterogeneous Thin Film Electrodes

Work on thin film heterogeneous membranes utilizing polyimide grew out of efforts aimed at developing high temperature sulfide electrodes. The results of a literature search during the summer of 1983 indicated that most of the standard solid state sulfide electrode materials did not possess low enough solubilities at higher temperatures. Even those that had small solubilities presented the further difficulties associated with the development of a simple, high quality, low cost deposition technique. The merits of the heterogeneous membrane approach are:

1. Just about any electrode material could be ground-up and included into a polyimide matrix.
2. Solubility of electrode materials would be reduced because of the protection offered by the surrounding polymer matrix.
3. The compatibility of polyimide deposition and pattern definition to standard IC planar technology is well established.

The initial experimental efforts have been directed towards preparation of AgCl-polyimide films rather than sulfide-polyimide films. AgCl was in stock and electrochemical potential measurements of chloride ion solution concentrations are easily accomplished in calibrated chloride salt solutions. The first attempt to reduce AgCl particles to powder in a ball mill did not meet with success. Silver chloride particles evidence a strong tendency to agglomerate. The

integrity of 3 μ m thick polyimide films with 20-35 μ m AgCl agglomerates is questionable. The second effort, precipitating AgCl from a AgNO₃ solution with HCl titration, failed to yield uniformly small particle size. Selective filtering to recover the smallest particles proved non-trivial.

The third effort which precipitated AgCl from a pyridine solution yielded the smallest particle size and the best film uniformity. The initial thought was to find a solvent for AgCl that would be miscible with the prepolymer polyimide solution. If the two solutions, one containing AgCl and the other polyimide precursor, were mixed together and spun-on to the wafer surface, then evaporation of the solvent during spinning would result in the AgCl precipitating out. We hoped that the precipitant would be of small size, comparable with the polyimide film thickness. We did find a solvent for AgCl, but the AgCl precipitated out when the AgCl/pyridine solution was mixed with the N-methyl-pyrrolidone based polyimide solution. Fortunately, if the solution mixing is done with either a high rpm sheer mixer or an ultrasonicator probe, particle size is quite small (<1 μ). The high viscosity of the polyimide solution component appears to limit particle size and agglomeration. This viscosity also assists in suspending the desired microparticulate while the larger particles are centrifuged out.

Both a sheer mixer and an ultrasonic microtip cell disruptor were tested for particle agglomeration reduction. Neither technique was very effective. Later these two methods were used to mix the AgCl and polyimide solutions. Both methods were roughly equivalent,

however, the sheer mixer has slight advantages. The ultrasonic tip was able to transfer only partial power to the solution, because the viscosity tended to pull the solution away from the tip, while the mixer could be run at full speed of 25,000 rpm. The ultrasonicated sample also tended to heat up faster as well. This heating could be minimized by some sort of cooling bath, but the price differential between the two pieces of equipment eventually dictated the purchase of the high speed sheer mixer.

The solubility of AgCl in pyridine merits extended comment. The solubility varies substantially with temperature. As indicated in Table 1 and graph 1, the maximum solubility of 5.60 gm AgCl per 100 gm pyridine, occurs at -1°C . Solubility is significantly less only a few degrees either warmer or colder from -1°C . Below 0°C pyridine and AgCl produce a solid phase in equilibrium with the solution of the complex $\text{AgCl} \cdot \text{C}_5\text{H}_5\text{N}$. We have observed this experimentally. As the pyridine solution is cooled from room temperature, more and more AgCl goes into solution. The maximum achieved was 3.5 gm AgCl/100 gm pyridine, less than the literature indicated. However, as the solution is cooled to below 0°C by adding alcohol to the ice bath, crystallites form in the solution indicating the formation of the solid phase complex $\text{AgCl} \cdot \text{C}_5\text{H}_5\text{N}$. This crystalization phenomenon is undesirable.

Experimental Procedure

1. Preparation of the pyridine solution
 - a. Cool known quantity of pyridine to 0°C
 - b. Add 3.5 gm AgCl per 100 gm pyridine

- c. Most of the AgCl should slowly go into solution.
 - d. It is important to maintain anhydrous conditions.
2. Mixing of the pyridine and polyimide solutions (Hitachi PIQ-13).
 - a. Pipet off an aliquot of pyridine solution
 - b. Add to a known cooled quantity of polyimide solution.
 - c. Mix rapidly in a high speed sheer mixer or with a high power ultrasonic microprobe. The AgCl should precipitate out of solution during the mixing and not before, except at the interface of the solutions.
3. Remove larger AgCl particles by centrifugation. The majority of the AgCl particles remain suspended; only the largest are eliminated if centrifugation is not too long or carried out at too high a speed.
4. Following centrifugation, the suspension is ready for spin-on application. Several layers were spun on top of one another.
5. Figure 5 illustrates to scale the electrode structure used to evaluate the electrochemical properties of the films. Encapsulation and active area definition were achieved with "EPOXI-PATCH" manufactured by Hysol Division, Dexter Corporation, Olean, New York, 14760.

Experimental Results

Several films with varying percentages of polymer to silver chloride were prepared and characterized by measuring their open circuit electrical potentials with respect to a double junction reference electrode. The earliest attempts which included films with

large particle sizes, greater than 10 μm particles in a nominally 3 μm thick polyimide film, had characteristically Nernstian responses to $[\text{Cl}^-]$, 10^{-4} - 10^{-1} Molar KCl. The films with very small silver chloride concentrations, less than 20% by weight, did not exhibit Nernst responses. Presumably the electrochemical response observed can be attributed to large silver chloride particles which were in direct contact with both the solution and the gold ohmic contact.

The second set of films prepared from pyridine solutions contained particles generally less than 2 μm in size. These films exhibited high impedance, drift and in all cases but the most highly doped film, a non-Nernstian response. All of the smaller ratios of AgCl/PIQ, produced films of very high impedance. The single electrode that did work contained 4 gm of AgCl to 1 gm of PIQ solids, which corresponds to a matrix filling ratio of 1:1.¹ The open circuit electrochemical measurements of this electrode are recorded on Figure 6.

Remarks

A close to Nernst response on a single electrode does not justify the conclusion that the heterogeneous material synthesized is a candidate for a broad range of high temperature electrochemical measurements. A number of unanswered questions await further investigation:

1

The density of AgCl is 5.56 gm/cm³ and 1.42 gm/cm³ for polyimides.

1. What particulate to polymer ratios are necessary to produce useful films? Presumably, the greater the polymer fraction, the greater the durability of the films.
2. What are the properties of these composites in high temperature aqueous environments? Does electrical and ionic conductivity increase at high temperature? Are the films rugged?
3. What is the mechanism for the electrochemical response? What is the nature of the ionic and electronic conduction in these films? In-situ film impedance measurements would provide some answers.
4. Will other powdered solids produce electrochemically sensitive thin films? The original aim to build high temperature sulfide electrodes has not yet been accomplished.

The preliminary results do encourage further investigation. The concept of heterogeneous thin films for chemical sensing has enormous potential, particularly if these films have relatively low electrical impedances.

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(pp. 35 → 41 removed and cycled separately)

IV. CONCLUDING REMARKS

The work detailed in this thesis represents a small contribution towards the task of developing effective geothermal and high temperature chemical sensing. Both the polyimide and the IrO_x work are only in a seminal stage. Both of these materials warrant continued investigation. This document exists to fulfil thesis requirements, document my contribution to the geothermal research grant and provide continuity for future graduate students work in this area.

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HIGH TEMPERATURE PH ELECTRODE STRUCTURE

FIGURE 1

AUTOCLAVE TEMPERATURE CYCLE

FIGURE 2

FIGURE 3

FIGURE 4

AgCl / POLYIMIDE ELECTRODE
TEST STRUCTURE

CHEMICALLY SENSITIVE
AgCl / POLYIMIDE MEMBRANE

FIGURE 5

OPEN CIRCUIT VOLTAGE PLOT
4:1 AgCl/PIQ Electrode #5

1-2-84

FIGURE 6

TABLE 1

SOLUBILITY OF SILVER CHLORIDE IN PYRIDINE
(Kahlenberg and Wittich, 1909)

t°	Gms. AgCl per 100 Gms. Pyridine	Solid Phase	t°	Gms. AgCl per 100 Gms. Pyridine	Solid Phase
-57 Eutec.		AgCl·2C ₅ H ₅ N + C ₆ H ₅ N	0	5.35	AgCl
-49	0.77	AgCl·2C ₅ H ₅ N	10	3.17	"
-35	0.99	"	20	1.91	"
-30	1.36	"	30	1.20	"
-25	1.80	"	40	0.80	"
-22	2.20	"	50	0.53	"
- tr. pt.	2.75	" + AgCl·C ₅ H ₅ N	60	0.403	"
-20	3.75	AgCl·C ₅ H ₅ N	70	0.32	"
-18	3.85	"	80	0.25	"
-10	4.35	"	90	0.22	"
- 5	5.05	"	100	0.18	"
- 1	5.60	"	110	0.12	"

SOLUBILITY OF AgCl IN PYRIDINE

GRAPH 1