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FUEL CELL OXYGEN SENSOR FOR TRACE OXYGEN ANALYSIS

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**FUEL CELL OXYGEN SENSOR FOR
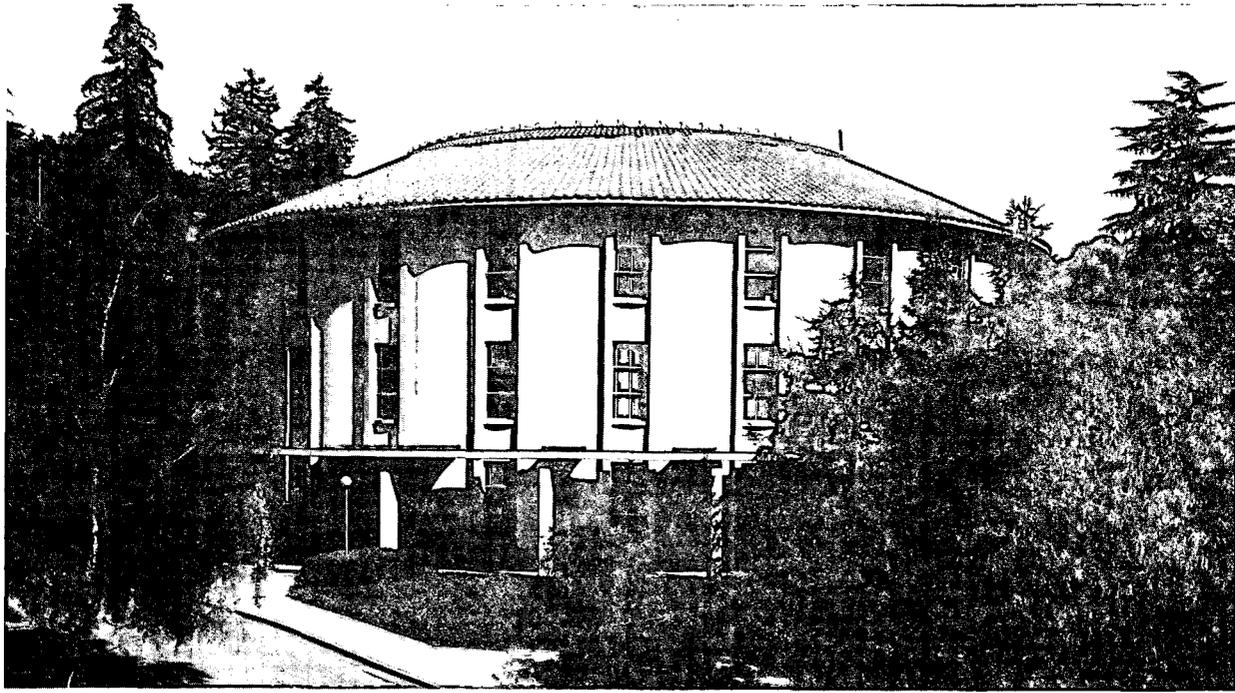TRACE OXYGEN ANALYSIS**

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June 1987

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FUEL CELL OXYGEN SENSOR FOR TRACE OXYGEN ANALYSIS

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Abstract

For photochemical studies of oxygen generation we have built an
on-stream, gas phase oxygen detector based on a commercially available
sensor, which has a detection limit of .002 Torr. If oxygen is generat-
ed in the solution phase, we can take account of the time-constant of
the vapor-liquid equilibration to obtain accurate time course data for
oxygen production.

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Introduction

In our research on "artificial photosynthesis", which involves the mimicking of the natural process with inorganic components and the attempt to photolyze water to hydrogen and oxygen, the detection and measurement of small quantities of oxygen product has proved to be a difficult problem. Gas analysis by the common method of sample withdrawal by syringe and subsequent GC measurement is inadequate because of uncontrollable air leaks and the necessity of maintaining a low detection limit. We have constructed and tested a satisfactory, airtight, on-stream gas phase oxygen analyzer based on a commercially available oxygen sensor. The sensor has a detection limit of ca. .002 Torr, or about 2 ppm at atmospheric pressure. It measures the oxygen in the gas space above the solution in the reaction vessel. By proper data manipulation we can compensate for the time-constant of the apparatus, which is a result mainly of the slow transfer of O_2 across the liquid-gas interface. Thus, an instantaneous measurement gives the total oxygen content of the reaction system.

Fuel Cell Oxygen Sensor

The Teledyne class B-2 (trace oxygen analysis) micro fuel cell is an electrochemical input transducer. Its function is to convert the chemical free energy of the prepackaged reactants within the cell and the oxygen molecules that permeate the sensor into electrical energy. The oxygen molecules that reach the cathode within the sensor accept electrons and are thus reduced. A current is generated in the external circuit that is directly proportional to the rate of diffusion of O_2 molecules (which, in turn, is related to the concentration of oxygen in

the surrounding gas phase) through the teflon membrane and thin film of electrolyte solution within the sensor assembly. The sum of the electrochemical half-reactions occurring in the cell (shown below) when oxygen is present represents a transfer of electrons from lead to O_2. When the lead anode is consumed the cell is discarded and replaced with another unit. Each unit must be calibrated as described below before use.

$$2Pb + 4OH^- \longrightarrow 2PbO + 2H_2O + 4e^-$$
$$4e^- + O_2 + 2H_2O \longrightarrow 4OH^-$$
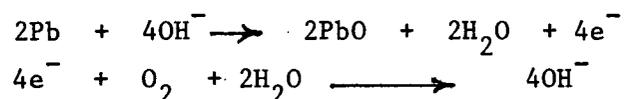
Calibration

Since the net reaction is $2Pb + O_2 \longrightarrow 2PbO$, the sensor exhibits an absolute zero (in the absence of oxygen the cell produces no current). A plot of O_2 concentration versus current is found to be linear to this zero point. In practice the cell is exposed to different gas phase concentrations (e.g., full scale pure oxygen and air), and the corresponding current response is measured. These three points were found to be co-linear for the three cells tested in our laboratory (see Figure 1). The slope of the line determines the sensitivity of the particular cell being used. The currents for these calibration concentrations for each cell are compared with specifications provided by Teledyne in the table below.
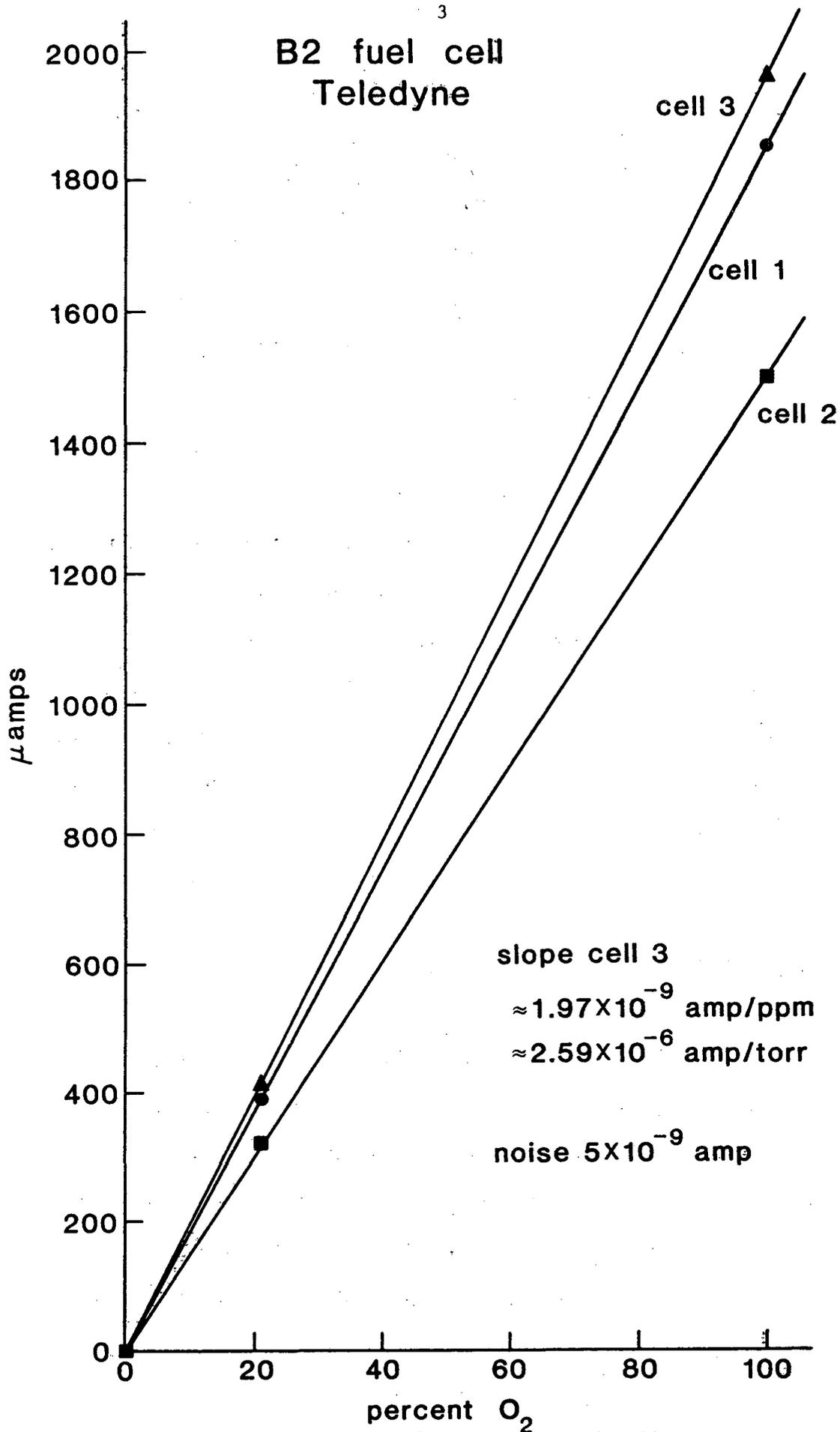
Figure 1. Calibration Curves for Teledyne Fuel Cell

Data set	O_2 (current, amp)	Air (current, amp)
Teledyne spec.	2500	500[*]
Cell #1[*]	1850	388
Cell #2[*]	1500	310
Cell #3[**]	1965	410

[*] Manufactured Oct. 1984 (measured April 22, 1986 [1] and

May 23, 1986 [2]).

[**] Manufactured Nov. 1985 (measured June 27, 1986).

The slope of the calibration line (the sensitivity S) determined

for cell #3 was found to be 2.6×10^{-6} amp/Torr O_2 or 2.0×10^{-9} amp/ppm O_2

at 1 atm. and 25°C. The detection limit was determined by the noise

level in the most sensitive measuring range. The magnitude of this

noise level is typically 5×10^{-9} amp. which imposes a detection limit of

2×10^{-3} Torr O_2. In the process of measurement of a given steady-state

concentration of oxygen, the fuel cell will consume oxygen. Since the

rate of consumption at a given partial pressure can be determined by the

current response of the sensor, an estimate of the fractional loss due

to the measurement process can be given. The consumption of oxygen is a

4 e^- process. Therefore 4 x 96,500 coulombs are passed per mole of O_2

consumed. Hence, 3.86×10^5 amp. = 1 mole O_2/second or 1 μamp =

2.59×10^{-12} moles O_2/second. A current of ∿400 μamp is generated if the

containment vessel contains air. A measurement of this concentration

over a period of one hour would consumed (1×10^{-9} moles/sec) x (3600 sec)

= ∿4×10^{-6} moles. This is only 0.5% of the number of moles of oxygen

(8×10^{-4}) in the 100 ml of air in the vessel. Since both the amount of

oxygen present and the rate of consumption are linearly dependent on

partial pressure, this loss value of 0.5% per hour is pressure independent.

Electronics

The anode and cathode of the fuel cell are attached by two solder welds to platinum wires, which are sealed in through the top of the glass containment vessel. A pin clip/BNC cable connects these wires to the input of the current-to-voltage amplifier. As stated earlier, the reduction of oxygen molecules within the sensor results in the production of a current in the external circuitry. The precise measurement of small currents can be accomplished by the null comparison function of an operational amplifier (Op.Amp.) (see schematic diagram Figure 2).

In practice, a reference current source is used to offset the unknown current source. The reference adjusts itself to bring the null detector to a zero difference indication. The unknown fuel cell current i_c flows into the (virtual ground) inverting input of the amplifier. The noninverting input is grounded. The output voltage adjusts in such a way that the feedback current i_f (drawn through the near zero impedance output of the Op.Amp. from the power lines) is equal and opposite to the cell current, yielding a net null current at the input junction (ideally of infinite impedance and actually of the order of 10^{12} ohms). The output voltage generates this comparison current i_f through a resistor R_f selected in the multiplier. The sensitivity is selectable by means of a front panel switch that controls the multiplier allowing an appropriate feedback resistance for the desired range. The bias and offset currents in the LF356 (FET) Op.Amp. are in general negligibly small (picoamp) compared to the cell currents i_c (greater than nanoamp) measured in these experiments, and, therefore, the feedback current is
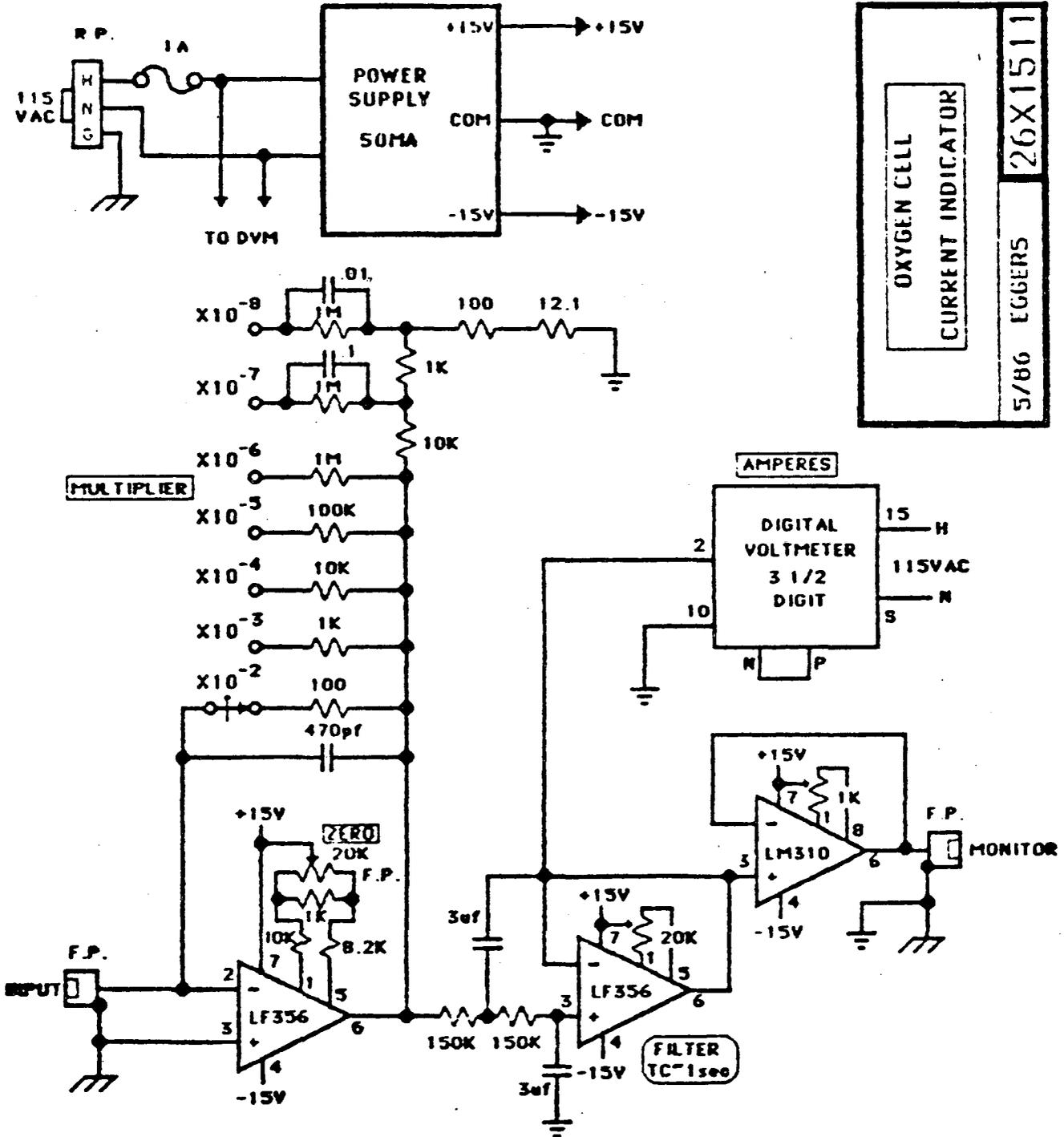
Figure 2. Operational Amplifier for Measurement of Fuel Cell Currents

equal in magnitude to the cell current. The feedback current follows the cell current and produces an output voltage proportional to this latter unknown current described by the expression $V_{out} = i_c R_f$. By appropriate selection of R_F, full-scale ranges of between 10^{-2} amp/V to 10^{-8} amp/V are possible.

The second stage amplifier is a low pass active filter. This stage is necessary to eliminate noise picked up by the sensor, which is a very sensitive current detector. The most serious component of noise we found was the current induced by the magnetic stirrer in the containment vessel. The output voltage of the filter lags the input by a phase angle and attenuates (rejects) signals higher than a characteristic threshold frequency. The filter used in the present device has a one-second time constant, which is the time required to attain 1/e of its final signal value. This filter has a gain of 1 for frequencies below $\sim$1 Hz. One output from this filter goes directly to a digital voltmeter (DVM) for direct readout. The filter is also connected to a voltage follower (monitor output) which can be used as an output terminal for a recorder or other device capable of handling up to 10 volts. The monitor output is isolated by the voltage follower circuit so external hookups will not influence the DVM reading.

Handling and Care of the Fuel Cell

1. The cell should remain in a humidified environment to prevent drying of the thin film of electrolyte solution.

2. When exposed to air for any duration the cell should be disconnected to prevent the consumption of the lead anode. Connection should be re-established after purging the reinstalled vessel and a burn-out under deaerated conditions should precede any measurements.

Measurement of O_2 in a Gas/Liquid Reaction System

The specific use for the Teledyne fuel cell in this laboratory is to measure the solution phase generation of oxygen (as a product of either an electrochemical or photochemical reaction). The sensor is placed in the gas phase above the aqueous mixture of reactants in a sealed containment vessel (see Figure 3). This vessel is then placed into a glove bag purged with an overpressure of nitrogen. The vessel is purged with tank argon which is passed through a BTS catalyst and Nanochem oxygen scavengers. After sufficient purging the vessel is closed and left overnight (with the fuel cell connected to provide a current path) to burn out any residual oxygen above a given baseline concentration still present in the vessel. The next morning a baseline current is measured in time by a stripchart recorder connected to the monitor output. After the establishment of the baseline, a chemical reaction is initiated and the current is monitored as a function of time. In order for oxygen molecules that are formed as a result of reaction in the aqueous phase to be detected, they must be transferred across the phase boundary. Once in the gas phase they rapidly diffuse to the teflon surface of the sensor and then permeate the membrane and thin layer of electrolyte solution within the fuel cell. The transfer across the phase boundary is the slow step in the evolving system. A simple model was developed that relates the value of the current and slope of the current/time plot at a given time to the total moles of oxygen in the containment vessel. The model was checked quantitatively by doing an electrolysis experiment with use of platinum electrodes built into the apparatus (Figure 3) and relating the coulombs passed to the moles of O_2 present.
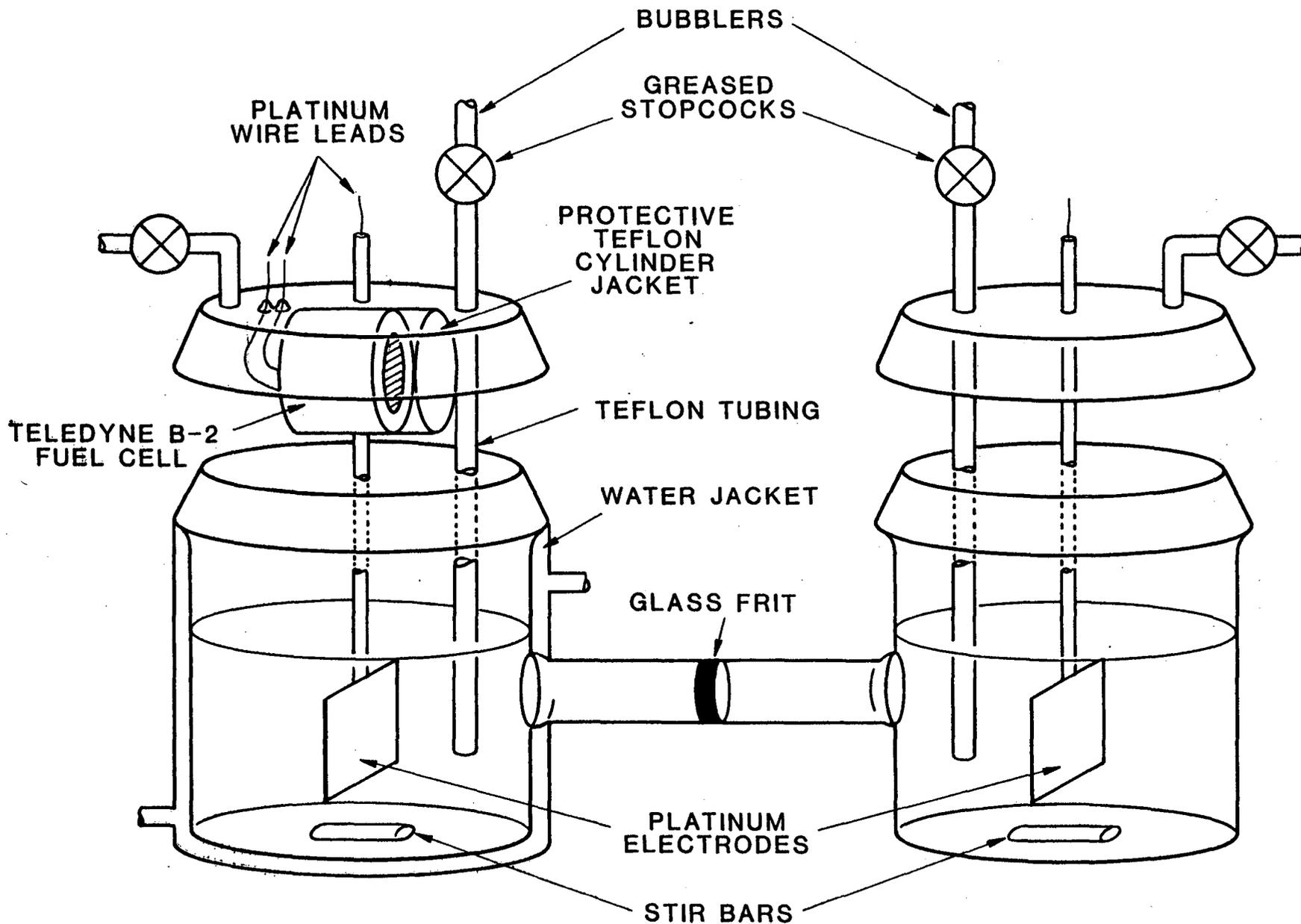
Figure 3. Apparatus for Measurement of Oxygen Generation in Solution

Model of the Reaction System

The current and time rate of change of current can be related to the partial pressure of oxygen in the gas phase by the sensitivity 1/S Torr/current) described above. This partial pressure at 25°C can be easily converted to moles of O_2. The Ostwald distribution coefficient describes the partitioning of oxygen between the phases at equilibrium as a ratio of the concentrations in the liquid and gas phase. The value of this equilibrium constant at 25°C is 35. A closed system ($C_s V_s + C_g V_g = n$), not necessarily in equilibrium, is described by the generating equation:

$$\frac{dC_g}{dt} = \text{constant} \times (KC_s - C_g)$$

where C_s and C_g are the concentrations in solution and gas, respectively, and V_s and V_g are the volumes. n is the number of moles of O_2 in the entire solution. Using these relations, one can generate an equation which, after rearrangement, relates the observables to the total number of moles in the containment vessel.

$$n = (1 + V_s/V_g K) \left(\frac{1}{B} \times \frac{dn_g}{dt} + n_g \right)$$

where n_g is the number of moles of O_2 in the gas phase, which is in turn determined from the current reading, i, and the sensitivity factor, S:

$$n_g = iV_g/SRT$$

Since V_s and V_g are comparable in magnitude and $K \gg 1$, the expression can be reduced to

$$n = \frac{1}{B} \frac{dn_g}{dt} + n_g$$

Thus, the total number of moles of oxygen, n, is the sum of two terms, one involving n_g and the other the slope of n_g vs t. From any small region on the chart, then, the instantaneous value of n an be obtained provided B is known. B is the rate constant that parameterizes the transfer of oxygen across the phase barrier. It is apparatus-dependent, involving V_s, V_g, the liquid-vapor surface area, and the degree of stirring. Therefore, it must be determined empirically under the same conditions as the experiment. The determination of B can be accomplished by quickly sweeping out the gas phase above a volume of air-saturated water and replacing it with argon.

The system is then closed and oxygen molecules within the aqueous solution begin to redistribute themselves approaching a new equilibrium. The gas phase concentration is monitored by measuring the current in time during this process until an asymptotic value, i_∞, is established. The value of $i - i_\infty$ is plotted on a logarithmic scale versus time. B is the slope of the plot and 1/B has the dimensions of time.