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IMPURITY TOLERANT ELECTROCATALYSTS

CONTRACT INFORMATION

Contract Number AA-45-35-00-0

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Period of Performance Oct. 1, 1989 to Sept. 30, 1990

Schedule and Milestones

FY89 Program Schedule

S O N D J F M A M J J A S

Novel Bimetallic Materials.
Sn/Pt(111) and Sr/Pt(100) Studies _____

PdAu Surface Reactivity and
Electrochemistry _____

Exhaust Gas Analysis(O₂ backinjection):
Polymeric Membrane Fuel Cells _____

Phosphoric Acid Fuel Cells _____

OBJECTIVES:

This project has two central goals. The primary research effort addresses fundamental aspects of Pt electrocatalyst poisoning by CO and an understanding of practical schemes for improving the CO tolerance of electrocatalytic materials. The second mission of this work is an attempt to address, on a fundamental level, the surface chemical properties that enhance the direct electrooxidation of methanol at binary Pt alloy electrode surfaces. More specifically each of these two objectives are described in bullet form as follows:

- We have explored the physical and chemical basis of elimination of CO poisoning effects by direct injection of low levels (~1%) of O₂ into the anode feed stream of working single fuel cells. The fuel cell systems examined include both polymer electrolyte (PEFC) and phosphoric acid fuel cells (PAFC). This examination has included model studies of O₂ coinjection with low levels of CO at Pt rotating disk electrodes and exhaust gas analysis on working fuel cells.
- We have examined the surface structural properties and reactivity of Sn/Pt surface alloys prepared by vapor deposition of Sn onto single crystal substrates followed by annealing (1000K). These studies have included a variety of surface analysis characterization studies. In addition, the reactivity of these templates with respect to small molecule adsorbates and the electrochemical reactivity towards direct methanol electrooxidation have also been examined.
- The surface properties and reactivity of

other bimetallic electrocatalytic materials (e.g., PdAu, PdSn) will also be examined using the same set of techniques and methods as described for the PtSn surface alloys.

BACKGROUND STATEMENT:

The rationale for studying the first programmatic area is that CO severely poisons the hydrogen electrode reaction in fuel cells for temperatures below 150°C. This is a difficult problem to overcome for Pt based fuel cells operating at low temperature or under cold startup conditions. Recent progress at Los Alamos (Pafford and Gottesfeld) has demonstrated a practical solution for a supported Pt anode electrocatalyst operating on hydrogen with up to 0.05% CO at temperature <100°C. This scheme of CO cleansing relies on coinjecting low levels of oxygen or air into the anode compartment. We are in the process of fully examining the range of parameters that contribute to this technologically important finding.

In addition, we are attempting to gain a fundamental understanding of how and why certain (reported) bimetallic electrode combinations display less poisoning by CO than pure Pt. This knowledge should, in turn, allow us to suggest (and try) other materials that may display better anode operating characteristics in the presence of CO. In addition, these same electrocatalysts have been used for the direct electrooxidation of methanol. These fundamental studies should allow a better understanding of how surface chemical reactivity depends on the properties of the bimetallic surface.

RESULTS

EXHAUST GAS ANALYSIS:

We have performed anode exhaust gas analysis for operational single fuel cells (PEFCs) using FTIR and GC methods to elucidate the effects of added O_2 . We have examined the effects of gas flow rate, membrane thickness and feed gas composition on the cleansing effect of O_2 added to a CO-contaminated anode feed stream of PEFCs. Our results indicate that under every condition where O_2 was blended at a level of 2% into the anode feed stream complete removal of CO (at the hundreds of ppm level) from the exhaust stream was achieved. On the basis of these results, and comparison with literature values for the heterogeneous oxidation of CO by O_2 , a model in which the CO impurity is oxidized in a heterogeneous process, possibly at nonelectrochemically active Pt sites within the electrode assembly, is proposed. Representative data from these analysis is shown in the following paragraphs.

Several methods of quantitatively analyzing for CO and CO_2 at ppm levels were suggested (e.g., GC, MS, IR). For ease of operation, reproducibility and lack of interferences, analysis by IR was determined to be the method of choice for CO and CO_2 analysis. For quantifying the loss of injected O_2 , by interaction with H_2 to form H_2O , GC was utilized. The IR analysis was conducted using a Mattson Cygnus FTIR spectrometer configured with a DTGS detector and a variable (2.25 - 20.25 M) path length IR cell. Quantification of the CO and CO_2 levels was achieved through the use of a primary gas standard containing 100 ppm each of CO and CO_2 (supplied by Scott Specialty Gases). Other concentration ranges (usually the higher concentrations) were prepared by blending CO and/or CO_2 mixtures with N_2 .

Absorbances were determined at 5-7 different path lengths to insure that background CO_2 levels (~330 ppm in air) did not introduce any systematic error into the observed absorbance readings. The entire IR beam path was flushed with dry N_2 to lower background CO_2 levels to less than 0.0005 absorbance units. In most cases the exhaust gas streams were passed through a coiled Cu tubing trap immersed in an ice bath with added salt ($T \sim -2-4^\circ C$). This step was taken to lower the water content going into the IR analysis cell and to prevent nonlinear absorbance behavior arising from severe IR transmittance losses. Water was, however, always present in the IR spectra. A representative spectrum recorded after purging the IR cell for 45 minutes with anode exhaust gas is shown in Fig. 1. Note that the CO (2130 cm^{-1}) and CO_2 (2360 cm^{-1}) bands are quite distinct and sufficiently well separated from the prominent water bands. Prior to examining the the anode exhaust, the IR gas cell was purged with dry N_2 at a high (~50 CFM) flow rate for 5-10 minutes. This is to insure that the measurement is not contaminated from prior sampling and to preclude a potential explosion in cases where the cathode side cell exhaust is sampled. A flow rate of 400 sccm through a 50 cm^2 PEFC corresponds roughly to a stoichiometric gas flow of ~2x the gas required to sustain the load of 20A employed.

A series of PEFC experiments were conducted in an attempt to address the following questions. (A) Does O_2 coinjection at the anode successfully convert all of the CO impurity to CO_2 ? (B) In the absence of O_2 coinjection is any of the CO oxidized by the low levels of O_2 cross-over from the cathode side of the fuel cell structure? (C) Are there flow rate dependencies to the observed disappearance of CO for both cases (with and without coinjected O_2)?

We begin by describing the exhaust gas

analysis for 100ppm CO injection using a 7 mil membrane separator with and without O₂ coinjections. For all cases examined, when O₂ was coinjected at a level of 2% with the 100ppm CO in H₂, the CO was completely converted to CO₂ (detection limit < 5 ppm CO). Representative IR data taken at a cell path length of 20.25M are shown in Fig. 2. The gas flow input parameters are listed on the figure. Note that there is no evidence of CO in the exhaust gas. In the Fig. 2 inset the CO₂ concentration is also plotted versus anode input gas flow rate through the cell. Note that the CO₂ level is considerably higher than that expected from a total conversion of CO to CO₂. However, it should be pointed out that an exact mass balance on the CO conversion requires accounting for the loss of H₂ due to the electrochemical oxidization in the anode electrocatalyst structure. To address the accounting issue and to examine appropriate control experiments for CO₂ production we have also examined the effect of added O₂ in the absence of CO and an exhaust gas analysis using only H₂ as the anode gas feed.

In Fig. 3 the CO and CO₂ levels in the exhaust gas are shown plotted versus flow rate through the anode structure for the case of no O₂ coinjected in the feed stream (100 ppm CO in H₂). Two observations are immediately apparent from inspection of Fig. 3. Firstly, at close to stoichiometric utilization of the anode gas input, the CO levels are observed to be very low (<10ppm). As the flow rate is increased the amount of CO observed in the anode exhaust increases in linear fashion up to nearly the input level of 100 ppm. Secondly, the CO₂ levels increase as expected from a stoichiometric oxidation of the initial CO level. At the highest flow rate (700 sccm) the CO₂ levels are also

observed to drop off slightly.

This puzzling behavior, namely the loss of CO measured at the PEFC anode exhaust gas at low flow rates (high stoichiometric gas utilization) when injected at a level of 100ppm is speculated to be due to low levels of O₂ crossing from the cathode compartment through the membrane separator and reacting at exposed Pt sites to produce CO₂. The degree of reactant cross-over (O₂ penetration) will depend on the O₂ partial pressure at the cathode, the membrane thickness, and on the possible presence of flaws (e.g., pinholes) in the membrane. It should also be mentioned that for the PEFC assemblies used in this work, the cathode side is held at a higher pressure than the anode.

For the experiments with no added CO, the CO₂ concentration was measured to be 55 ± 20ppm at several anode input flow rates (no CO was observed) We hypothesize that at low flow rates of H₂ with 2% O₂, this level of CO₂ production in the absence of added CO is derived from some low level of gasification of the C support. This rate of C gasification is insignificant in the context of long term stability of the carbon material in the PEFC.

The fate of the coinjected O₂ was examined by GC analysis and will be briefly discussed. Surprisingly, for all of the fuel flow rates examined (200-800 sccm) the O₂ was not completely converted to H₂O. Significant levels of O₂ remained after passing through the anode assembly. In addition, no clear cut dependence of the O₂ conversion to H₂O with flow rate was observed. Typical conversion levels of O₂ to H₂O were around 50%. The data are being further examined to assess the effect of flow rate on reaction product partial pressure.

Further experiments are in progress to complete this description of the complex

interfacial chemistry occurring in PEFC assemblies when O_2 is coinjected with low levels of CO in the anode feed stream. In addition, phosphoric acid fuel cell (PAFC) assemblies are being constructed to test the beneficial effects of O_2 coinjection in scrubbing the anode feed gas of low levels of CO. Several avenues will be explored in this upcoming venture, among them are the effects of CO on the low temperature operation of the PAFC and the effects of coinjection of O_2 . An exhaust gas analysis identical to that done for the PEFC assemblies will also be conducted for the PAFC.

MODEL ELECTROCHEMICAL REACTIONS AT Pt RDEs

In addition to following the combustion of the CO impurity by heterogenous reaction at the supported Pt anode electrocatalyst, we have performed more carefully controlled electrochemical experiments using rotating disk electrodes to delineate parameters that influence CO poisoning of both the hydrogen electrooxidation and O_2 reduction processes at polycrystalline Pt surfaces immersed in aqueous acid solutions over the temperature range 25-75°C. Examining both the hydrogen oxidation and O_2 reduction processes has allowed us to suggest alternative reaction pathways that result in the removal of the electrode poison CO. This work has been submitted for publication ((a)Paffett, Pafford, and Gottesfeld, and (b) Paffett, Hawker, Tobias, Valerio, and Gottesfeld). The primary conclusion of this work is that at Pt electrode surfaces at temperatures of 80°C, CO adsorbed at potentials of $<+0.35V$ vs NHE (in the upd-H region) can apparently be effectively removed by O_2 in solution. At potentials above $+0.35V$ or in the absence of O_2 , electrode performance (towards

either ORR or H_2 oxidation) was completely poisoned.

In summary, there appear to be at least two viable mechanisms for the removal of CO by coinjected O_2 in these fuel cell systems. The first process is a heterogenous process in which the well known rates of CO oxidation by O_2 can account for observed removal rates. The second process (that may be occurring simultaneously) is a CO oxidation process that is occurring at the surface of Pt particles in contact with electrolyte whenever the electrode potential is negative of $+0.35V$ and above 75°C.

SURFACE CHEMISTRY AND ELECTROCHEMISTRY OF Sn/Pt SYSTEMS

We have completed a study of the interactions of vapor deposited Sn at Pt(100). The motivation for this body of work stems from a more complete picture of surface alloy behavior for the Sn/Pt systems. Previous work on the Sn/Pt(111) ((a)Paffett and Windham, (b) Overbury, Mullins, Paffett, and Koel) systems has indicated that clean ordered surface alloys can be conveniently and reproducibly prepared by this method. These surfaces in turn display rather unique reactivity (Paffett, Gebhard, Windham, and Koel) that lends insight into the surface chemical process occurring when these bimetallic surfaces are used to achieve higher electrochemical rates of methanol electrooxidation. In the present case, the Sn/Pt(100) system was chosen to complete the preparation methodology and to determine whether a more open starting template (Pt(100)-FCC) would produce ordered surface alloys that might be similar to bulk terminated SnPt alloys. The roles of surface order and stoichiometry are then directly addressed in attempting to answer

specific questions regarding surface chemical reactivity.

Specifically, Sn/Pt(100) interfaces prepared by vapor deposition of Sn onto Pt(100) surfaces were examined using Auger and x-ray photoelectron spectroscopy (AES, XPS), low energy electron diffraction (LEED), and inert gas low energy ion surface spectroscopy (LEISS) (Paffett, Simonson, and Koel). The Sn depositions have been performed at 300K and 600K and the surface composition and order were examined as functions of further annealing to 1200K. The AES uptake plots at 300K indicate that a fairly uniform layer deposition process occurs up to 2 adlayers. For the 600K depositions AES data indicate significant interdiffusion and surface alloy formation. LEED observations indicate that the characteristic 5×20 Pt(100) reconstruction disappears with Sn exposures of 0.35 monolayer (ml). Further Sn depositions result in a $c(2 \times 2)$ LEED pattern starting with an exposure of slightly above 0.5 ml. The $c(2 \times 2)$ LEED pattern becomes progressively more diffuse with increasing Sn exposure with eventual loss of all LEED features above 2.2 ml exposure. AES, LEED, and LEISS results were obtained after annealing various precoverages of Sn on Pt(100). For specific Sn precoverages and annealing conditions $p(3\sqrt{2} \times \sqrt{2})R45^\circ$ and $c(2 \times 2)$ LEED patterns were observed. Plausible real space models, based on overlayer structures, are suggested with idealized Sn surface coverages of 0.67 and 0.50 ml, respectively. However, further analysis is being performed to determine whether these results might not also be consistent with surface alloys in which the Sn adatoms reside in the surface layer as opposed to on top of the surface Pt(100) template. These surfaces when examined in conjunction with the Sn/Pt(111) ordered surface alloys should provide interesting templates for examining the surface

electrochemical reactivity towards small fuel molecules (e.g., CH_3OH).

The electrochemical reactivity of the ordered Sn/Pt(111) surface alloys has been examined using a microreactor coupled to a ultra-high vacuum (UHV) chamber. A schematic drawing of the apparatus used in this study is shown in Fig. 4. The surface analysis techniques were used to adequately prepare and characterize the surface alloys as described in manuscripts on the Sn/Pt(111) ordered surfaces (Paffett and Windham). The surfaces of interest were transferred to the microreactor region where this smaller region (volume=100 ml) was backfilled with Ar, electrolyte introduced and the prepared surface alloy was then used as an electrode surface for the electrocatalytic activity towards methanol electrooxidation. The electrolyte solution was removed from the surface(s), the electrode was rinsed with ultrapure water (no electrolyte) and then were transferred back into the UHV environment. At this juncture the surface was examined using the same surface analytical techniques utilized to prepare and characterize the surface originally. We have at this point in time repeated the preliminary experiments reported previously (quarterly report (1/89)) and describe the results in outline form below. All of the electrochemical results described below were obtained in 0.1M H_2SO_4 solutions and potentials are referenced with respect to a Pd/H reference electrode that had been charged galvanostatically in 0.1M H_2SO_4 solution prior to assessing the methanol electrochemical activity.

1) In 0.1M H_2SO_4 solutions the electrochemical stripping of the vapor deposited Sn proceeds above approximately +0.6V and no sharp, strong electrochemical features were seen in cyclic voltammograms of the specifically prepared surfaces. Experimental evidence for the above statement is supported by the AES spectra

recorded over the region 100-550 eV. AES traces have been recorded from Pt(111), an unannealed Sn overlayer on Pt(111) ($\Theta = 0.7$ ml), and the $(\sqrt{3} \times \sqrt{3})R30^\circ$ Sn/Pt(111) surface alloy prior to and after electrochemical cycling in 0.1M H_2SO_4 . After exposure to the electrochemical environment an appreciable O content builds up at the interface. In addition, a slightly variable C concentration is present after exposure to electrochemical environments. This C content was essentially the same (to within $\pm 20\%$) regardless of whether methanol was present in the electrolyte. For surfaces that have been electrochemically cycled to potentials greater than +0.6V the surface concentration of Sn was drastically decreased (<5% atomic concentration).

X-ray photoelectron spectroscopy (XPS) recorded from the Sn overlayer and the $(\sqrt{3} \times \sqrt{3})R30^\circ$ Sn/Pt(111) surface alloy after electrochemical potential excursions below +0.6V indicates that the surface contains a hydrated Sn oxide (most likely either $SnOH_x$ or $SnO_2 \cdot nH_2O$ - quarterly report 1/90). Potential excursions above this resulted in a loss of Sn in agreement with the AES data.

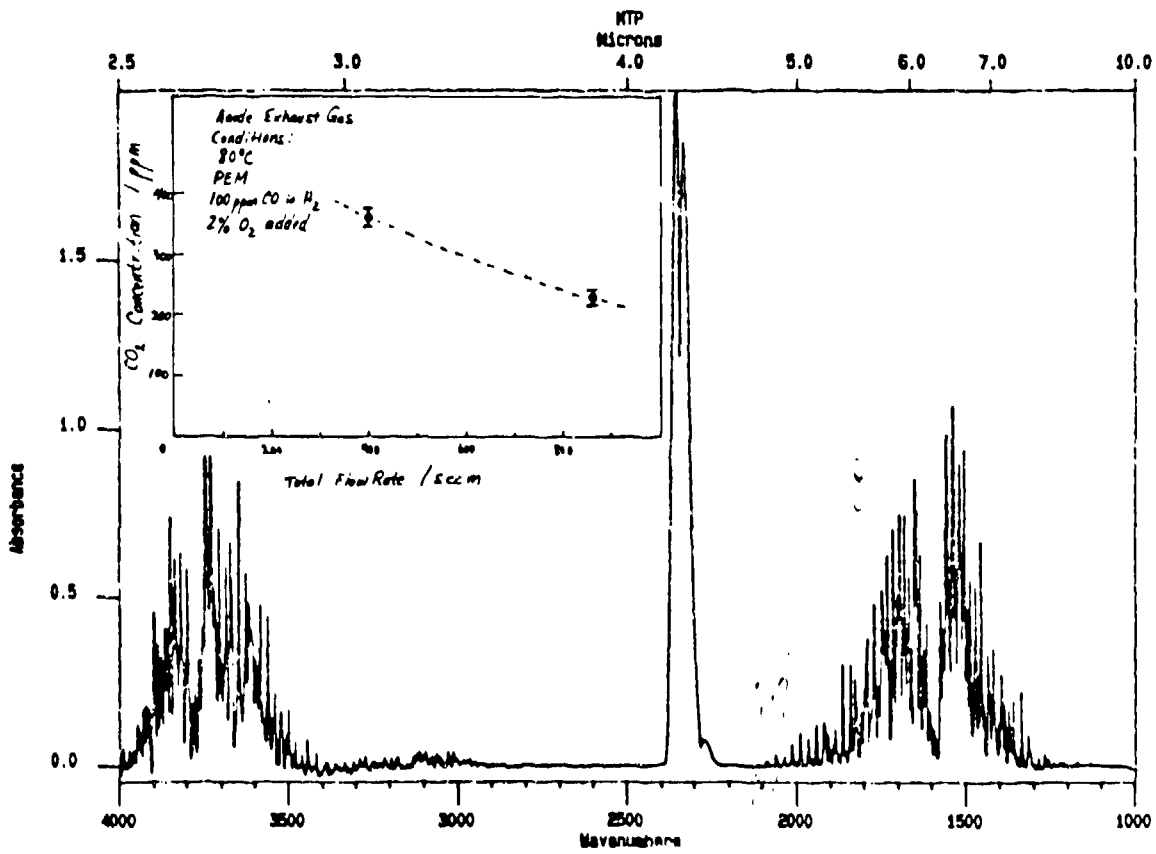
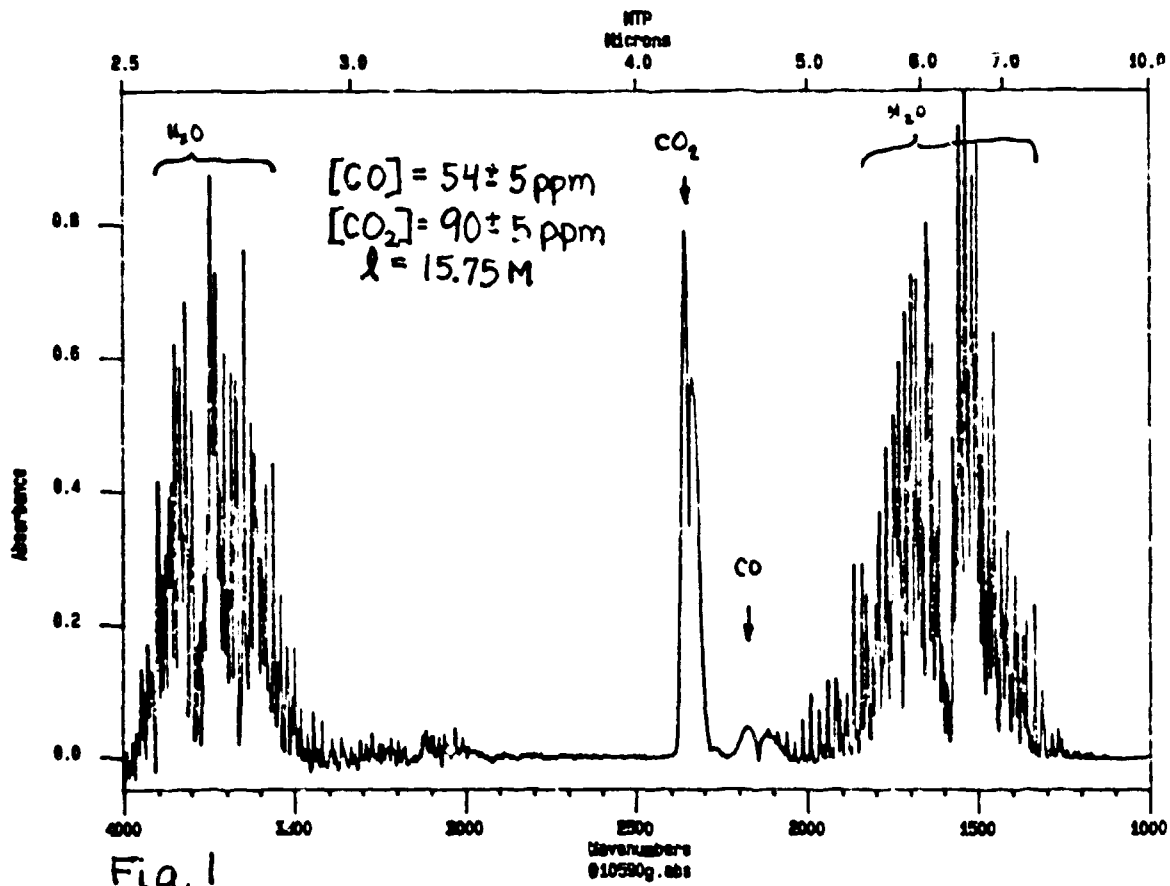
The actual electrochemical enhancement for methanol electrooxidation was probed using cyclic voltammetry. These preliminary results will be discussed and have been reported in prior quarterly report (1/90).

In summary, the overlayer surfaces appeared to be rather unreactive with respect to methanol electrooxidation and in all cases a carboneaceous residue was readily detected by AES. The Sn/Pt(111) surface alloys, however, do appear to more reactive towards methanol electrooxidation. Work is currently in progress to further delineate the role that specifically prepared bimetallic surfaces (in the form of ordered surface alloys) have on the observed

electrooxidation behavior towards methanol.

REFERENCES

- J. Pafford and S. Gottesfeld, *J. Electrochem. Soc.*, **135** (1988) 2651.
- M.T. Paffett, J. Pafford, and S. Gottesfeld, Extended Abstract of the Electrochemical Society, Spring Meeting of the Electrochemical Society, May 1989, Los Angeles, CA.
- M.T. Paffett, D. Hawker, H. Tobias, J. Valerio, and S. Gottesfeld, submitted to ?.
- M.T. Paffett and R.G. Windham, *Surface Sci.*, **208** (1989) 34.
- M.T. Paffett, S. Gebhard, R. Windham, and B. Koel, *Surface Sci.*, **223** (1989) 449.
- M.T. Paffett, S. Gebhard, R. Windham, and B. Koel, *J. Phys. Chem.*, in press, 1990.
- S. Overbury, D. Mullins, M.T. Paffett, and B. Koel, 3rd International Conference on Surface Structure, Milwaukee, WI, July, 1990.
- M.T. Paffett, R.J. Simonson, and B.E. Koel, manuscript in preparation.



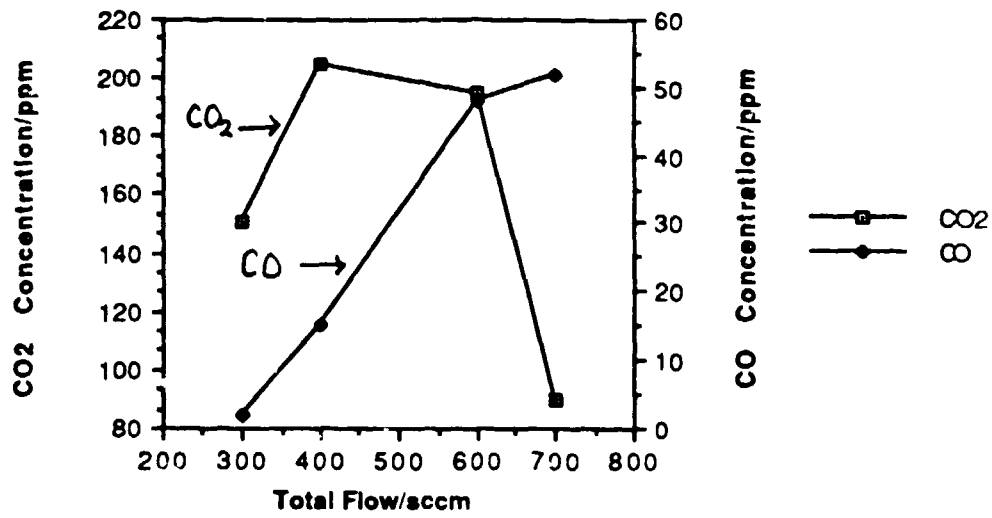


Fig. 3

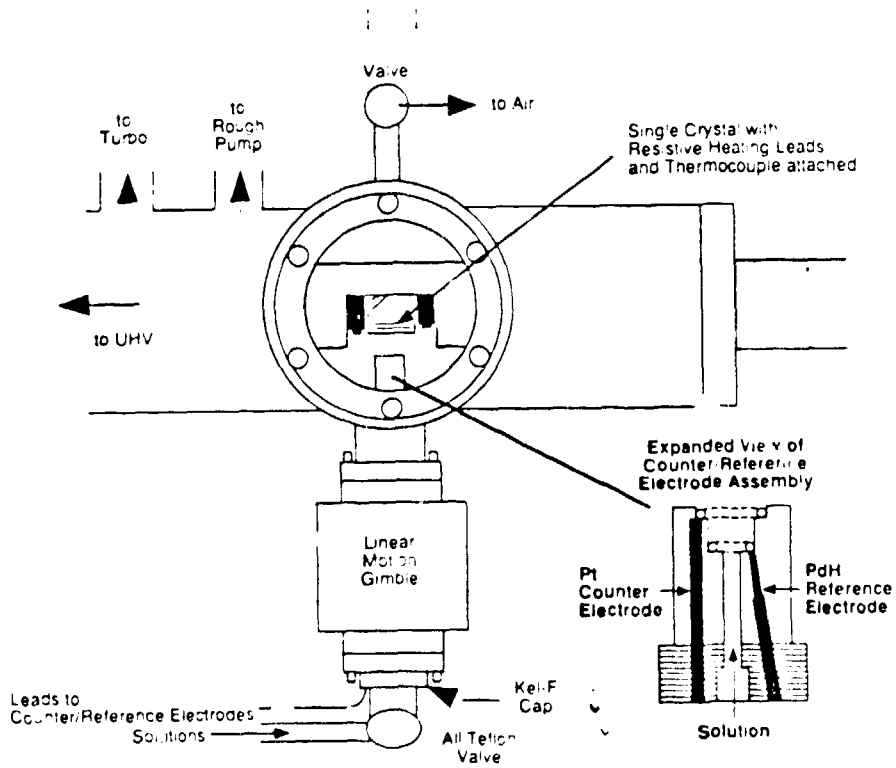


Fig 4