Control and Measurement of Low Oxygen Partial Pressures in H_2 or N_2 Gas Using Calcia-Stabilized Zirconia Cells

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Introduction

Calcia-stabilized zirconia (CSZ) cells have been designed and fabricated to operate as an oxygen gauge to measure oxygen partial pressures in a gas flow (H_2 or N_2), and as an oxygen pump to increase or decrease oxygen partial pressures in it. In the atmosphere of H_2 flow, oxygen incorporation in it usually takes the form of $H_2O(g)$, whereas in N_2 oxygen can exist either as $O_2(g)$ or $H_2O(g)$ since there is a trace amount of H_2 in commercially supplied N_2. Control and measurement of low oxygen partial pressures were carried out over varying flowrates and pump currents in both flowing H_2 and N_2 gas. The results were presented and discussed for both gases.

Cell Operation

Calcia-stabilized zirconia (CSZ) is commercially available in various sizes, shapes and doping concentrations. Impurity doping causes defects in pure zirconia (ZrO_2) and is responsible for electrical (mainly ionic) conductivity. When pure zirconia is doped with divalent metal oxide such as calcium oxide (CaO), oxygen vacancies are created, one for each Ca atom. These doubly charged oxygen vacancies ($V_O^{\cdot\cdot}$) are formed to maintain electrical neutrality with substitutional calcium. In the substitutional defect, a Ca^{2+} ion occupies a nominal Zr^{4+} ion site (represented by Ca_{Zr}'') and has a relative charge of -2 [3]. When gases with different oxygen activities are present at the two opposite sides of the CSZ electrolyte and the temperature is raised sufficiently high, diffusion of oxygen ions will take place due to an oxygen concentration gradient across the electrolyte. This results in a reverse electric field which develops across the electrolyte in order to maintain equilibrium. The electric field can be equivalently described as being caused by the migration of oxygen vacancies in the direction opposite to that of oxygen ions until equilibrium is reached. Although electron diffusion is in general present, essentially all charge conduction is ionic at a cell operating temperature of 500°C. With one gas having a known amount of oxygen content, the cell emf represents a measure of the oxygen content in the other gas according to the relation [1,5]:

$$E = \frac{-RT}{4F} \ln \left[\frac{P_{O_2}}{P_{O_2}(\text{ref})} \right] \tag{1}$$

In H_2 gas, equation (1) can be modified to [1]:

$$E = \frac{-RT}{2F} \ln \left[\frac{(P_{H_2O}/P_{H_2})}{(P_{H_2O}/P_{H_2})\ \text{ref}} \right] \tag{2}$$

where

$$R = \text{gas constant}$$

$$T = \text{cell temperature in K}$$

$$F = \text{Faraday equivalent}$$

$$P_{O_2(ref)} = \text{reference oxygen partial pressure}$$

$$(P_{H_2O}/P_{H_2})ref = \text{reference ratio of water partial pressure to hydrogen partial pressure}$$

$$P_{O_2} = \text{unknown oxygen partial pressure}$$

$$\frac{P_{H_2O}}{P_{H_2}} = \text{ratio of unknown partial pressure of water to hydrogen partial pressure}$$

When an electrical potential is applied across the cell, oxidation and reduction reactions will take place at the two electrolyte surfaces (electrodes) depending on the polarity of the applied potential. Oxygen is released at one electrode and captured at the other as a result of oxidation and reduction respectively. Thus a CSZ cell can be used as a pump to pump oxygen from one gas to the other through the electrolyte.

A CSZ gauge and a CSZ pump were fabricated using a 6″ long by 1/4″ O.D. and a 12″ long by 1/4″ O.D., respectively, slip cast tube made of ZrO_2 with 7.5 w/o CaO (Figures 1 and 2). Cell temperature was kept constant at 500°C by Eurotherm model 931 and 913 temperature controllers. The component layout and flow path of the gas flow system is illustrated in detail in Figure 3.
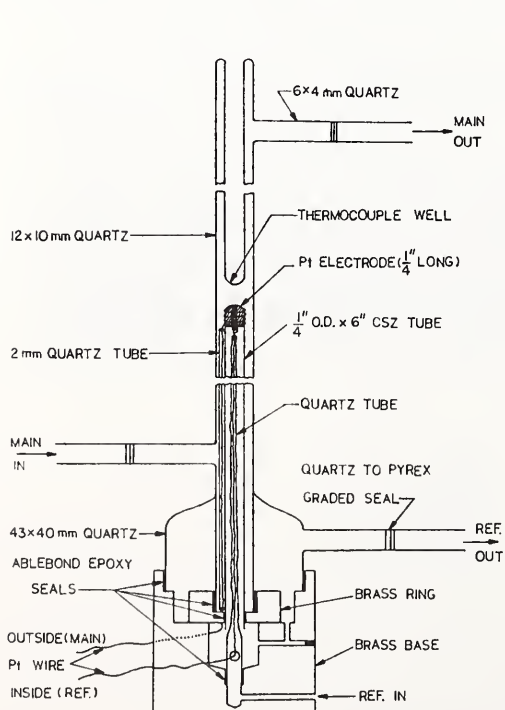

FIGURE 1. *CSZ Gauge Design*
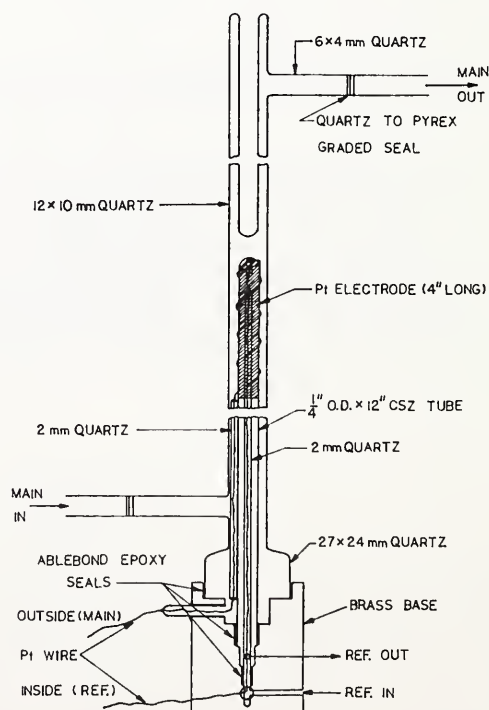
FIGURE 2. *CSZ Pump Design*
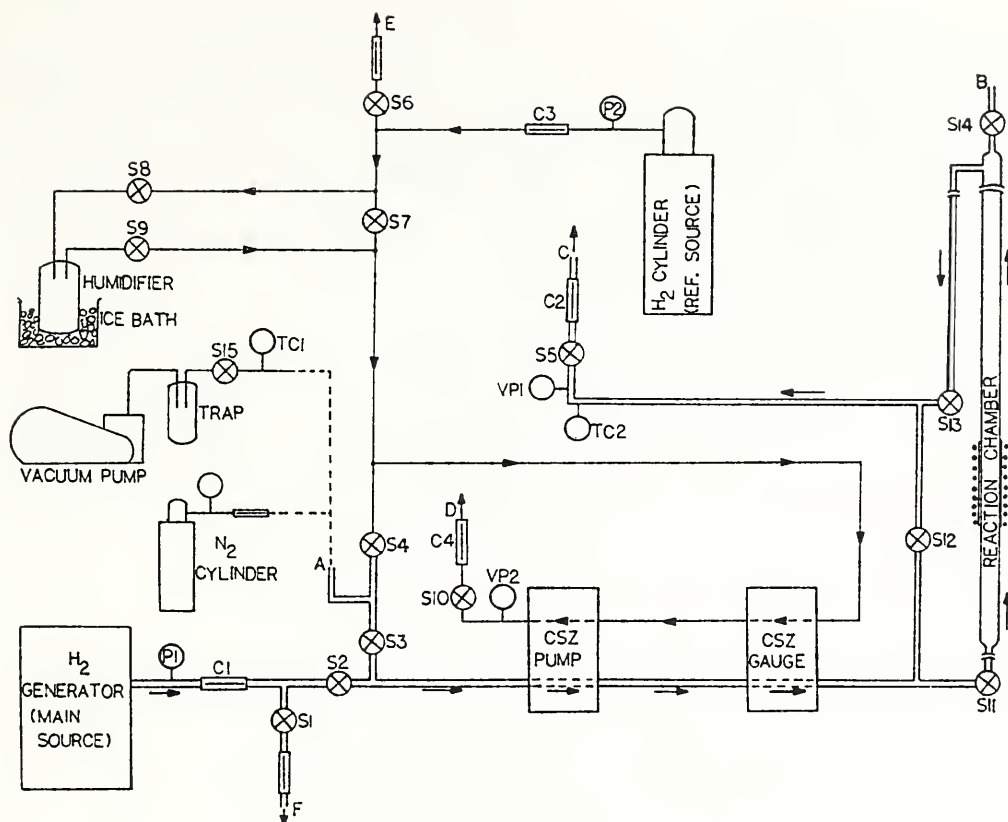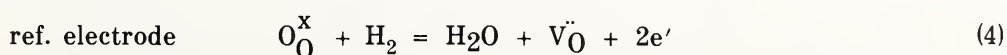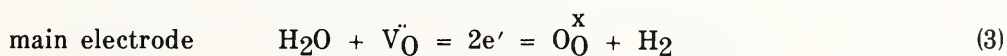
Figure 3. *Gas Flow System*

Results and Discussion
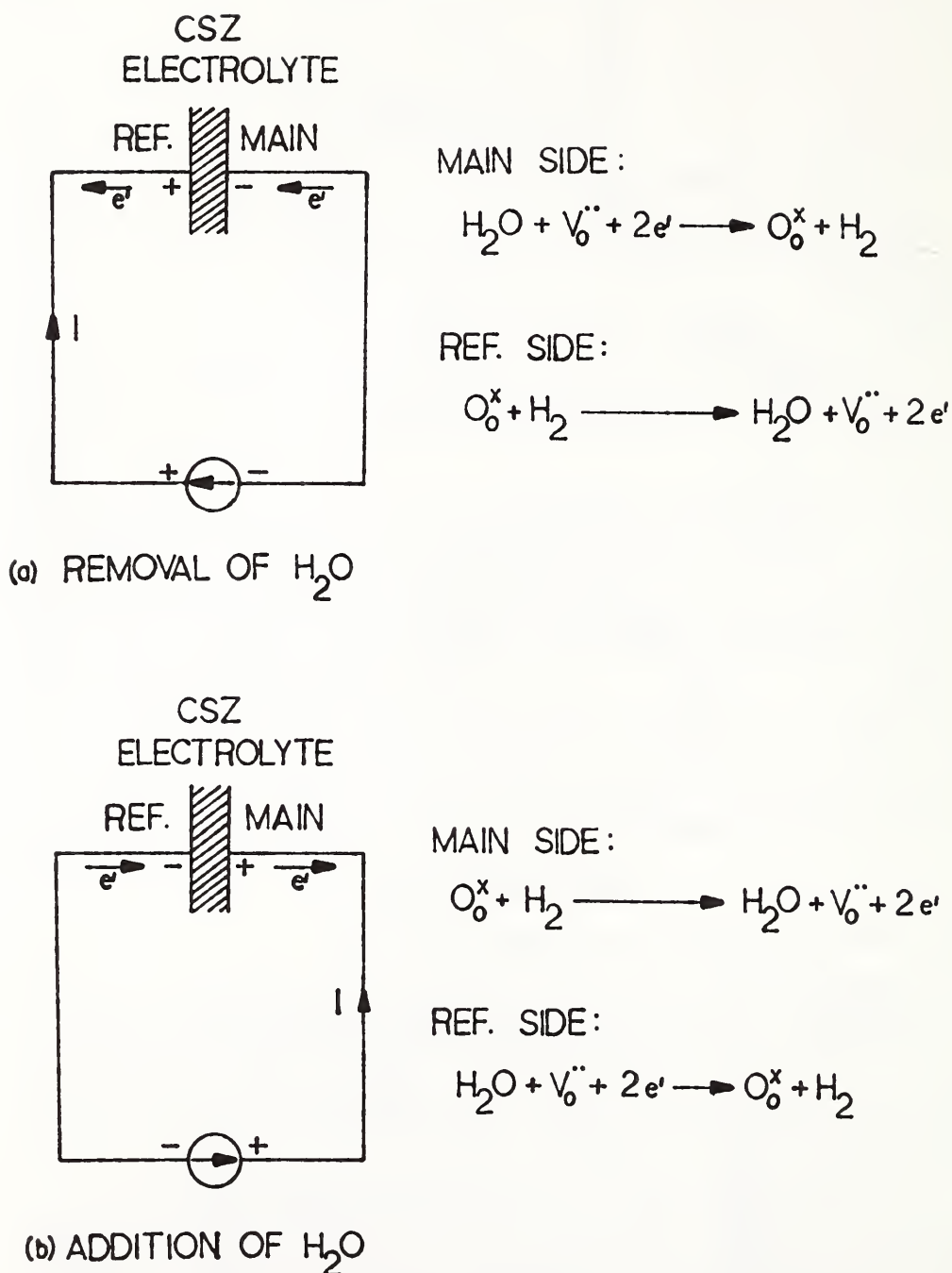
3.1 *Control and Measurement of $H_2O(g)$ in $H_2(g)$ Flow*

In the control and measurement of H_2O concentrations in an H_2 gas stream, an ultra high purity (UHP) H_2 gas was generated by an Elhygen Mark V hydrogen generator with a built-in palladium diffuser. A cylinder of UHP H_2 was employed as a source of the reference gas. The oxygen activity of the reference gas was established by passing $H_2(g)$ through a water saturator which was kept at 0 °C [3] where P_{H_2O} was known to be 6.025 x 10^{-3} atm [4].

The The H_2O concentration in the main H_2 gas may be altered by applying an electrical potential across the CSZ pump surfaces. In practice, however, a constant current source (Keithley model 227) was used because it provided a very steady and more convenient means of controlling the amount of $H_2O(g)$ to be added to or removed from the gas stream. When a current source is connected to a CSZ pump so that the positive and negative terminals are connected to the reference and main electrodes on the pump surfaces respectively (Figure 4), $H_2O(g)$ is removed from the main gas as follows:

main electrode $\qquad H_2O + V_O^{\cdot\cdot} = 2e' = O_O^x + H_2 \qquad\qquad$ (3)

ref. electrode $\qquad O_O^x + H_2 = H_2O + V_O^{\cdot\cdot} + 2e' \qquad\qquad$ (4)

At the main electrode, oxygen removed from H_2O molecules combines with oxygen ion vacancies on the electrode surface and electrons to become electri-

CSZ
ELECTROLYTE

REF. ▨ MAIN

MAIN SIDE:

$$H_2O + V_o^{\cdot\cdot} + 2e' \longrightarrow O_o^x + H_2$$

REF. SIDE:

$$O_o^x + H_2 \longrightarrow H_2O + V_o^{\cdot\cdot} + 2e'$$

(a) REMOVAL OF H_2O

CSZ
ELECTROLYTE

REF. ▨ MAIN

MAIN SIDE:

$$O_o^x + H_2 \longrightarrow H_2O + V_o^{\cdot\cdot} + 2e'$$

REF. SIDE:

$$H_2O + V_o^{\cdot\cdot} + 2e' \longrightarrow O_o^x + H_2$$

(b) ADDITION OF H_2O

FIGURE 4.   *Electrode Surface Reactions*

cally neutral oxygen sites. At the reference electrode, oxygen atoms from oxygen sites near the electrode surface react with H_2O and form $H_2O(g)$. This in turn creates oxygen ion vacancies and electrons are released. These electrons flow back to the current source while oxygen ion vacancies migrate to the main electrode surface to provide a continuous supply of $V_O^{\cdot\cdot}$ in reaction (3). To add $H_2O(g)$ to the main gas stream, the polarity between the current source and the CSZ pump electrodes are reversed. The amount of current required to add or remove lppm (10^{-6} atm) of H_2O to or from the main gas stream is 0.1436 Q μA [2] where Q is the flowrate in scc-atm/min.

At a flowrate of 100 cc/min, the H_2O concentration in the main gas stream without pumping (i.e. background level) was found to be ~ 3.3 ppm. About half of the H_2O measured was furnished by the hydrogen supply and was fixed regardless of a flowrate. The remaining H_2O was believed to be the result of outgassing from various glass epoxied and O-ring joints, and it varied inversely with flowrates. When electric current was applied to the pump (Table 1), the H_2O concentrations were shown to be adjustable from 0.0223 ppm to above 100 ppm. The lower and upper limits can be extended further by increasing and decreasing the flowrate respectively. Note that the current required to add 1 ppm of H_2O was 13.29 mA since the flowrate of 100 cc/min at room temperature (22°C) implied that the standard flowrate was $(100 \times 273)/(273 + 22) = 92.54$ scc/min. Figures 5-7 show the plots of measured ppm versus background $\pm$ pumped ppm. The pump efficiency decreased significantly after a few ppm of H_2O had been removed from the main gas since there was a near complete depletion of H_2O in the gas stream. When the current was applied in the direction so that H_2O was added to the main

TABLE 1

	Pump Current (μ A)	Pumped ppm	Background $\pm$ Pumped ppm	Measured Emf (mV)	Measured ppm
Increase $H_2O(g)$	1328.63	100	103.31	134.7	105.56
	930.04	70	73.31	144.7	78.18
	664.32	50	53.51	155.7	56.18
	389.59	30	33.31	172.3	33.73
	265.73	20	23.31	184.6	23.59
	132.86	10	13.31	202.9	13.62
	93.00	7	10.31	211.7	10.42
	66.43	5	8.31	219.1	8.37
	53.15	4	7.31	223.6	7.30
	39.86	3	6.31	228.7	6.27
	26.57	2	5.31	234.5	5.27
	13.29	1	4.31	241.7	4.25
	0	0	3.31	250.0	3.31
Remove $H_2O(g)$	10	−0.753	2.56	262.3	2.28
	13.3*	−1.000	2.31	271.0	1.76
	20	−1.505	1.81	273.5	1.64
	26.57*	−2.000	1.31	297.5	0.795
	30	−2.258	1.05	283.9	1.195
	40	−3.011	0.299	292.0	0.924
	39.86*	−3.000	0.31	347.5	0.177
	50	−3.763	−0.45	393.0	0.045
	60	−4.516	−1.21	396.3	0.041
	70	−5.289	−1.98	406.5	0.0301
	80	−6.021	−2.71	410.5	0.0267
	90	−6.774	−3.46	411.5	0.0259
	100	−7.527	−4.22	415	0.02335
	110	−8.279	−4.97	415.8	0.0228
	120	−9.032	−5.72	416.0	0.0225
	130	−9.785	−6.48	416.4	0.02234
	150	−11.29	−7.98	416.5	0.02233

Q(T = 22°C, P = 1 atm) = 100 cc/min = 92.54 SCC-atm/min

*Extension of data obtained at the same time as data for the addition of H_2O to the background level.
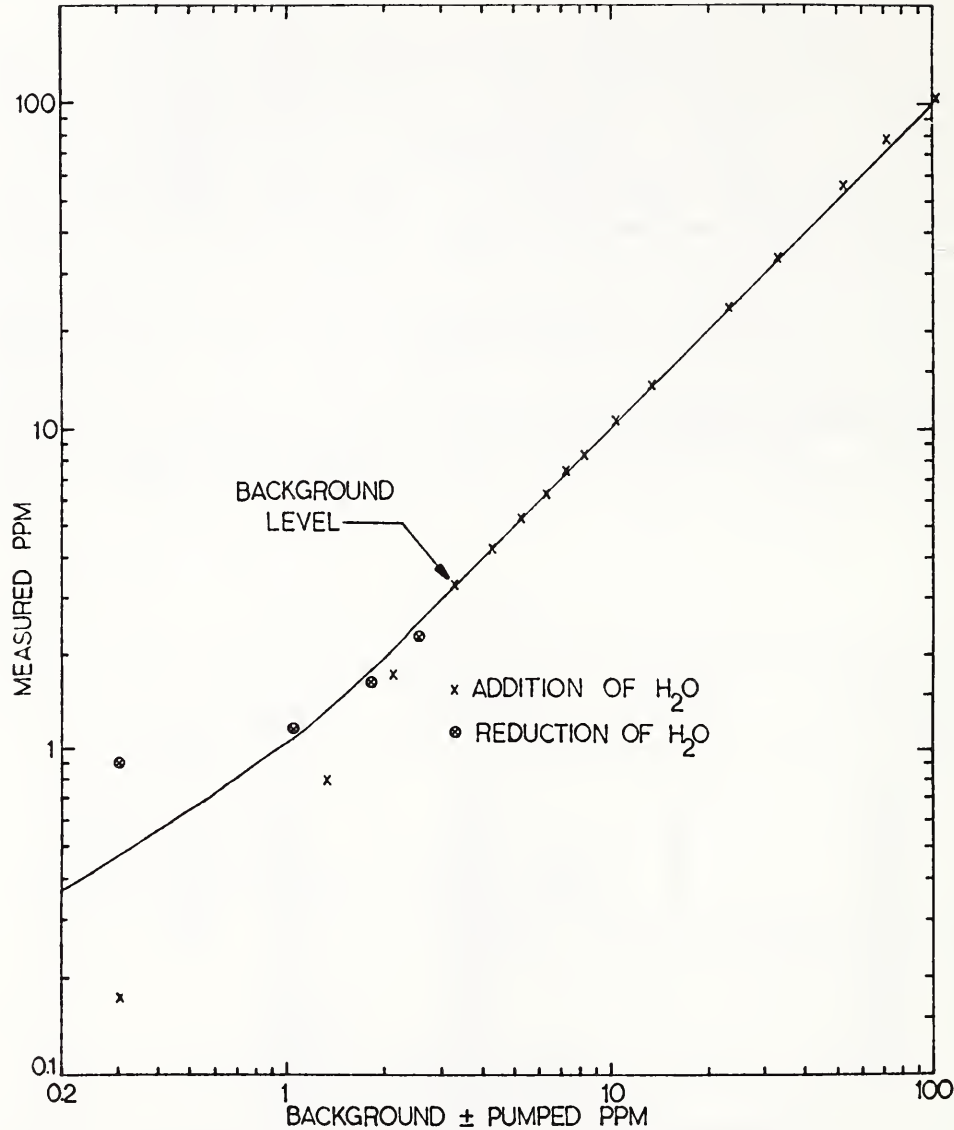
FIGURE 5.   *Plot of Pumped H_2O Versus Measured H_2O in H_2*
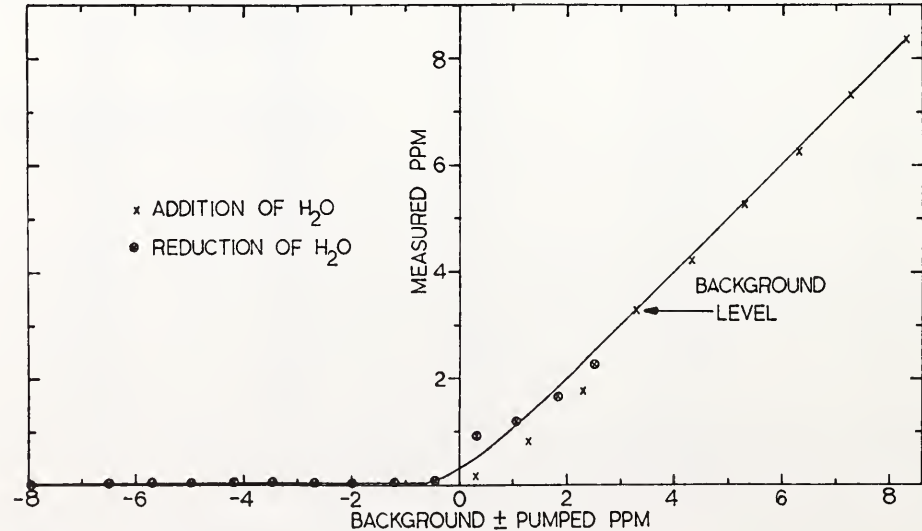
FIGURE 6.   *Plot of Pumped H_2O Versus Measured H_2O in H_2*
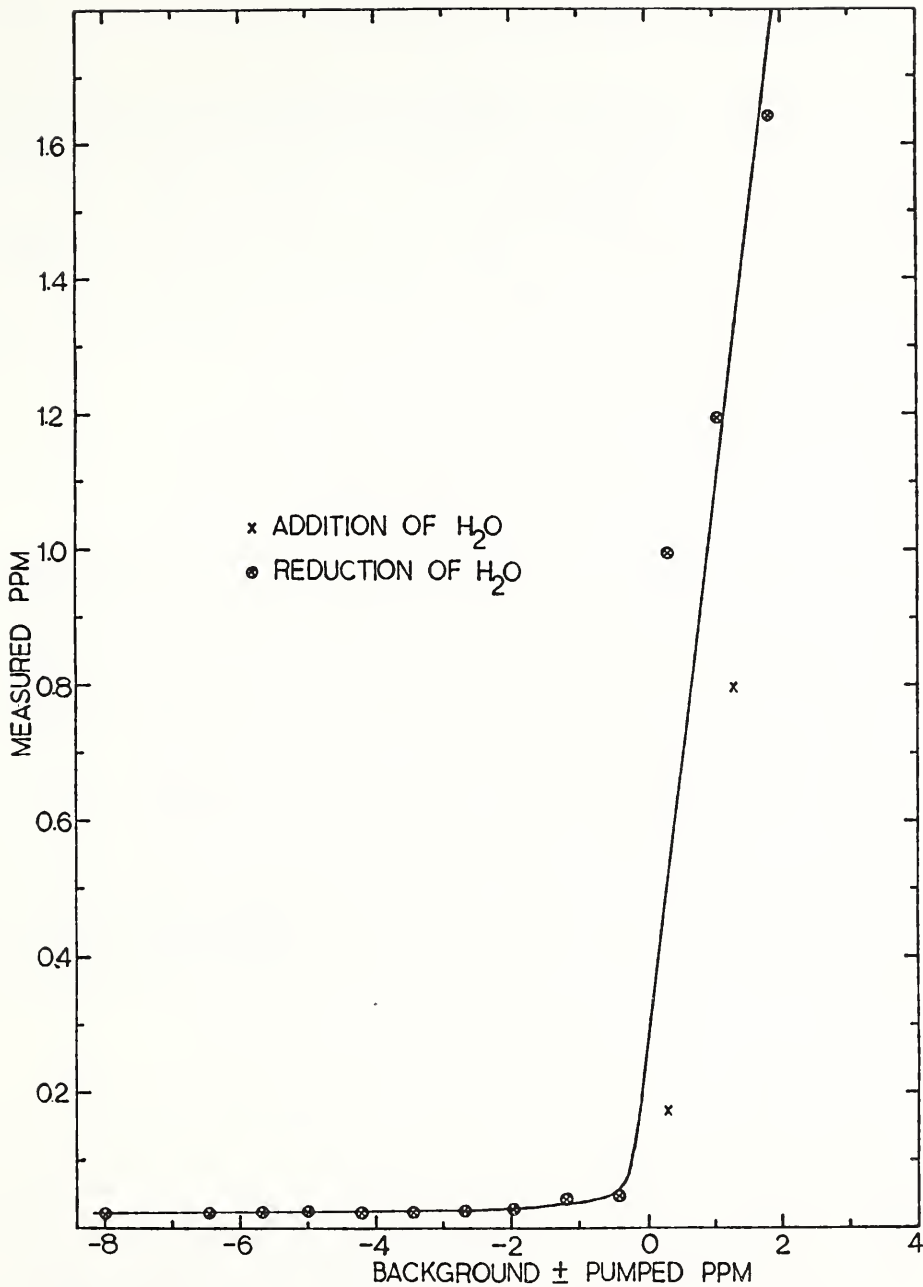
FIGURE 7. *Plot of Pumped H_2O Versus Measured H_2O in H_2*

gas stream, the pump exhibited an almost linear relationship between the pump current and the measured amount of H_2O being pumped. Some discrepancies were observed between 1 and 2.5 ppm since this was the area most sensitive to environmental changes. Fluctuation of H_2 flowrates from the H_2 generator due to line voltage fluctuations, slight variation from 0 °C of the ice bath (if the bath temperature was -1 °C, for instance, the H_2O level from the reading would be a few tenths ppm higher then the actual level), fluctuation of room temperature, and inaccuracies of the equipment used (voltmeters and ammeter) were all thought to be responsible for the recorded errors.

3.2   *Control and Measurement of $O_2(g)$ in $N_2(g)$ Flow*

The experimental set-up for the control and measurement of oxygen content in N_2 gas stream was essentially the same as that for the control and measurement of H_2O concentrations in H_2 gas. N_2 gas from a UHP-N_2 cylinder was fed into the main path through a capillary tube at point A (Figure 3). Again H_2 gas from a UHP-H_2 cylinder, saturated with $H_2O(g)$ at 0°C was used as a reference gas. Since we wish to interpret the measured emf's in terms of oxygen partial pressure (P_{O_2}), equation (1) was used here. P_{O_2} is the equilibrium oxygen partial pressure of (P_{H_2O}/P_{H_2}) ref and is found to be $7.1364933 \times 10^{-33}$ atm at 500°C [4]. Equation (1) thus becomes

$$P_{O_2} = \exp \left\{ - \frac{4FE}{RT} + \ln(7.1364933 \times 10^{-33}) \right\} \qquad (5)$$

At the flowrate of about 10 cc/min at 22°C (9.25 scc/min), P_{O_2} in N_2 flow was measured to be 1.36×10^{-30} atm at the gauge electrode surface. This was equivalent to P_{H_2O}/P_{H_2} (in flowing N_2) = 0.126 at 500°C [4]. Upon application of electric current to the CSZ pump in the direction to add oxygen to the main N_2 gas stream, P_{O_2} began to rise (Figure 8). Initially oxygen added to the N_2 gas stream combined with trace $H_2(g)$ impurity to form $H_2O(g)$. The rise of P_{H_2O}/P_{H_2} or its equivalent P_{O_2} was gradual but steady as the pump current increased. At about 330 μA of applied current $(P_{O_2} \cong 2.5 \times 10^{-25}$ atm), a sharp rise of P_{O_2} was observed. This was most likely due to the exhaustion of the available $H_2(g)$ in the flowing N_2 gas. The curve then began to flatten at the onset of addition of O_2 to the main gas stream where P_{O_2} is about mid-10^{-6} atm. P_{O_2} could be pumped to about mid-10^{-4} atm at 1000μA pump current. Plots for flowrates of 20, 30 and 50 cc/min yielded a very similar characteristics and little change in values of P_{O_2} and hence are not shown here.

Conclusion

A CSZ pump and a CSZ gauge were designed, fabricated and built into a gas flow system to control and measure oxygen partial pressures (or H_2O) in N_2 or H_2 gas streams. In streaming H_2, $H_2O(g)$ content could be varied from 0.0223 ppm (equivalent $P_{O_2} = 1.067 \times 10^{-43}$ atm) to over 100 ppm (equivalent $P_{O_2} < 1.97 \times 10^{-36}$ atm) with a background level at 3.3 ppm at 100 cc/min flowrate. This range can be expanded by varying flowrates. In an N_2 flow, the background (equilibrium) oxygen partial pressure was found to be 1.36×10^{-30} atm at 10 cc/min flowrate. When current was applied to the pump to add oxygen to streaming N_2, P_{O_2} rose gradually with pump current until it reached $\sim 2.5 \times 10^{-25}$ atm. A sharp rise of P_{O_2} due to exhaustion of $H_2(g)$ in N_2 was then observed. The curve began to flatten out at $P_{O_2} \cong$ low-mid 10^{-6} atm due to the onset of addition of oxygen to N_2. P_{O_2} of about mid 10^{-4} atm were achieved with 1000 μA pump current. Since the breakpoint from low to high P_{O_2} value when pumping oxygen into N_2 apparently depends on the H_2 concentration in the N_2, one should be able to adjust the breakpoint upward by adding more H_2 to the N_2. Observe that below the breakpoint the curve (Figure 8) is nearly linear such that one order of magnitude change in P_{O_2} corresponds to $\sim 50 \mu$A pump current.
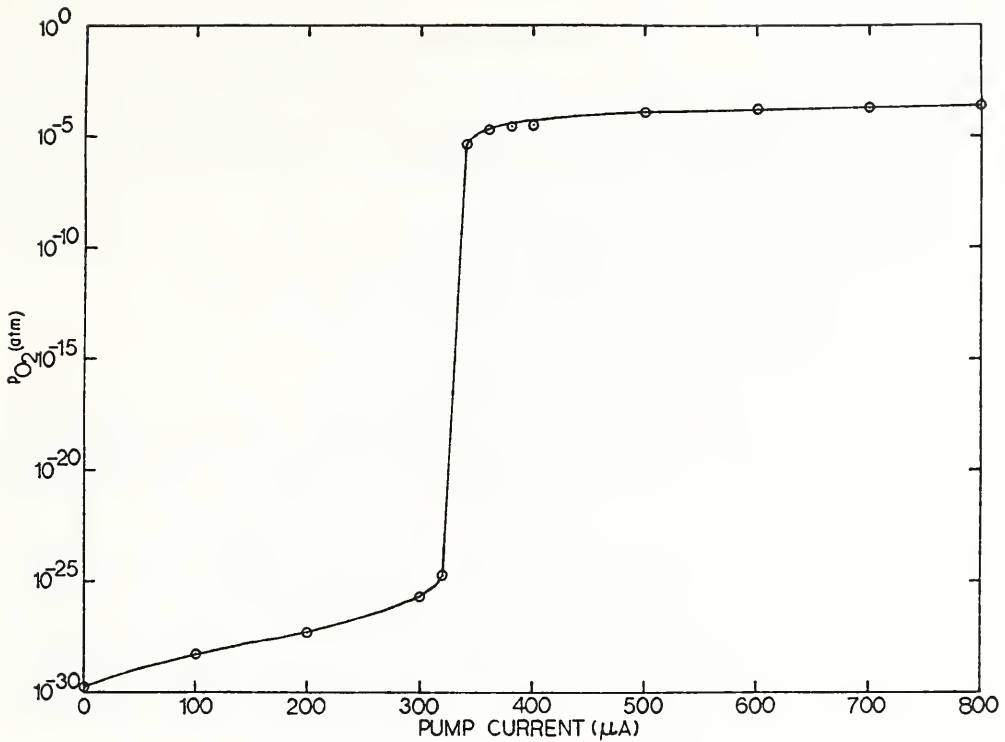
FIGURE 8.   *Plot of Pump Current Versus Oxygen Partial Pressure in N_2*

Thus one can vary the oxygen partial pressure in flowing N_2 or H_2 to create a wide range of conditions for oxidation or reduction in a reactor located as shown in Figure 3.

Acknowledgment

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