Hydrogen Detection via Polarography

Kennedy Space Center

ASRC Aerospace Corp.

Jesús A. Dominguez
Ron Barile

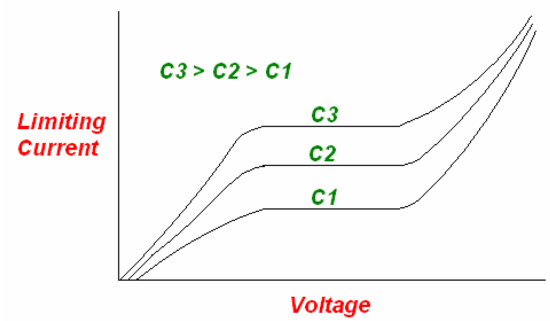
photo: NASA/Pat McCracken

Outline

- ***Background.***
- ***Sensing Approach.***
- ***Mathematical Model.***
- ***Results.***
- ***Conclusions & Future Work.***

Background

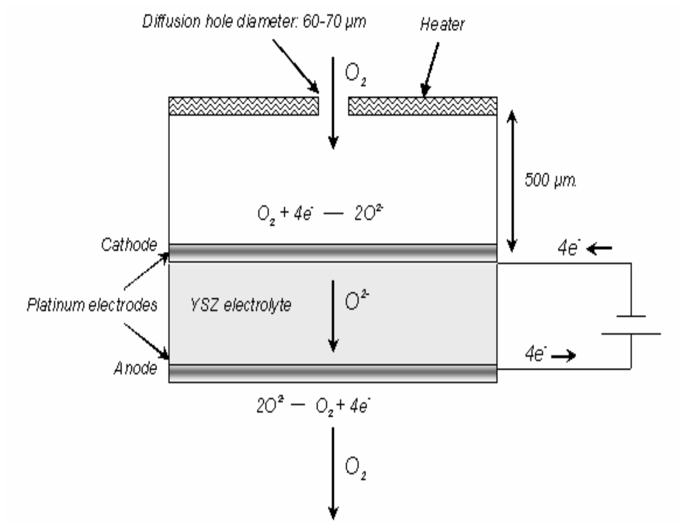
- *Polarography is the measurement of the electrical current that flows in solution as a function of an applied voltage.*
- *The actual form of the observed polarographic current depends on not only the applied voltage but also on the characteristics of the electrolyte and electrodes.*



- *Polarography is traditionally applied to electrolytes in the liquid phase having a solution of metal ions.*
- *H_2 sensing via polarography is performed using an electrolyte in the solid phase and shows a current level increment with gaseous H_2 concentration similar to those relating to metal ions in liquid electrolytes.*

Background (Cont.)

- ***A commercially available gas polarographic O_2 sensor was converted to a gas polarographic H_2 sensor.***
- ***The O_2 sensor consists of a solid electrolyte disk made of yttria-stabilized zirconia (YSZ), two porous platinum electrodes attached to both sides of the electrolyte disk, and a cylindrical cap with a gas diffusion hole for the artificial diffusion control of the gaseous O_2.***
- ***A tiny heater is mounted on top of the cylindrical cap to keep the sensor temperature at 350-450 ℃.***
- ***The voltage is applied so that the electrode in the sensor cavity is negative (cathode) to control the diffusion of gaseous O_2 and reduce it to negative O^{-2} ions.***
- ***O^{-2} ions pass through the YSZ electrolyte and reach the positive electrode (anode), where they subsequently reform to gaseous O_2.***



Commercially available gas polarographic O2 sensor

ASRC Aerospace Corp.

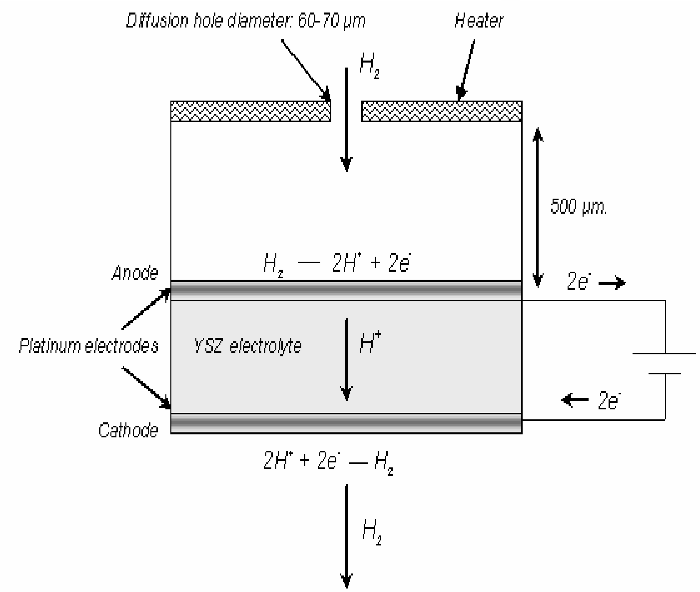
Sensing Approach

- *In existing and commercially available gas polarographic O2 sensors, the electrode in the sensor cavity has to be negative (cathode) as gaseous O2 is reduced to negative ions (O-2) at the cathode.*

- *In contrast, a gas polarographic H2 sensor should have the positive electrode (anode) in the sensor cavity as gaseous H2 needs to release electrons and generate H+ ions or protons.*

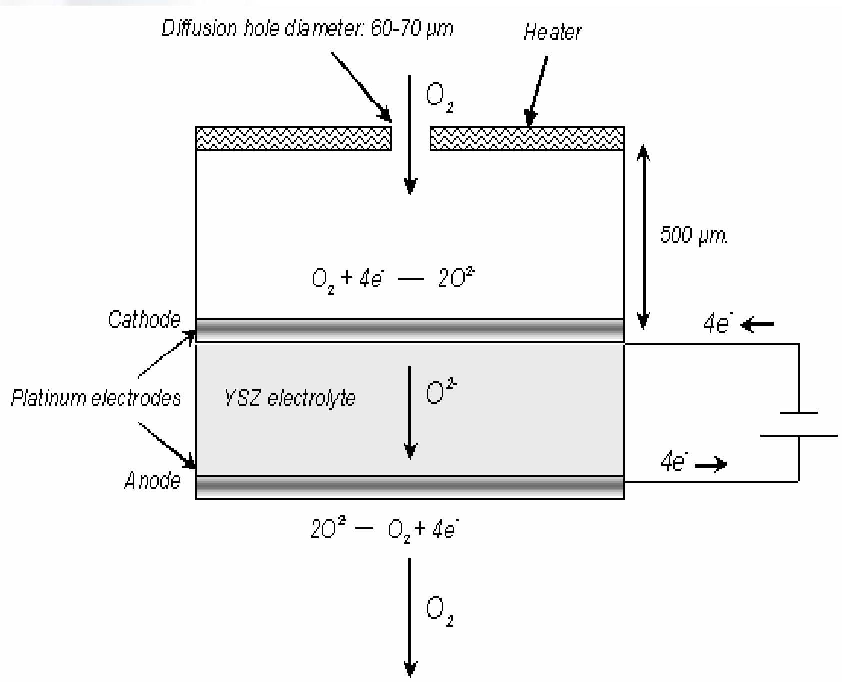
- *These H+ ions (or protons) should pass through the YSZ electrolyte to the negative electrode (cathode), where they subsequently reform to gaseous H2.*

- *This gas polarographic hydrogen sensor is actually an electrochemical-pumping cell since the gaseous H2 is in fact pumped via the electrochemical driving force generated between electrodes.*

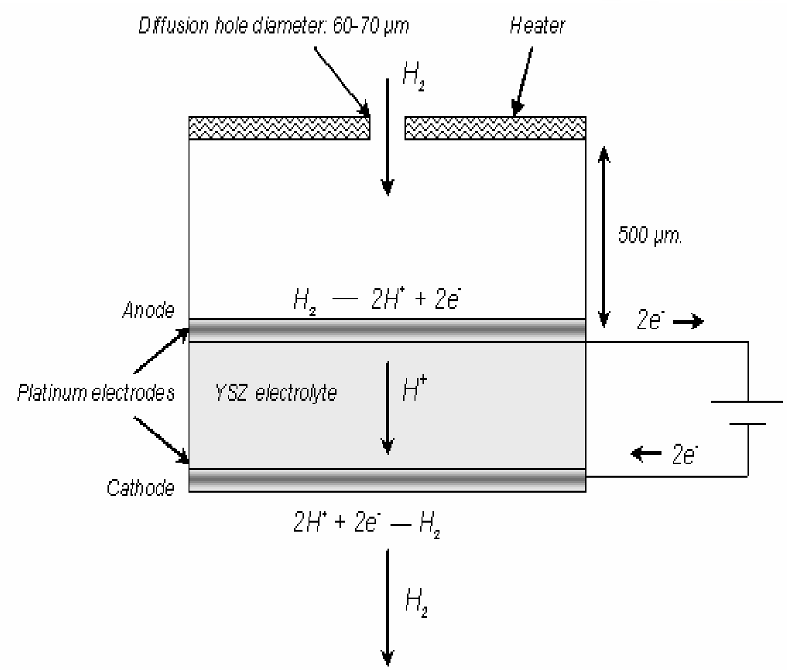


H2 sensor

Sensing Approach (Cont.)



Commercially available gas polarographic O2 sensor



H2 sensor

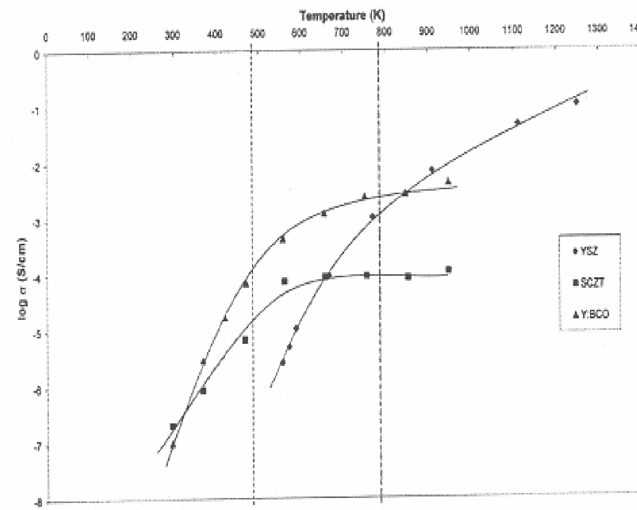
Sensing Approach (Cont.)

- ***YSZ is used as solid electrolyte in most of the commercial gas polarographic O2 sensors as well as in Solid Oxide Fuel Cells (SOFC) because of its excellent oxygen ion (O^{-2}) conductivity. YSZ is also a protonic (H^+) conductor and can be used as solid electrolyte in the new gas polarographic H2 sensor.***

- ***Research and development on solid materials that can perform proton conducting at intermediate temperature have dramatically increased due to the renewed interest in the industry for solid-electrolyte fuel cells.***

- ***Commercially available Proton Exchange Membranes (PEM) might be utilized as solid-electrolyte in the gas polarographic H_2 sensor. PEM performs proton conducting at relatively low temperature (5-120 ºC).***

- ***Research on new zirconia materials are currently focus on obtaining materials that can perform proton conducting at intermediate temperature***



Proton Conductivity of BCY, SCZT85 and YSZ with Temperature[1]

ASRC Aerospace Corp.

Mathematical Model

Kennedy Space Center

Assumptions:

1) ***Gas binary system.***
2) ***Steady-state conditions.***
3) ***No reaction.***
4) ***Stagnant background gas.***
5) ***Mass transfer only one direction***
6) ***Rate-limited at the diffusion hole.***

Terms:

Y_A ***Background concentration.***

S ***Electrode Cross Area***

L ***Cavity length.***

P ***Gas pressure.***

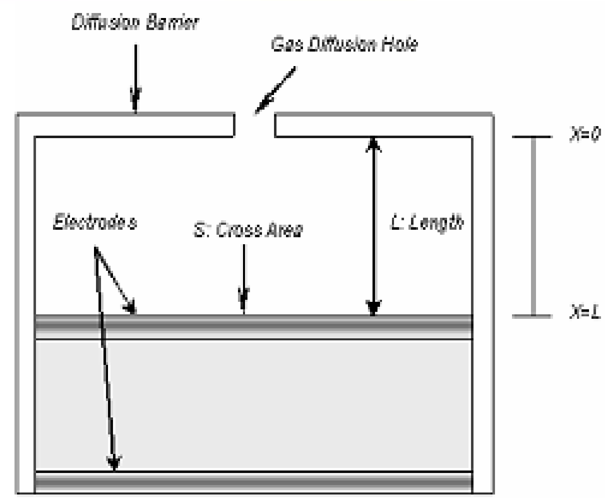
T ***Gas temperature.***

D_{AB} ***Diffusion coefficient of the gaseous specie in the binary gas mixture.***

F ***Faraday constant.***

η ***Number of electrons/mole of the gaseous specie transferred between electrodes (4 for O2 and 2 for H2).***

R ***Gas Constant.***



$$I_l = -\frac{\eta FSPD_{AB}}{RTL} Log_N(1 - Y_A)$$

Linear function of the logarithm of the background gas concentration.

ASRC Aerospace Corp.

Mathematical Model

Kennedy Space Center

For a binary mixture of A and B (background gas) the limiting current is expressed as:

$$I_l = \eta F S \overbrace{N_A}^{x=L} \quad (1)$$

- I_l Limiting current.
- η Number of electrons per mole of specie A transferred from the anode to the cathode.
  - = 4 if A specie is O_2 ($O_2 + 4e^- \rightarrow 2O^{-2}$).
  - = 2 if A specie is H_2 ($2H^+ + 2e^- \rightarrow H_2$).
- F Faraday constant.
- S Electrode cross area.
- $\overbrace{N_A}^{x=L}$ Molar flux of specie A at the electrode.

General equation for molar flux N_A:

$$\frac{\partial C_A}{\partial t} + \left(\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial x} + \frac{\partial N_{Az}}{\partial x} \right) = R_A \quad (2)$$

- C_A Molar concentration of specie A.
- N_{Ai} Molar flux of specie A in i = x, y, & z.
- R_A Reaction of specie A.

Assuming steady state conditions, no reaction, and mass transfer only in one direction (x direction) equation 2 becomes:

$$\frac{\partial N_{Ax}}{\partial x} = 0 \quad (3)$$

Assuming a binary system denoting A as the specie being measured and B as the background gas, N_{Ax} in equation 3 can be expressed as:

$$N_A = -CD_{AB} \frac{\partial Y_A}{\partial x} + Y_A (N_A + N_B) \quad (4)$$

- N_A Molar flux of specie A.
- N_B Molar flux of specie B.
- C Molar concentration.
- D_{AB} Diffusion coefficient of A into B.
- Y_A Molar fraction of specie A.

Assuming specie B (background gas) is stagnant ($N_B = 0$), equation 4 becomes:

$$N_A = -CD_{AB} \frac{\partial Y_A}{\partial x} + Y_A N_A \quad (5)$$

ASRC Aerospace Corp.

Mathematical Model (Cont.)

Expressing equation 5 in terms of N_A

$$N_A = -\frac{CD_{AB}}{(1-Y_A)}\frac{\partial Y_A}{\partial x} \qquad (6)$$

Substituting equation 6 into equation 3:

$$\frac{\partial\left(\frac{CD_{AB}}{(1-Y_A)}\frac{\partial Y_A}{\partial x}\right)}{\partial x} = 0 \qquad (7)$$

Integrating twice:

$$Log_N(1-Y_A) = k_1 x + k_2 \qquad (8)$$

Using the two boundary conditions and their respective assumptions:

$Y_{A(x=0)} = Y_A$ *(specie A at the orifice hole is the same as ambient)*

$Y_{A(x=L)} = 0$ *(specie A totally consumed at the electrode)*

Constants k_1 *and* k_2 *are determined and equation 8 becomes:*

$$N_A = -\frac{CD_{AB}}{L} Log_N(1-Y_A) \qquad (9)$$

Assuming ideal gas equation 9 becomes:

$$N_A = -\frac{PD_{AB}}{RTL} Log_N(1-Y_A) \qquad (10)$$

Substituting equation 10 in equation 1 becomes:

$$I_l = -\frac{\eta FSPD_{AB}}{RTL} Log_N(1-Y_A) \qquad (11)$$

Equation 11 states the linear relation between the limiting current and the concentration of the background gas when temperature and pressure remain constant.

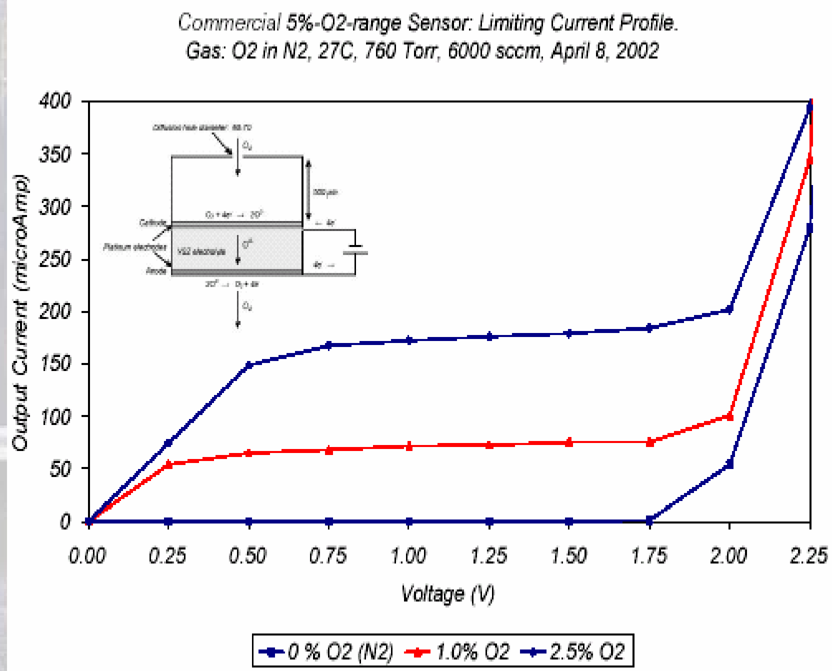
If temperature and pressure remain constant and a reference measurement is taken equation 11 becomes:

$$I_l = I_l^* \frac{Log_N(1-Y_A)}{Log_N(1-Y_A^*)}$$

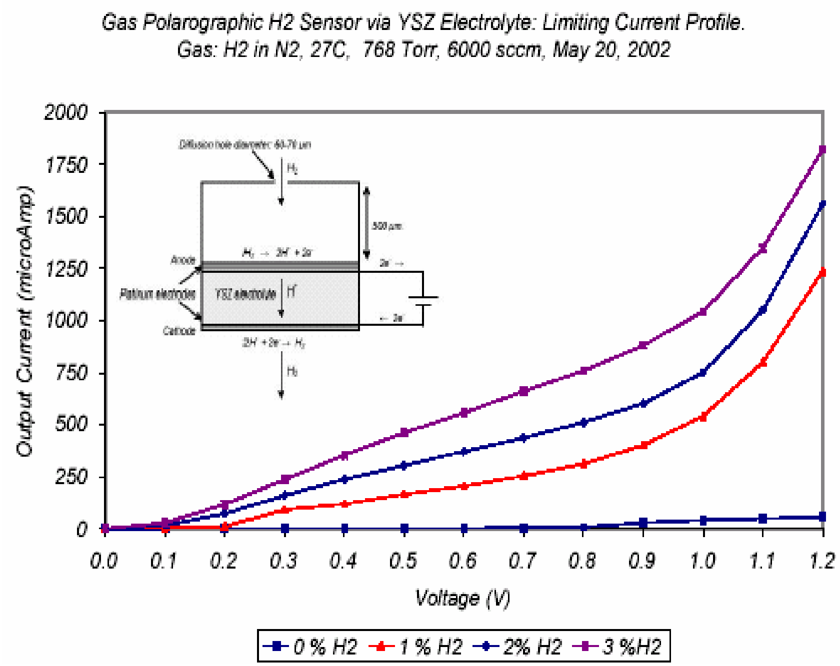
The asterisk are reference measurement.

ASRC Aerospace Corp.

Results



O_2 Limiting Current Profile

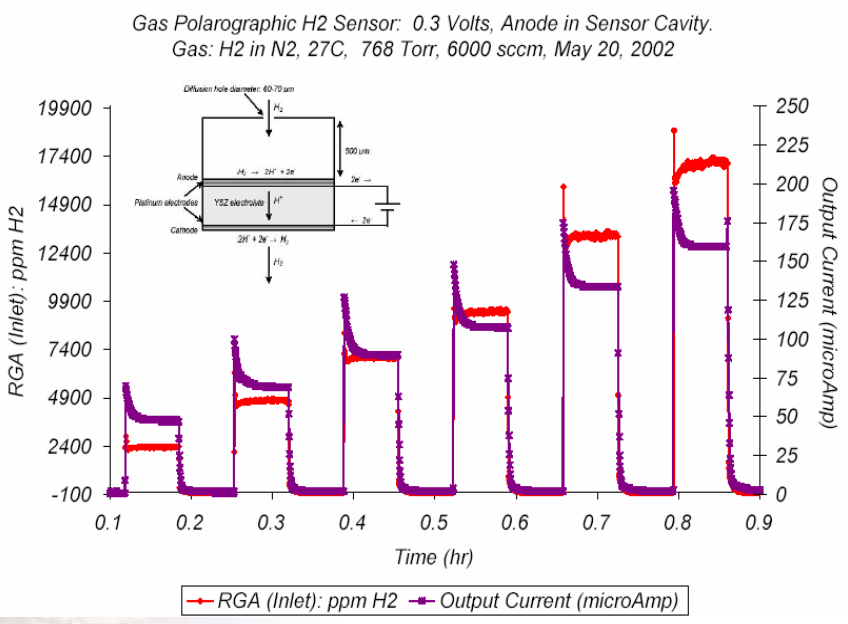


H_2 Limiting Current Profile

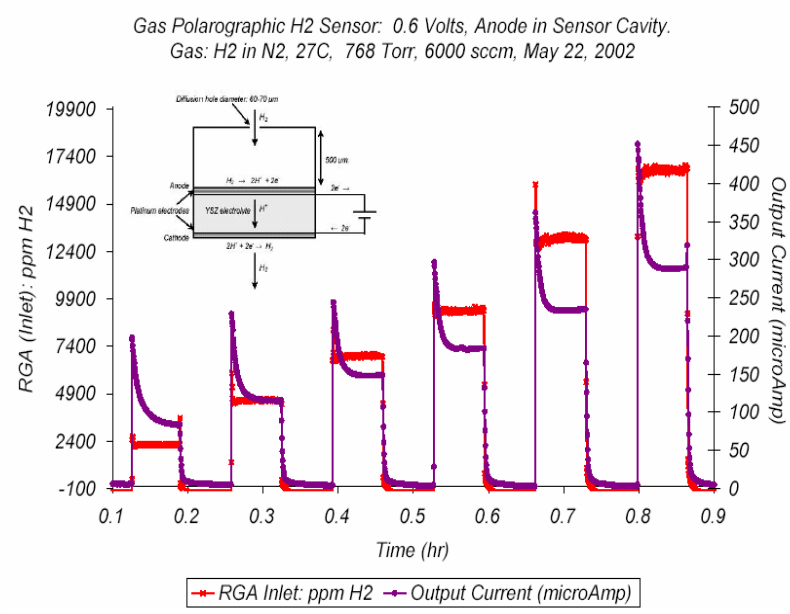
ASRC Aerospace Corp.

Results (Cont.)

Kennedy Space Center



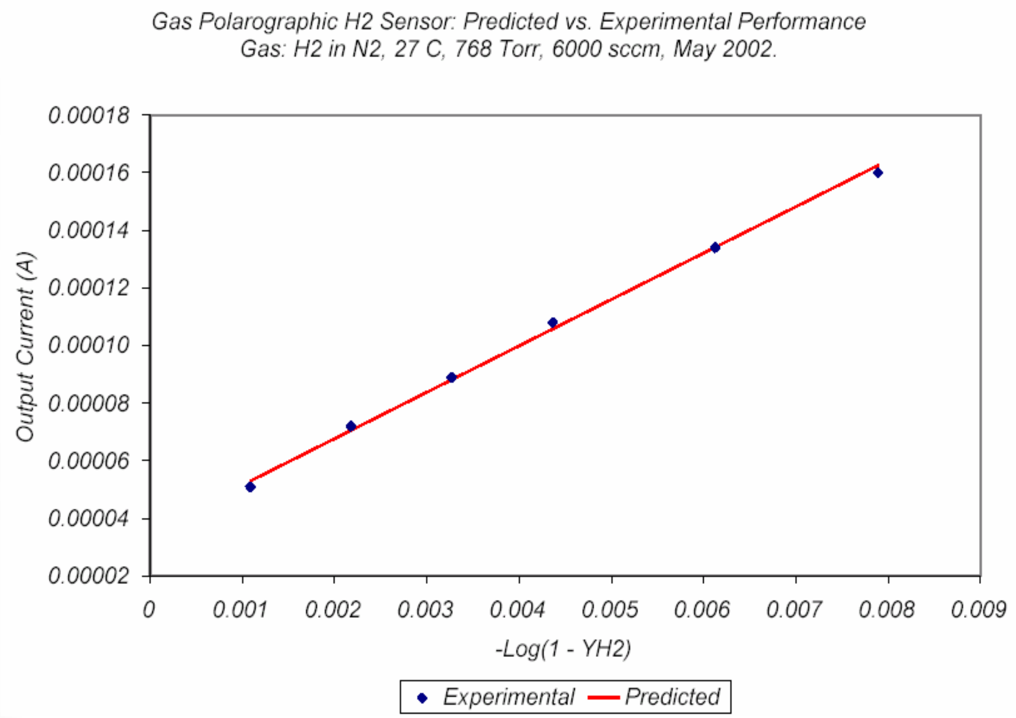
H2 measurement profile at 0.3 V with anode at the sensor cavity.



H2 measurement profile at 0.6 V with anode at the sensor cavity.

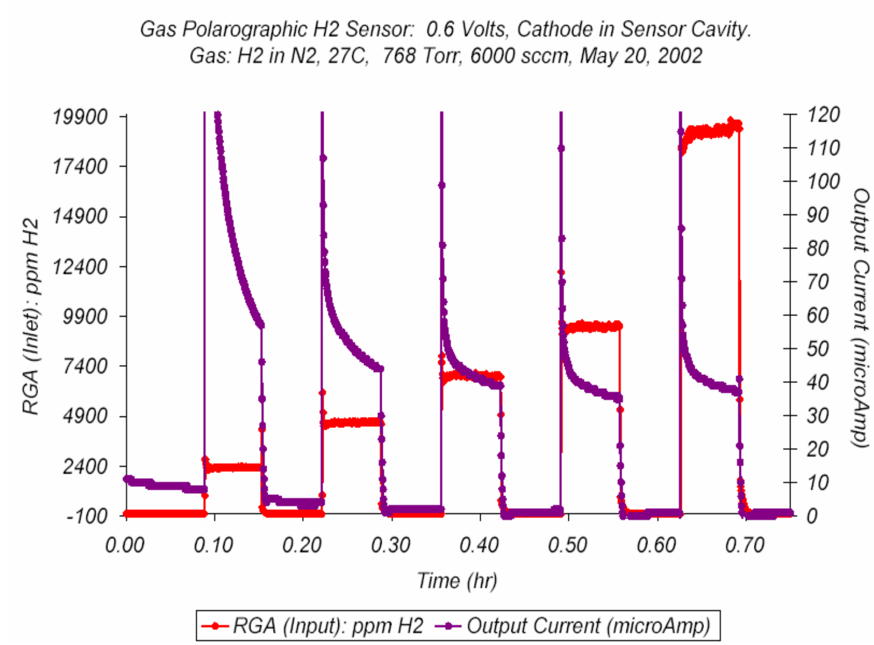
ASRC Aerospace Corp.

Results (Cont.)



Experimental vs Predicted results.

Results (Cont.)



H2 measurement profile at 0.3 V with cathode at the sensor cavity.

Conclusions & Future Work

Kennedy Space Center

- *The engineering and manufacturing requirements of this new gas polarographic H_2 sensor would be basically the same as those already in place for the commercially available gas polarographic O2 sensors.*
- *Further research is needed to determine the proper size of the diffusion hole and evaluate different types of solid electrolytes including solid electrolytes with more H^+ and less O^{-2} ion conduction selectivity and capable of conducting protons (H^+) at lower temperatures.*
- *An array of two gas polarographic sensors with different diffusion hole sizes and voltage polarities might be able to detect O_2 and H_2 using the same sensing mechanism.*
- *A smart sensing system equipped with the proper algorithm might be able to extract mutual cross- sensitivity interference of H_2 on O_2 and O_2 on H_2 respectively.*

ASRC Aerospace Corp.