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(54) **PROCESS FOR PREPARING PALLADIUM  
ALLOY COMPOSITE MEMBRANES FOR  
USE IN HYDROGEN SEPARATION,  
PALLADIUM ALLOY COMPOSITE  
MEMBRANES AND PRODUCTS  
INCORPORATING OR MADE FROM THE  
MEMBRANES**

(76) Inventors: **Fernando Roa**, Golden, CO (US); **J.  
Douglas Way**, Boulder, CO (US);  
**Stephen N. Paglieri**, White Rock, NM  
(US)

Correspondence Address:

**CHRISTOPHER J. KULISH, ESQ**  
**HOLLAND & HART LLP**  
**P. O. BOX 8749**  
**DENVER, CO 80201-8749 (US)**

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427/383.1; 427/404

(57) **ABSTRACT**

The invention is directed to a method for producing Palladium alloy composite membranes that are useful in applications that involve the need to separate hydrogen from a gas mixture. Further, in one embodiment, a Pd alloy composite membrane is realized in which the Pd alloy film is 1  $\mu$ m or less in thickness and resistant to poisoning by sulfide compounds. Further, the Pd alloy composite membranes are applied to a number of applications, such a fuel reforming.

FIG.1

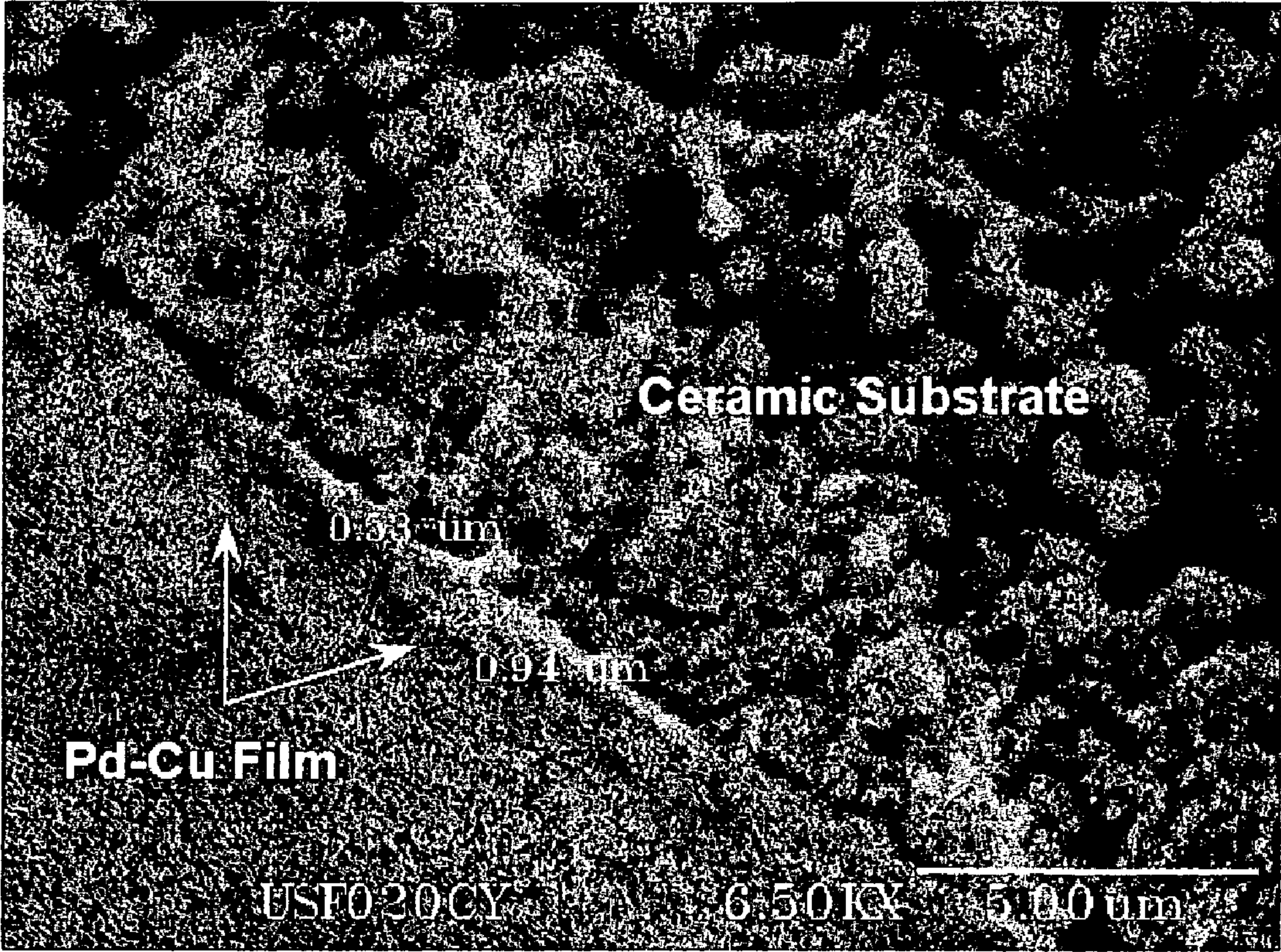


FIG.2

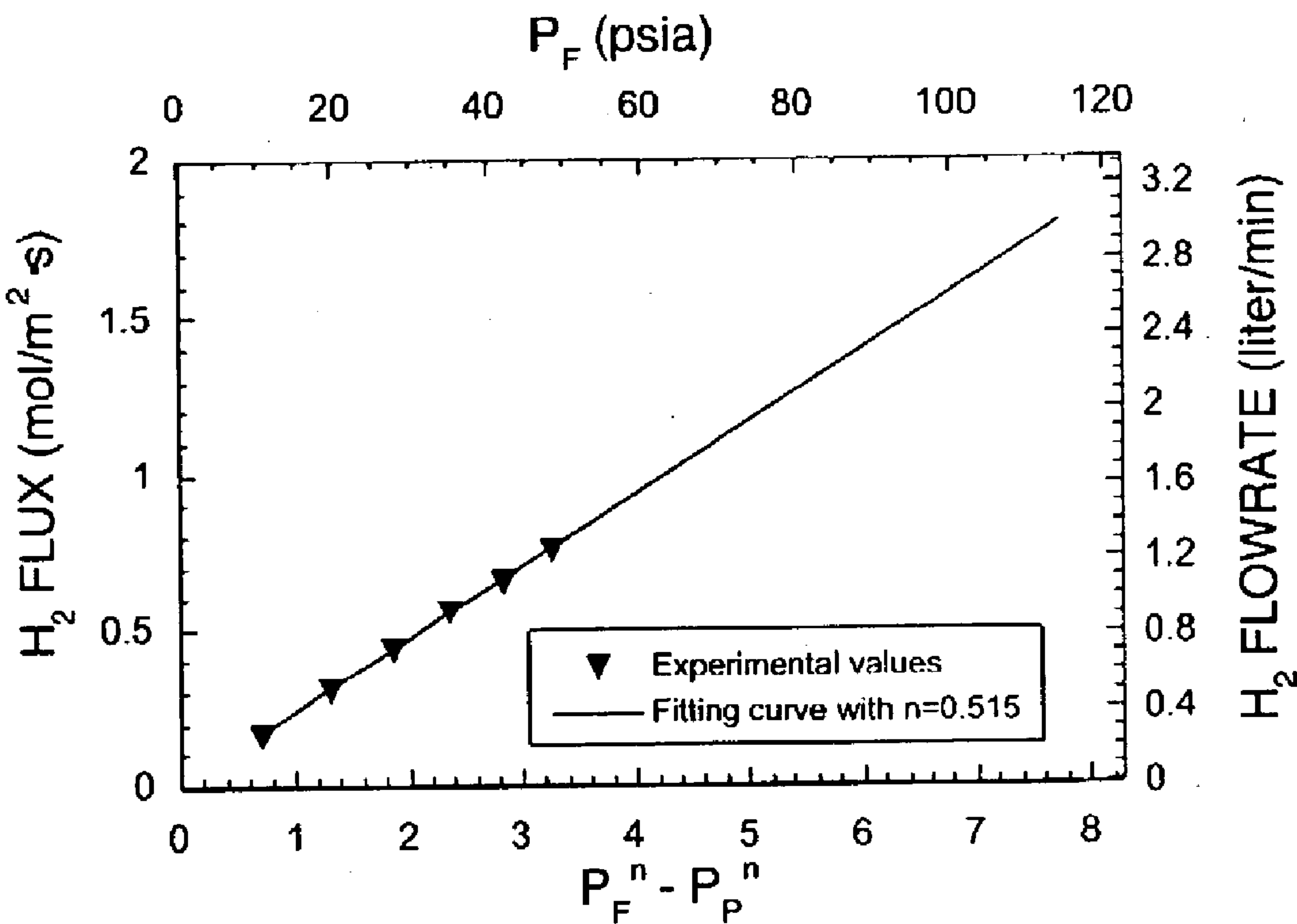


FIG.3

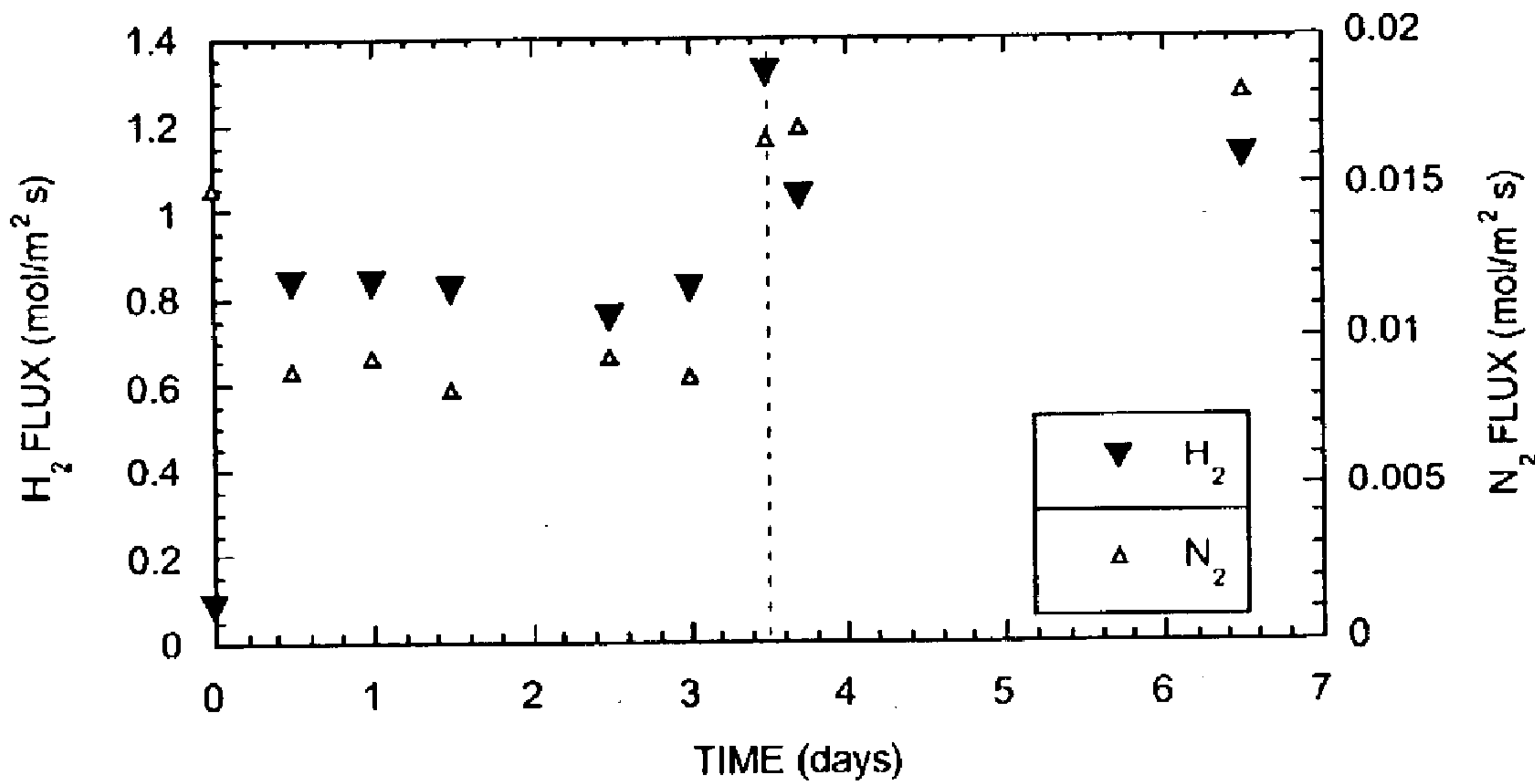




FIG.4

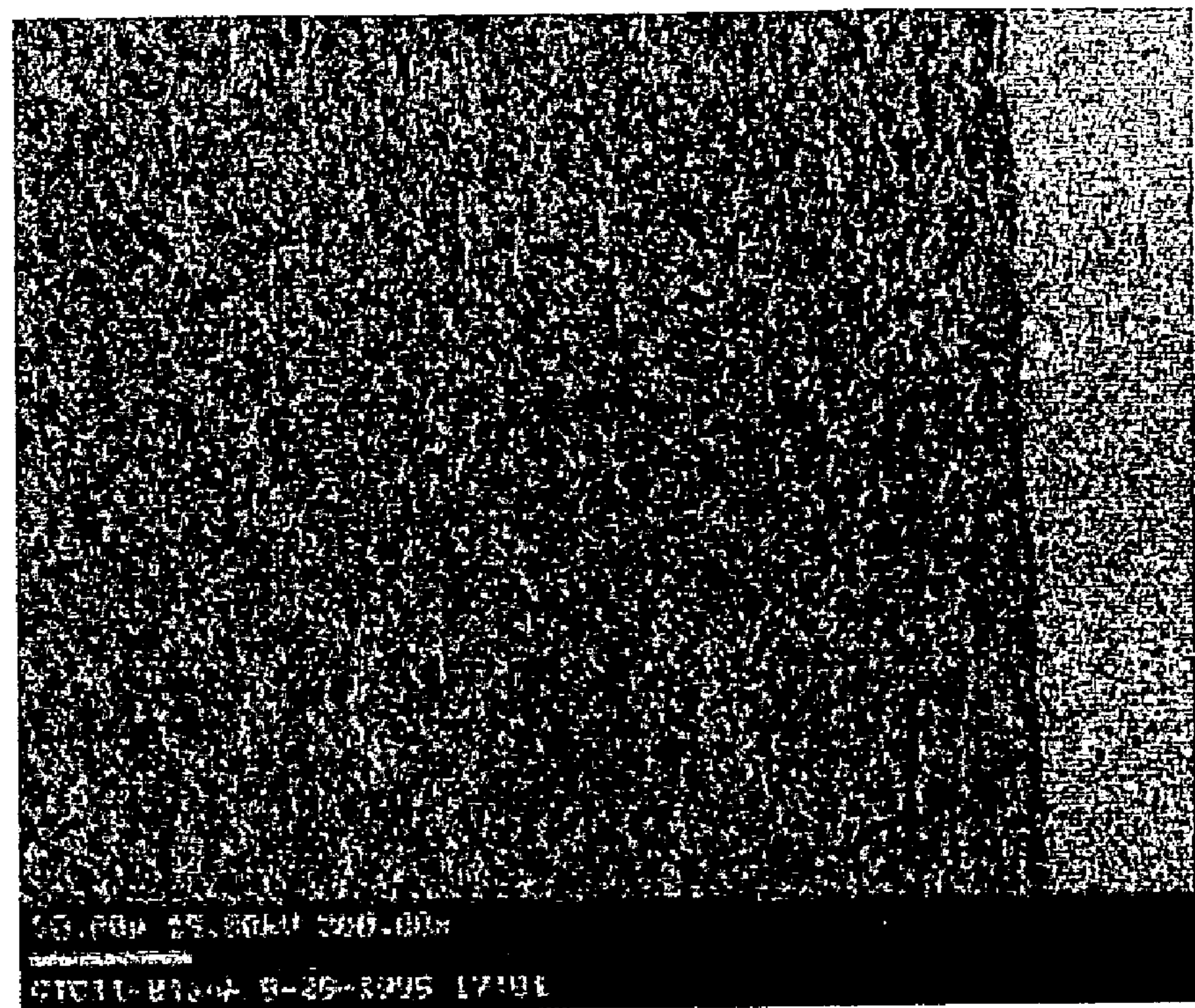


FIG.5

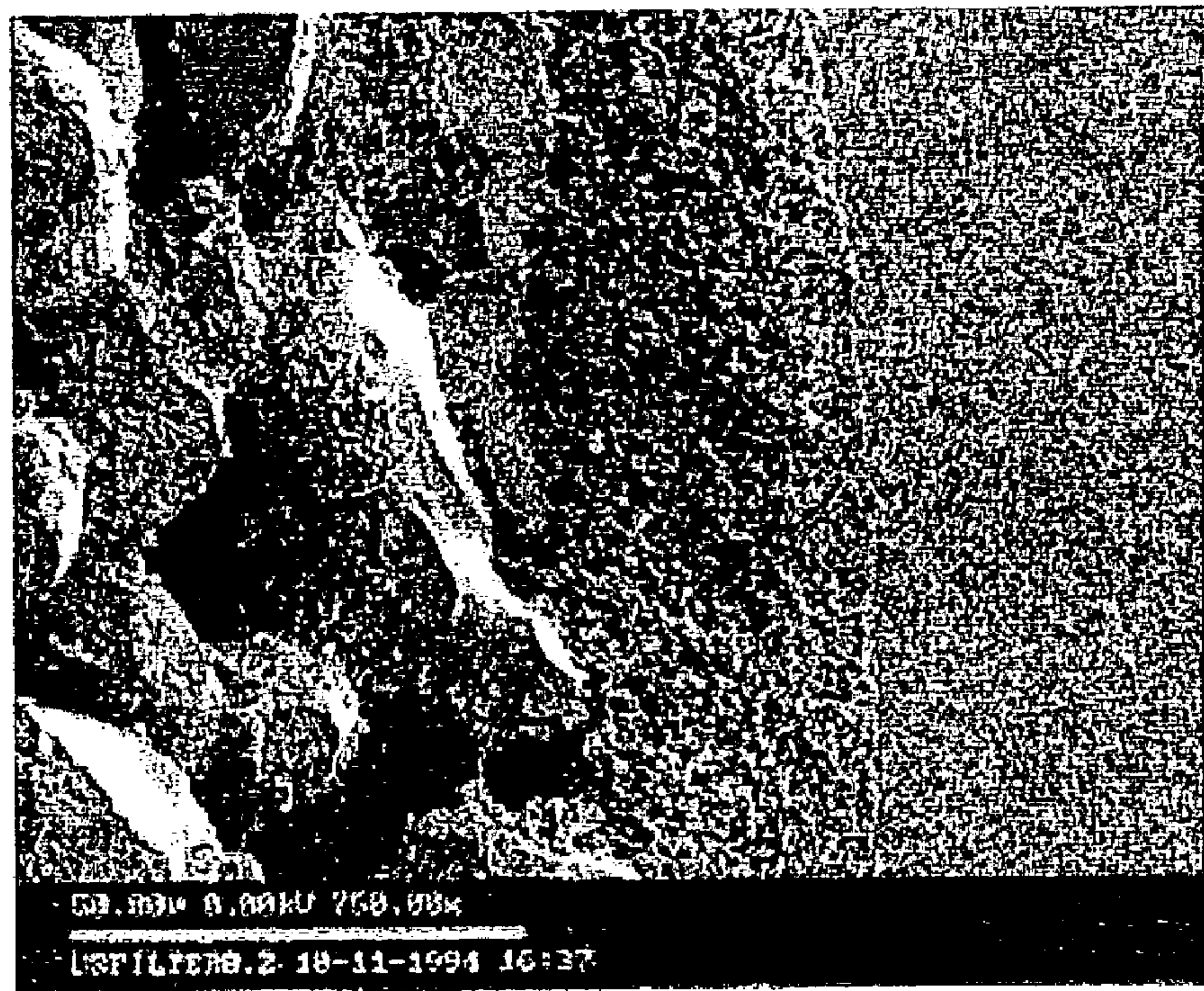


FIG.6A

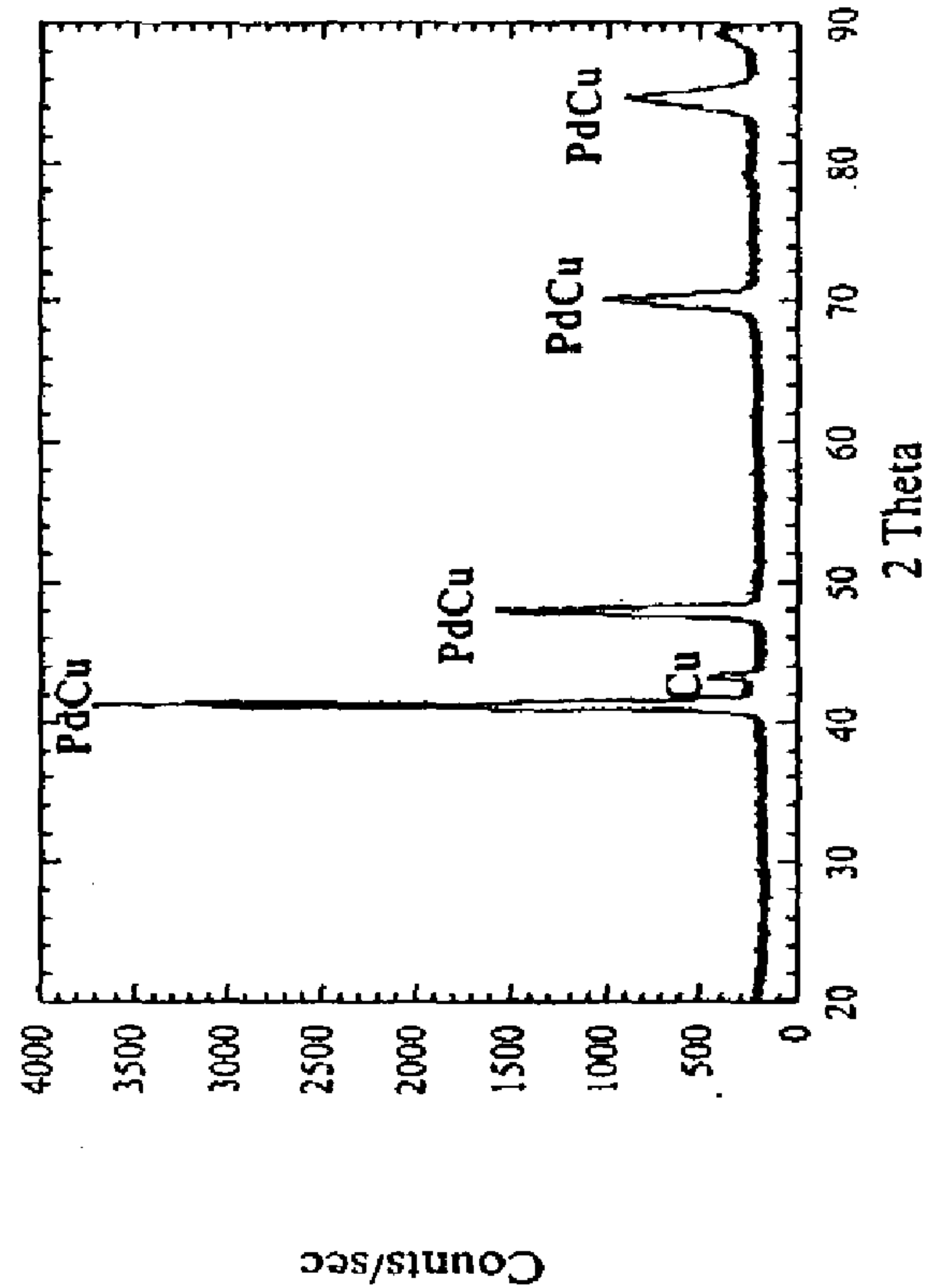


FIG.6B

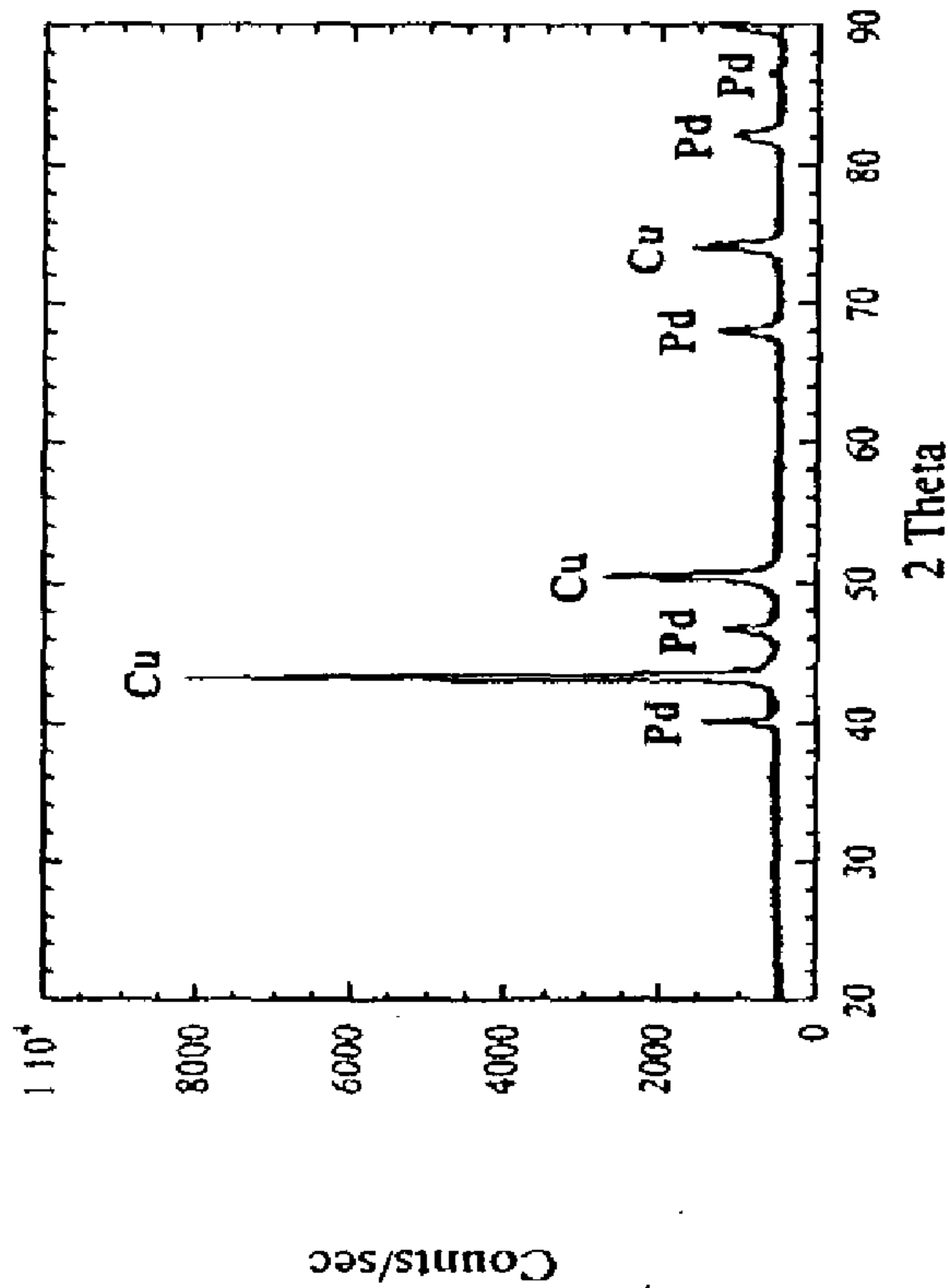




FIG.7

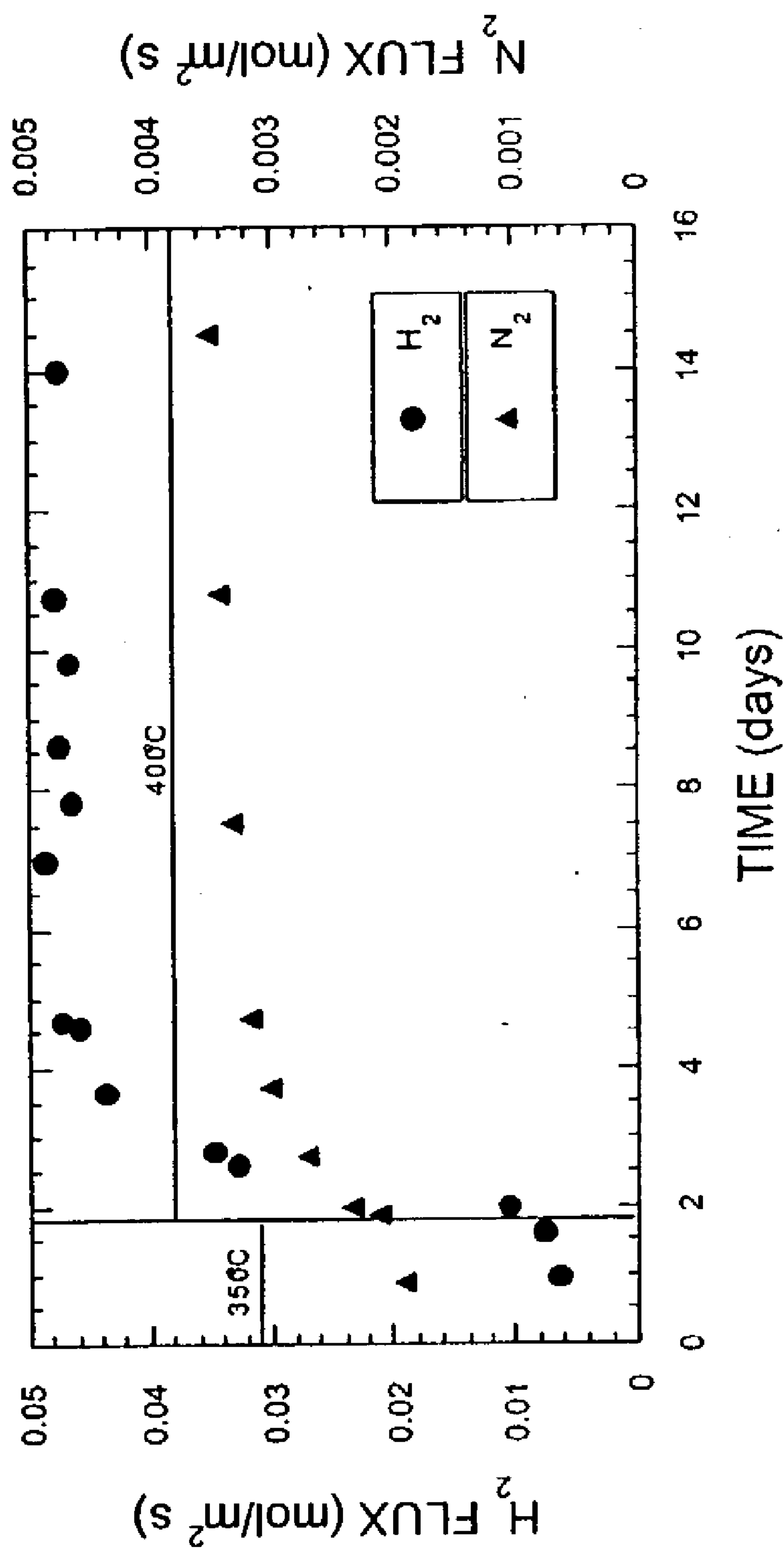


FIG.8

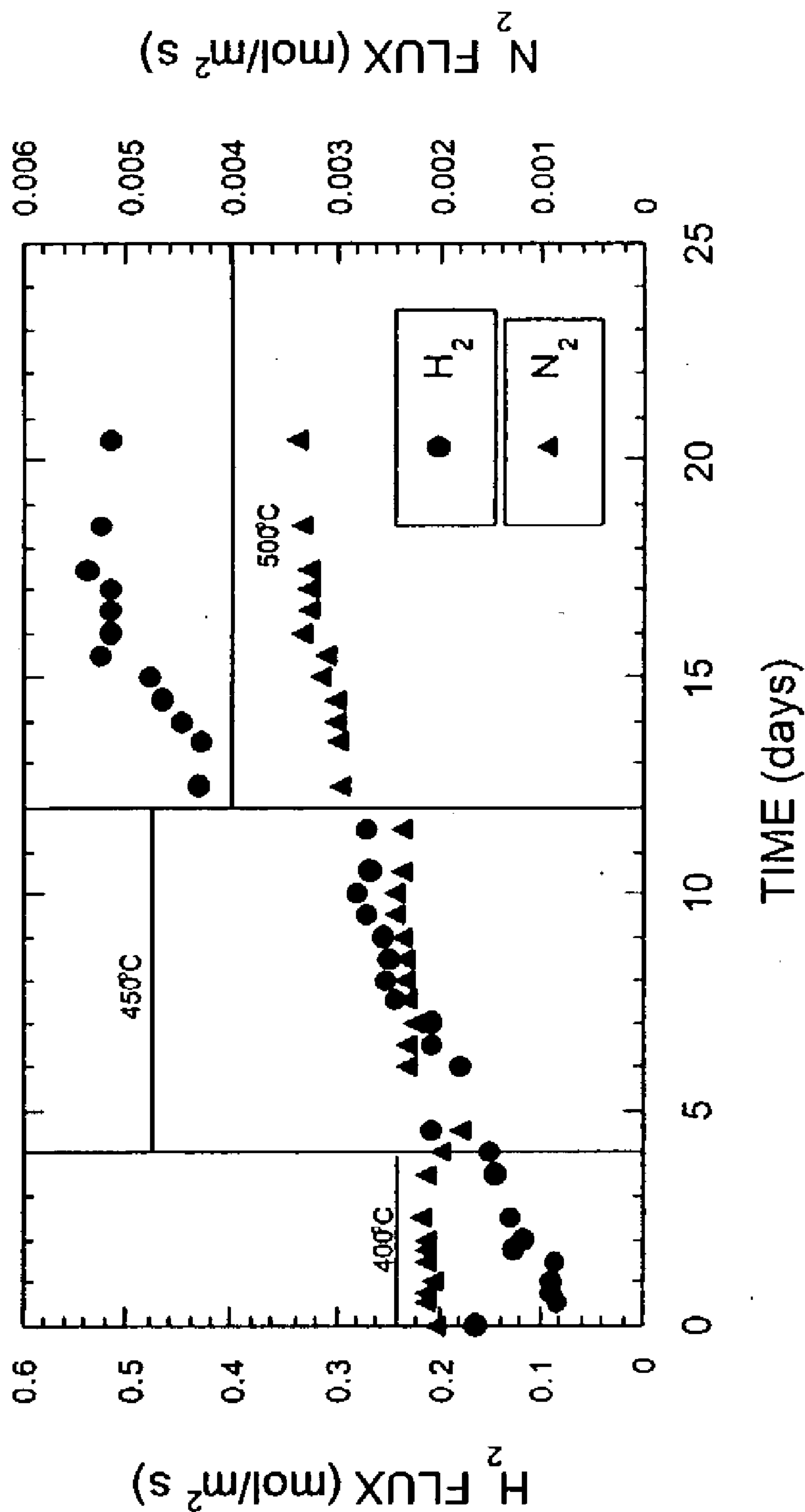


FIG.9A

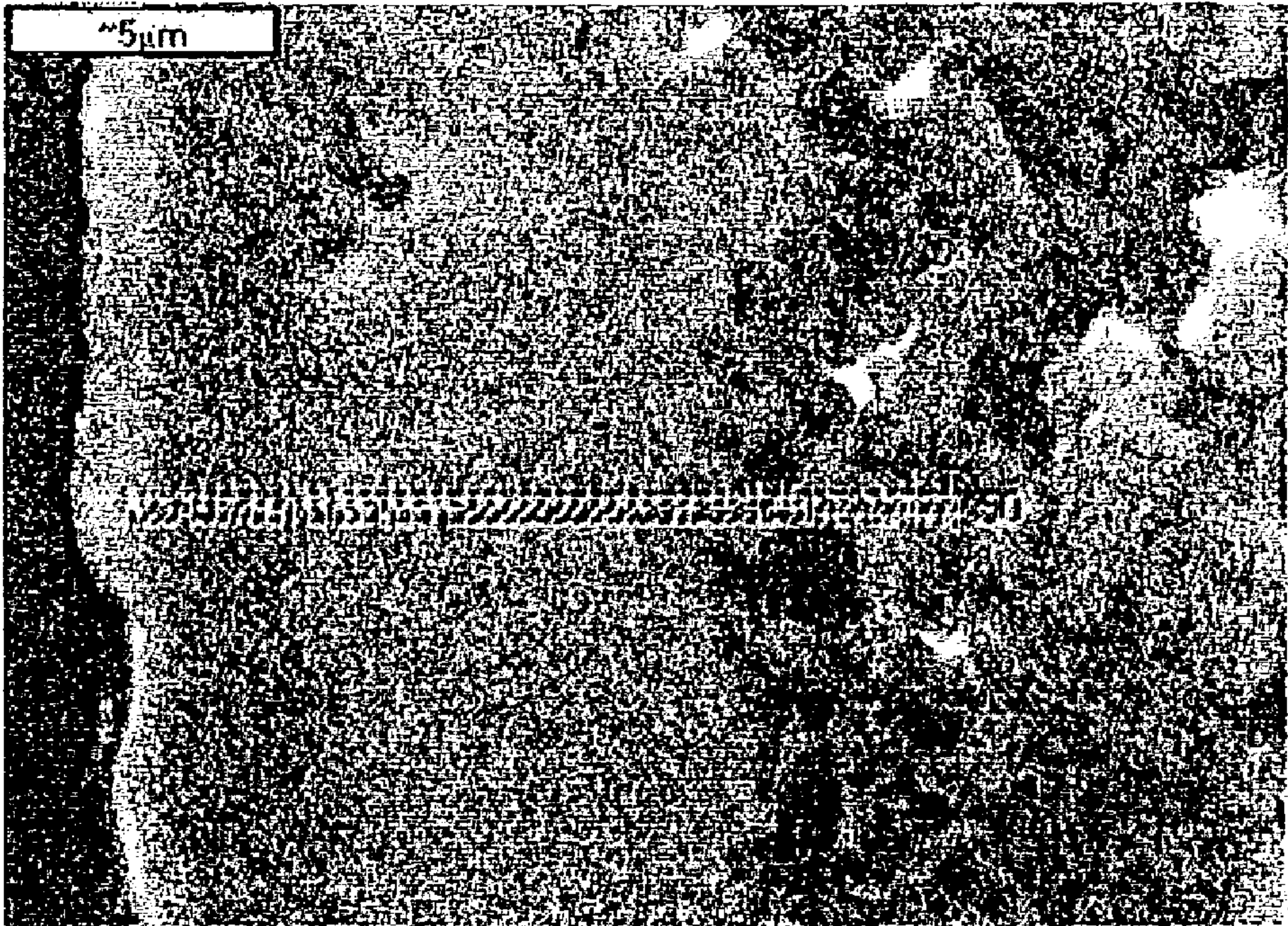




FIG.9B

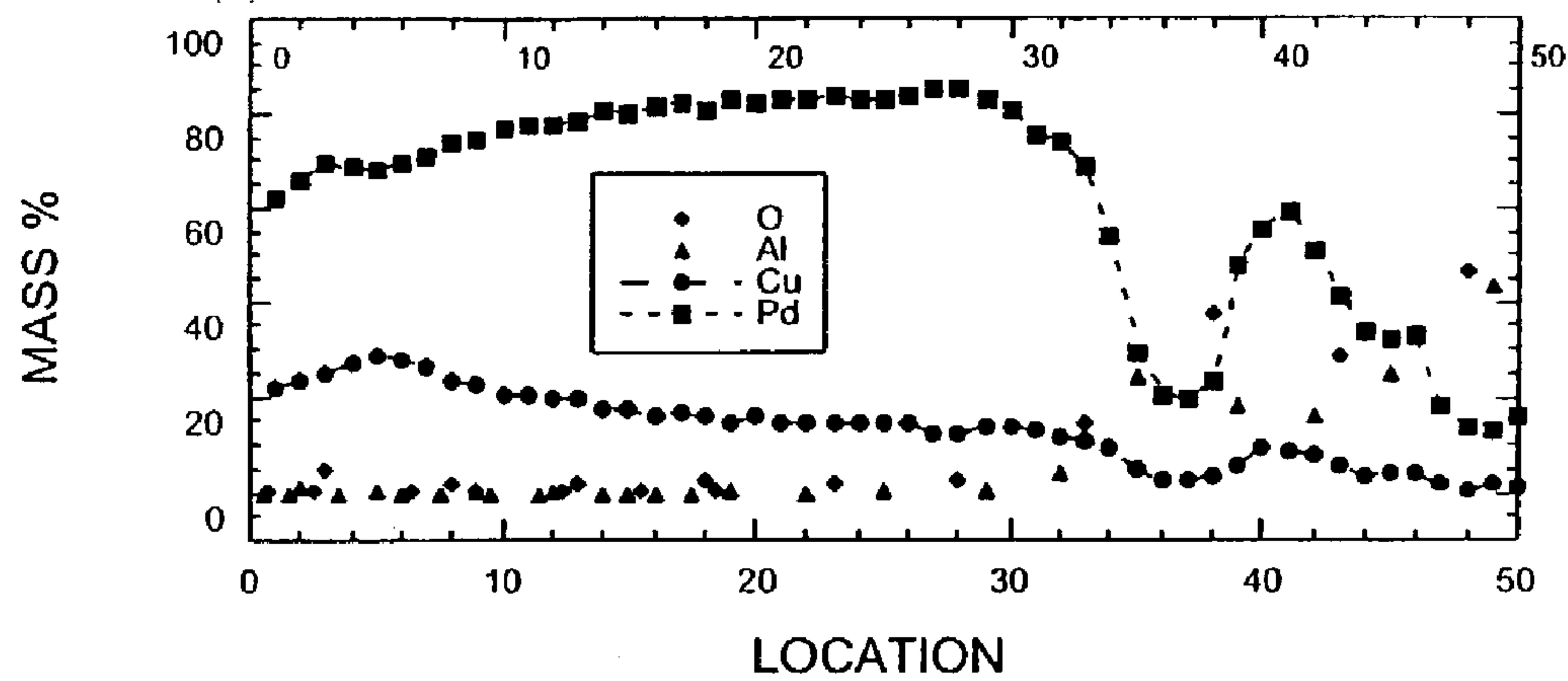


FIG.10

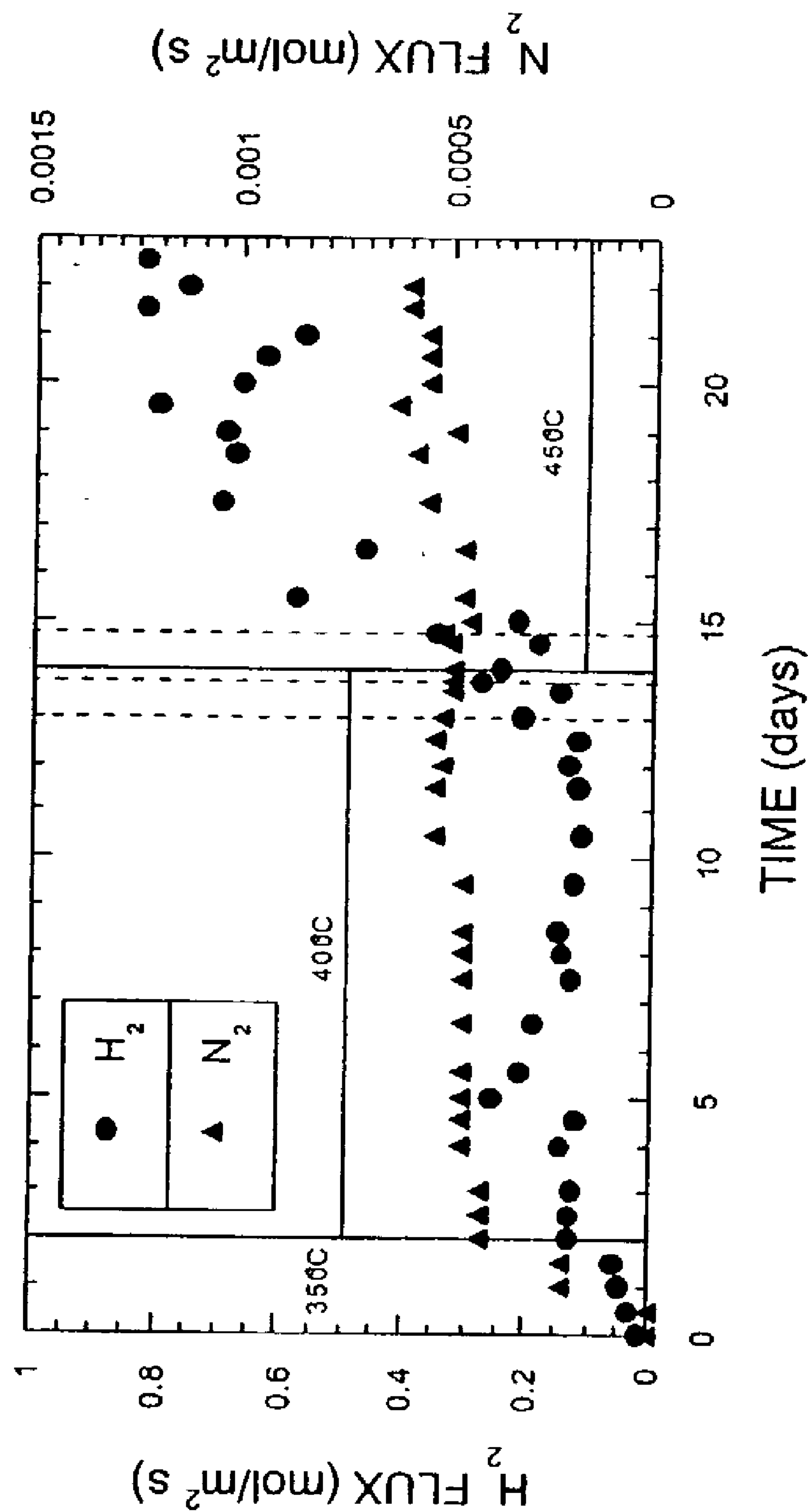




FIG.11A

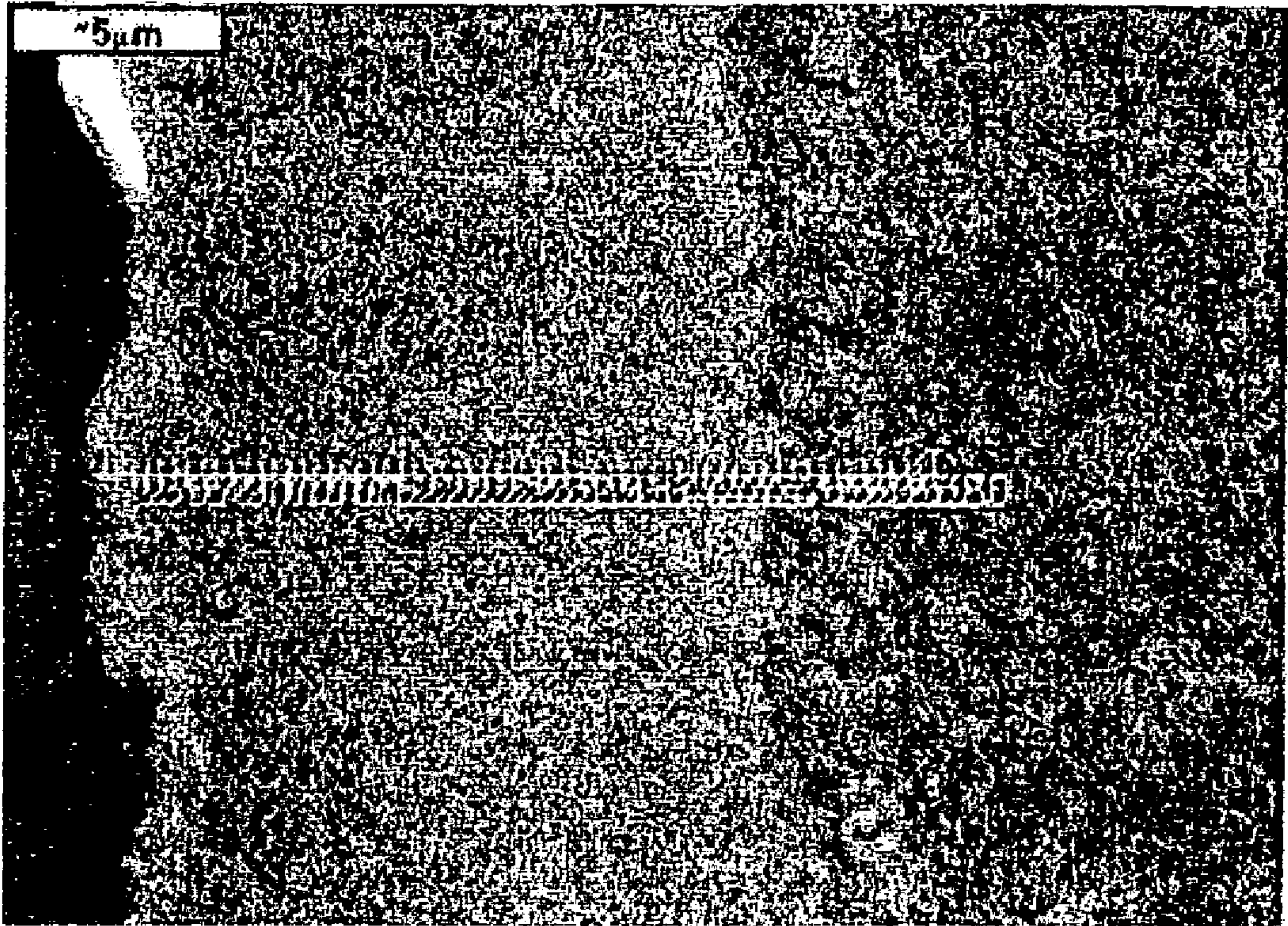


FIG.11B

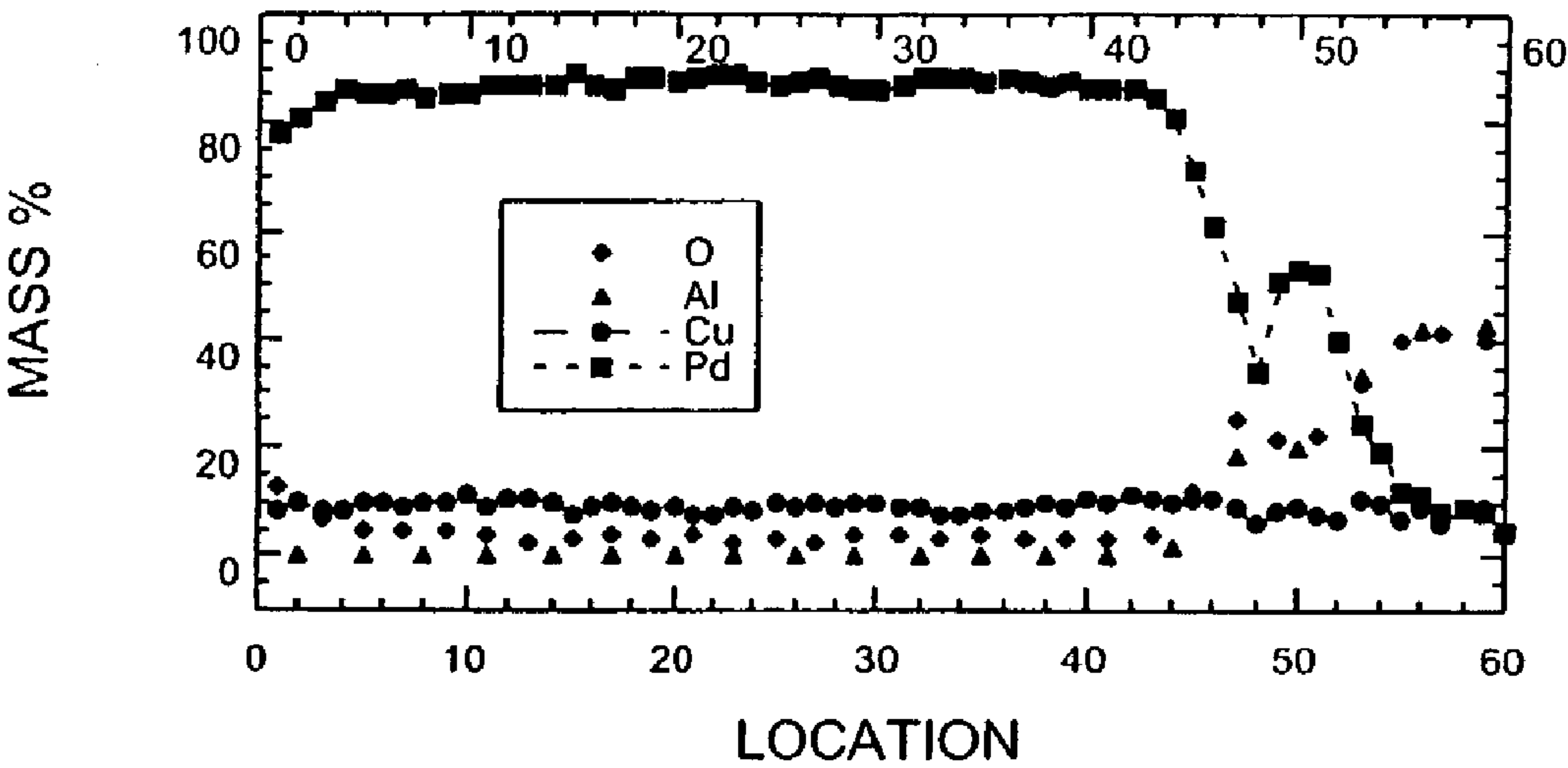




FIG.12

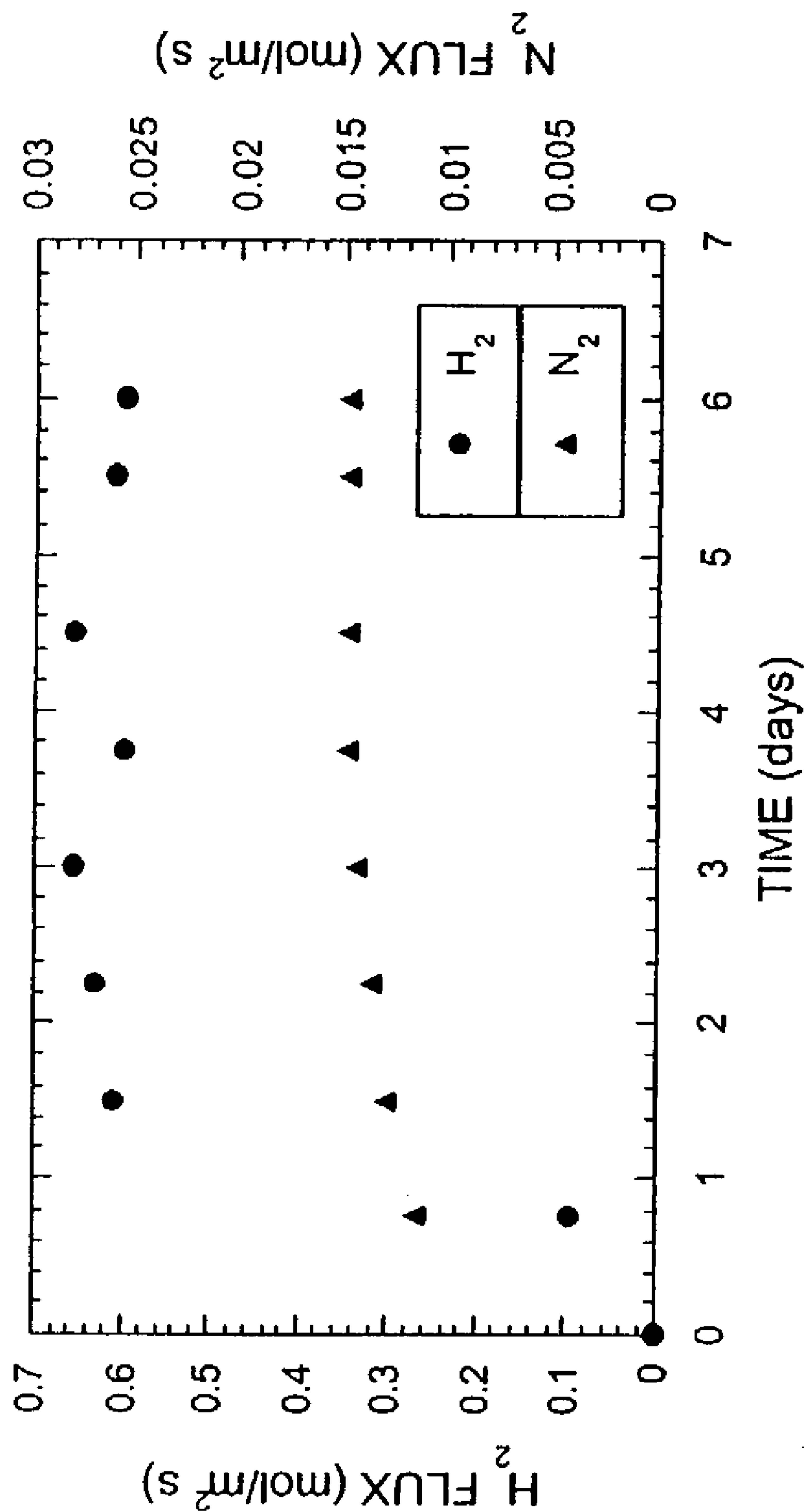


FIG.13

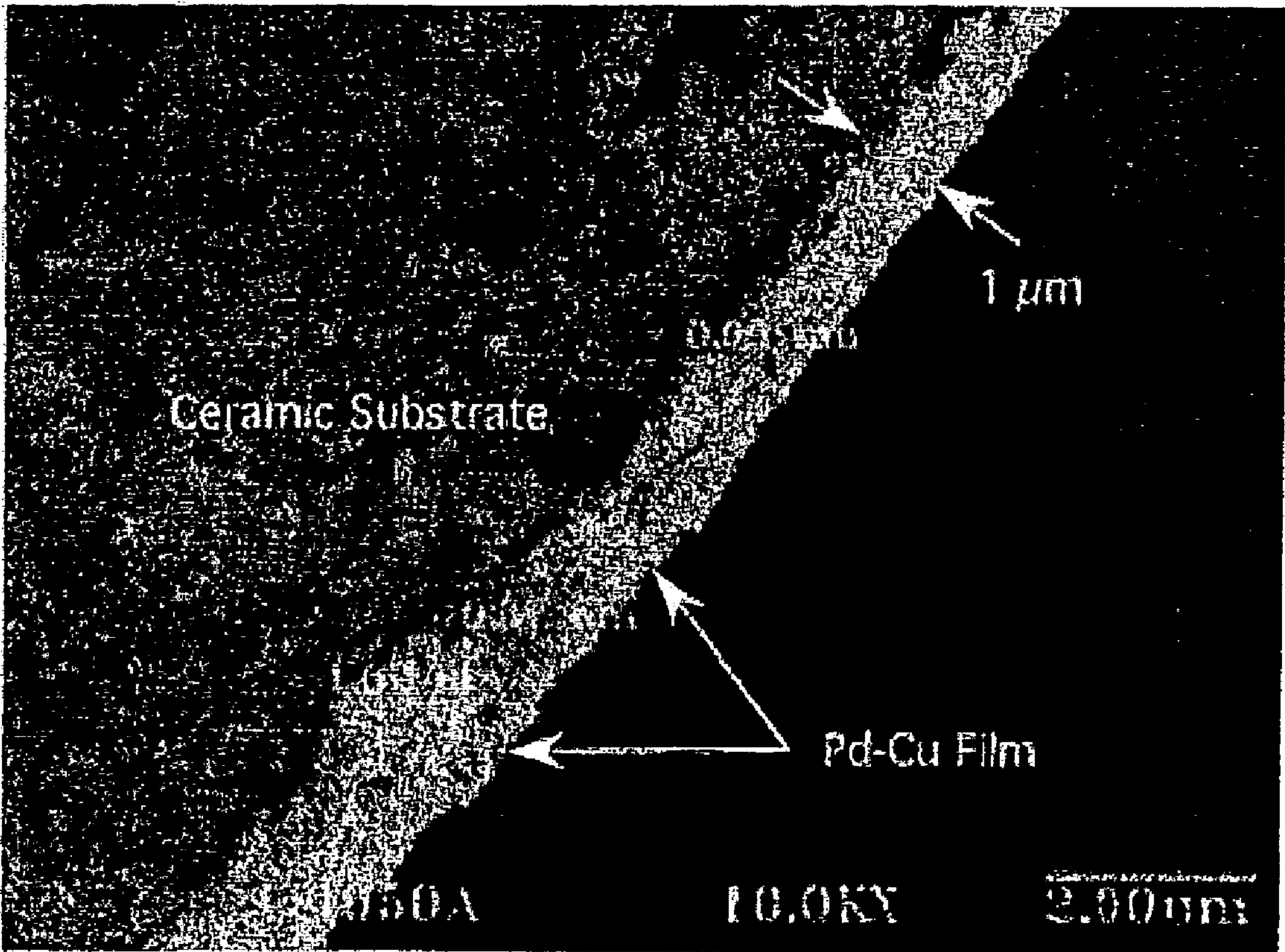




FIG.14



FIG.15

Solution	Constituent	Quantity
Pd Plating Bath	PdCl <sub>2</sub> , 99.9% pure	5.45 g/L
	NH <sub>4</sub> OH	389.6 mL/L
	Na <sub>2</sub> EDTA	70 g/L
	N <sub>2</sub> H <sub>4</sub> (1.0 M)	10 mL/L
	HCl	10.9 mL/L
Cu Plating Bath	CuSO <sub>4</sub>	6.225 g/L CuSO <sub>4</sub> •5H <sub>2</sub> O
	Na <sub>2</sub> EDTA	20.0988 g/L
	Formaldehyde (37%)	14.039 mL/L
	NaOH	20 g/L
	Triton X-100	25 mg/L
	2,2-bipyridyl	5 mg/L

FIG.16

Membrane No.	Type of support material	Support pore size (nm)	Estimated Thickness of Pd film	*N <sub>2</sub> Flux (mol/m <sup>2</sup> s) x 10 <sup>4</sup>	Estimated Thickness of Cu film	*N <sub>2</sub> Flux (mol/m <sup>2</sup> s) x 10 <sup>4</sup>
1	Symmetric α-alumina	200	47	-	10	-
2	Symmetric α-alumina	200	10	5.332	4	0.337
3	Symmetric α-alumina	200	6.5	1.073	4	0.105
4	Symmetric α-alumina	200	8	0.985	8	0.061
5	Asymmetric zirconia	50	8	0.438	6	0.021
6	Asymmetric zirconia	50	1.5	0.248	1	0.042
7	Asymmetric γ-alumina	5	10	very high	-	-

\* The membrane, coated with Pd, is pressurized with N<sub>2</sub> at 896.3 kPa. The time for the pressure to drop at 827.4 kPa is measured and the flux calculated.

\* As above but now the membrane is coated with both Pd and Cu.



FIG.17

Membrane No.	$\Delta P$ (kPa)	Heated to (K)	H <sub>2</sub> flux @ 500 °C (mol/m <sup>2</sup> s)	Highest Selectivity*	Thickness from SEM (μm)	Pd/Cu from EDAX (wt%)
1	689.5	723	0.048	14	27.6 ±8.5	72/28
2	344.7	973	0.35	70	11.0±1.0	80/20
3	344.7	773	0.52	170	11.6±1.0	81/19
4	344.7	723	0.18 <sup>§</sup>	270	12.5±1.5	78/22
5	344.7	723	0.80	1400	12±1.0	91/9
6	344.7	723	0.66 <sup>#</sup>	47	1.5 ±0.2	70/30

\* Selectivity = hydrogen flux/nitrogen flux.

<sup>§</sup> Measurement made at 450 °C

<sup>#</sup> Measurement made at 350 °C

FIG.18

ITEM	COST (\$)
Asymmetric ceramic support	125
Palladium	17.5
Other chemicals	5
Electricity and supplies	0.2
TOTAL	147.7

**PROCESS FOR PREPARING PALLADIUM ALLOY  
COMPOSITE MEMBRANES FOR USE IN  
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**CROSS REFERENCE TO RELATED  
APPLICATIONS**

**[0001]** This application claims the benefit of U.S. Provisional Patent Application Serial No. 60/369,674, entitled "PROCESS FOR PREPARING PALLADIUM ALLOY COMPOSITE MEMBRANES FOR USE IN HYDROGEN SEPARATION, PALLADIUM ALLOY COMPOSITE MEMBRANES AND PRODUCTS INCORPORATING OR MADE FROM THE MEMBRANES", and filed by Fernando Roa, J. Douglas Way and Stephen N. Paglieri on April 3, which application is incorporated by reference into this application in its entirety.

**FIELD OF THE INVENTION**

**[0002]** The invention is directed to a process for fabricating a palladium alloy composite membranes, the composite membranes and products incorporating or made from such membranes.

**BACKGROUND OF THE INVENTION**

**[0003]** The hydrogen separating capability of Pd alloy membranes is well known. Applications include hydrogenation and dehydrogenation reactions and recovery of hydrogen from petrochemical plant streams. Other applications are high temperature hydrogen separations, fuel cell power systems, hydrogen fueling stations, hydrocarbon reforming, and use in membrane reactors, devices that can simultaneously form a product and separate the reaction products.

**[0004]** There are several patented Pd and Pd/Ag alloy membrane devices and fabrication processes. All of these devices are poisoned severely by the presence of sulfur compounds, typically  $H_2S$ , in a reducing environment. Solving the  $H_2S$  poisoning problem is a necessity for application of metal membranes in the petroleum and petrochemical industries since all gas streams contain small amounts of  $H_2S$  (0.01 to 1 ppm) which will poison metal membranes made from Pd and Pd/Ag alloys. The  $H_2S$  poisoning problem will also be present for fuel cell power systems where hydrocarbons containing organic sulfur (such as gasoline, diesel fuel, and natural gas) are converted into synthesis gas.

**[0005]** Pd or Pd/Ag membrane materials useful for selectively separating hydrogen without poisoning the membrane have been actively pursued by the scientific community. A large base of technical literature exists specifically for Pd or Pd/Ag membranes and is the subject of numerous patents. Pd/Cu alloys and certain other Pd alloys are known to be much more resistant to  $H_2S$  poisoning than Pd or Pd/Ag alloys.

**[0006]** There are two types of Pd and Pd alloy membranes. The first type is a Pd or Pd alloy foil membrane, a foil being a "free-standing" or unsupported membrane. The second type is a composite membrane that includes a substrate and a film of Pd or Pd—Ag that is supported on the substrate.

With respect to the first type of membranes, McKinley is believed to have been the first to describe the beneficial properties of relatively thick palladium alloy foil membranes (25 to 100 microns in thickness). In U.S. Pat. No. 3,350,845, McKinley teaches the use of 0.1 mm thick (100 microns) Pd—Au alloy foil membranes for hydrogen separation which resist poisoning by sulfur compounds, including hydrogen sulfide. In U.S. Pat. No. 3,439,474, McKinley teaches the use of 25 micron thick 40 mass % Pd—Cu alloy foil membranes for the separation of hydrogen at elevated temperature and pressure. The primary benefits of the Pd—Cu alloy foil membrane include resistance to poisoning by  $H_2S$  and higher hydrogen permeability compared to pure palladium.

**[0007]** With respect to the first type of membrane, U.S. Pat. No. 3,881,891 describes a method for increasing the hydrogen permeability of Pd alloy foil membranes and reducing the poisoning effects of sulfur compounds. The method involves adding water vapor to the gas mixture. They observed an increase in the hydrogen permeability in the presence of steam for all membranes tested. Exposure to water vapor also restored the hydrogen permeability of membranes previously exposed to  $H_2S$ .

**[0008]** Also relating to the first type of membrane, U.S. Pat. No. 6,103,028 describes methods for reducing the thickness of palladium alloy (Pd—Cu, Pd—Ag, Pd—Ru, and Pd—Y) foil membranes to increase the hydrogen flux. The foil membranes are annealed at 320° C. under hydrogen and then etched by exposure to mineral acids or by electrochemically removing metal from the membranes.

**[0009]** Further relating to the first type of membranes, U.S. Pat. No. 6,152,995 describes a process to increase the flux of hydrogen through a metal foil membrane by chemical etching using a mineral acid such as  $HNO_3$  or mixtures of  $HNO_3$  and HCl. This patent also describes methods for finding leaks on metal foil membranes and techniques to repair such leaks.

**[0010]** The second type of membranes is comprised of a thin film of Pd deposited on a substrate that could be dense or porous. In this regard, U.S. Pat. No. 5,149,420 discloses a method for forming a thin, micron thick layer of pure Pd on supports of dense Group IV-B and V-B metals such as niobium, vanadium, or tantalum, or titanium. In operation, the palladium layer catalyzes the dissociation of hydrogen molecules to hydrogen atoms, which can subsequently permeate through the Pd layer and the dense metal support layer. A Pd coating on the other side of the membrane allows for the recombination of hydrogen atoms to form molecular hydrogen. It should be noted that the primary source of diffusional resistance in such a membrane is due to the metal support layer.

**[0011]** Further relating to the second type of membranes, U.S. Pat. Nos. 5,451,386 and 5,652,020 teach the preparation of supported Pd membranes for hydrogen separation by electroless plating of a dense layer of Pd that is 10 to 20 microns thick on porous ceramic supports. In these membranes, the primary source of resistance to hydrogen diffusion is the Pd layer, not the ceramic support.

**[0012]** Apparently, Kikuchi and co-workers have fabricated Pd—Cu alloy films on porous supports by chemical deposition of Pd and then Cu with subsequent annealing (500° C. for 12 hours).



## SUMMARY OF THE INVENTION

[0013] The invention is directed, at least in part, to a process for producing a composite membrane comprised of a substrate and a very thin Pd alloy film on the substrate. The ability to deposit a very thin Pd alloy film reduces the material cost of the film relative to membranes with thicker films and increases the  $H_2$  flux since to a first approximation, the flux is inversely proportional to membrane thickness. In one embodiment, the film is less than about 1 micron.

[0014] In certain embodiments, the resulting membrane is comprised of a Pd alloy film that is both thin and resistant to sulfur poisoning. Such a membrane is useful in applications that require the separation of hydrogen from hydrocarbon streams that contain sulfur or sulfur compounds. One such application is in fuel cell power systems that use sulfur containing hydrocarbon fuels. In such system, the membrane separates  $H_2$  from a product stream emanating from a fuel conversion reactor. In addition, at least in the case of a membrane with a Pd—Cu film, the membrane rejects carbon monoxide, a PEM fuel cell poison. Other applications for such a membrane include applications involving hydrogenation and dehydrogenation reactions, recovery of hydrogen from petrochemical plant streams, hydrocarbon reforming and coal gasification for power generation in fuel cells.

[0015] In one embodiment, the process comprises providing a porous substrate. Common porous substrates comprise ceramics, sintered metals, and sintered metals with ceramic outer surfaces. Typically, the size and shape of the substrate dictated by the application. For instance, in a fuel cell application, the substrate is likely to be an open-ended cylinder or a block with multiple, parallel shafts or holes extending through the block.

[0016] If required, the porous substrate is pre-processed, i.e., subjected to one or more operations that place the substrate in condition for plating related operations and/or one or more operations that are more readily accomplished before plating related operations. For example, if needed, the substrate is cleaned so as to be substantially free of salts and other materials that would interfere with the plating operations. Further, the substrate is shaped to the extent needed. Typically, shaping involves cutting the substrate to desired dimensions. Additionally, if needed, surfaces of the substrate through which hydrogen is not to permeate are sealed. For example, in the case of a cylinder for use in a hydrogen filtering application, the Pd alloy film is established on the inner surface of the cylinder and the end surfaces of the cylinder are sealed. The sealing assures that the hydrogen from a hydrocarbon stream passing through the cylinder cannot follow a path between the inner wall of the cylinder and the end walls but must follow a path between the inner and outer surfaces of the cylinder so that the hydrogen passes through the outer wall.

[0017] After any pre-processing operations have been completed, the portion of the porous substrate that is to support the Pd alloy film is subjected to a number of plating related operations. Initially, the noted portion of the substrate is “seeded” with Pd crystallites that form nucleation sites for subsequent plating of a Pd film on the substrate. There are a number of methods for “seeding” the substrate. For example, impregnation with an organic solution of Pd acetate or Pd acetylacetonate is feasible. Another possible method is ion exchange.

[0018] After the substrate has been “seeded” with Pd crystallites, the substrate is plated with a Pd film. There are several electroless methods for accomplishing the plating, including osmotic plating, vacuum pump plating and batch plating. Electro-plating is also feasible.

[0019] After the substrate has been plated with the Pd film, a second ingredient of the alloy is plated on top of the Pd film. Among the possible second ingredients that will yield an alloy with sulfur resistance are copper and gold. The second ingredient is plated on top of the Pd film by dipping or flowing the second ingredient over the substrate and Pd film. An osmotic plating technique is also feasible. By appropriately controlling the thermodynamic conditions and/or times under which the Pd and second ingredient are plated onto the substrate weight percentages of the constituents of the film can be achieved. These percentages are typically chosen so as to produce a film that has a hydrogen flux at or near the maximum for the constituents of the alloy. For example, for a Pd—Cu film, the maximum hydrogen flux occurs with a 40% Cu. A 40% Cu can be achieved by conducting the Pd and Cu plating operations under substantially the same thermodynamic conditions and over periods of time that produce layers of Pd and Cu that are approximately equal in thickness.

[0020] After the second ingredient has been plated over the Pd film, the structure is annealed to produce a Pd alloy of substantially uniform composition. In one embodiment, annealing is accomplished by gradually heating the structure up to at least  $350^\circ$  but less than  $600^\circ$  C. in an inert gas atmosphere (e.g., He, Ar or Ne) for 12 hours and then switching the atmosphere to hydrogen. The annealing permits intermetallic diffusion of the second ingredient layer into the Pd layer, thereby forming the Pd alloy. The use of hydrogen gas allows the progress of the annealing to be monitored. To elaborate, when hydrogen flux reaches a steady state value, the annealing step is substantially complete. To produce a film thickness of  $1\text{ }\mu\text{m}$  at the low end of the temperature scale, the annealing process takes at least 24 hours.

[0021] Once the Pd alloy film has been established on the substrate to produce the Pd alloy composite membrane, the membrane is subjected to air oxidation and reduction to improve the hydrogen flux of the membrane. In one embodiment, the membrane is subjected to air oxidation for a short duration (e.g., 5-30 minutes) at temperatures above  $350^\circ$  C., followed by exposure to hydrogen.

[0022] An advantage of the composite membrane approach is that membranes can be made by coating support materials to obtain a metal membrane typically thinner than most free-standing foil membranes.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0023] FIG. 1 is an SEM picture of the cross section of a Pd—Cu composite membrane (scale bar is  $5\text{ }\mu\text{m}$ ).

[0024] FIG. 2 shows the influence of  $H_2$  feed pressure on the hydrogen flux through Pd—Cu membrane 25b. The experimental temperature is  $350^\circ$  C. The membrane composition is 60 mass % Pd, 40 mass % Cu.

[0025] FIG. 3 shows flux data for Membrane #25b, 60 wt. % Pd. Film thickness  $\approx 1.5\text{ }\mu\text{m}$ , temperature  $\approx 350^\circ$  C. The



pressure differential for the permeation tests was 225 kPa. Note the flux increase due to the "air purge" treatment, shown as a dotted line.

[0026] FIG. 4 is a cross-section of symmetric,  $\alpha$ -alumina GTC 998 support with a nominal 0.2  $\mu\text{m}$  pore size. Scalebar is 50  $\mu\text{m}$ .

[0027] FIG. 5 is a cross-section of an asymmetric, alumina ultrafilter. Scalebar is 50  $\mu\text{m}$ .

[0028] FIG. 6 shows XRD results for the annealing of GTC Pd/Cu membrane. Film thickness  $\approx 22 \mu\text{m}$  (a) As electrolessly deposited. (b) Annealed at 600° C. for 12 hours under helium.

[0029] FIG. 7 shows flux data for Membrane 1. Film thickness  $\approx 28 \mu\text{m}$ . The pressure differential for permeation tests was 690 kPa.

[0030] FIG. 8 shows flux data for Membrane 3. Film thickness  $\approx 11 \mu\text{m}$ . The pressure differential for permeation tests was 345 kPa.

[0031] FIG. 9 is a scanning electron micrograph (a) and EDAX analysis profile (b) for Membrane 3. The crosses through the SEM image show the location of the individual EDAX analyses. Location 0 corresponds to the Pd—Cu membrane top surface and 50 corresponds to a point approximately 5  $\mu\text{m}$  into the alumina support.

[0032] FIG. 10 shows flux data for membrane 5. Metal layer thickness  $\approx 10 \mu\text{m}$ . The pressure differential for permeation tests was 345 kPa. Dotted lines represent 30 minute air purges.

[0033] FIG. 11 is a scanning electron micrograph (a) and EDAX analysis profile (b) for Membrane 5. The crosses through the SEM image show the location of the individual EDAX analyses. Location 0 corresponds to the Pd—Cu membrane top surface and 50 corresponds to a point approximately 5  $\mu\text{m}$  into the alumina support.

[0034] FIG. 12 shows flux data for Membrane 6. Film thickness  $\approx 1 \mu\text{m}$ , temperature  $\approx 350^\circ \text{C}$ . The pressure differential for permeation tests was 345 kPa.

[0035] FIG. 13 is a scanning electron micrograph of membrane 6. Scalebar  $\approx 2.0 \mu\text{m}$ .

[0036] FIG. 14 is a scanning electron micrograph of membrane 7. Scalebar  $\approx 20.0 \mu\text{m}$ .

[0037] FIG. 15 is a table relating to Electroless Pd and Cu Plating Baths.

[0038] FIG. 16 is a table relating to Room Temperature Leak Testing of Pd—Cu Membranes.

[0039] FIG. 17 is a table relating to a summary of Pd—Cu Membrane Performances and Characterization.

[0040] FIG. 18 is a table relating to retail costs to make a 30 cm long section of 2  $\mu\text{m}$  thick Pd—Cu membrane supported on an asymmetric ceramic ultrafilter.

#### Detailed Description

[0041] The invention is directed, at least in part, to a process for fabricating a composite membrane comprised of a substrate and a Pd alloy film supported on the substrate. Before describing the process, some of the characteristics of

Pd alloys that render them preferable to pure or substantially pure Pd, at least in some applications, are described. To begin with, the critical temperature for existence of the  $\beta$  phase hydride is lower in Pd alloys than in pure or substantially pure Pd. This significantly reduces membrane rupture due to warping or cracking, a failure that affects pure or substantially pure Pd members in applications involving temperature cycling. Many Pd alloys are also more permeable to hydrogen than pure or substantially pure Pd, including PdAg<sub>23</sub>, (compositions in wt. %), PdCu<sub>40</sub>, PdY<sub>7</sub>, and PdRu<sub>7</sub>. Further, Pd alloys containing Au or Cu are more resistant to sulfur compounds than pure or substantially pure Pd. Ternary and higher alloys of Pd are capable of providing higher operating temperature capability relative to pure or substantially pure Pd.

[0042] The process for fabricating a Pd-alloy film on a tubular substrate is described for a PdCu<sub>40</sub> film. It should, however, be understood that the process is to PdRu, PdAu, PdAg, PdNi, and PdFe and, in particular, Pd<sub>93</sub>Ru, Pd<sub>95</sub>Au, Pd<sub>77</sub>Ag, Pd<sub>93</sub>Ni and PdFe<sub>7</sub>, which are the compositions that are at or near the maximum hydrogen flux point for the alloy. The process is also applicable PdOs, PdCo, PdRh, PdIr and PdPt membranes. Generally, the process is applicable to alloys of Pd and elements other than Pd in Groups VIII and IB.

[0043] The use of the PdCu<sub>40</sub> alloy has a number of desirable characteristics. Namely, the hydrogen permeability of PdCu<sub>40</sub> passes through a maximum around 40 wt. % Cu. The high percentage of Cu significantly reduces membrane cost relative to pure Pd. Additionally, the PdCu<sub>40</sub> alloy exhibits increased resistance to H<sub>2</sub>S. Further, a bcc alloy phase formed below 600° C. is believed to be responsible for an increased permeability of the PdCu<sub>40</sub> film compared to pure or substantially pure Pd. Like PdAg<sub>23</sub>, PdCu<sub>40</sub> can withstand repeated temperature cycling with less distortion than pure Pd since at 40 wt. % Cu, the critical temperature for  $\beta$ -hydride phase formation is below room temperature.

[0044] Initially, a substrate is provided. Suitable substrates are made of oxide ceramics (e.g., alumina, titania and zirconia), non-oxide ceramics (e.g., SiC and SiN), sintered or porous metals (e.g., stainless steel and nickel), and sintered or porous metals with ceramic surfaces. The process is described with respect to a tubular substrate. However, the process is applicable to substrates of any geometry, provided the surfaces that are to bear the Pd—Cu film are adequately exposed. Further, presently, good results have been obtained with asymmetric substrates with a pore size gradient the extends over a 20-50 nm pore size range. Substrates that are not asymmetric, have pores of a different size, or have a different pore size gradient are also feasible.

[0045] If needed, the provided substrate is subjected to a pre-processing step in which the substrate is subjected to one or more operations that are needed to place the substrate in condition for plating related operations and/or one or more operations that more readily accomplished prior to plating related operations. If the substrate that is provided is not clean or becomes dirty before a plating operation, the substrate must be cleaned to remove any salts or other materials that could interfere with the subsequent plating processes. Typically, cleaning is carried out with isopropanol and deionized water but other cleaning procedures that remove the undesirable material or materials are also feasible.



[0046] Further, if the substrate that is provided does not have the appropriate dimensions, appropriate sizing operations are undertaken. Typically, this involves cutting the substrate but other form or shape altering methods are also feasible. It is also feasible to perform sizing operations at a different point in the process.

[0047] In addition, the surfaces of the substrate through which it is undesirable to have  $H_2$  flow when the finished membrane is in use are sealed. Typically, a low temperature glaze (e.g., potter's glaze) is utilized because many substrates are subject to damage if exposed to high temperatures. For example, if the U.S. Filter T1-70 5nm filter, an asymmetric ceramic filter, is exposed to temperatures above  $600^\circ\text{C}$ ., the thin top layer of the filter is subject to damage. Regardless of the sealant utilized, the sealant is either painted onto the surface to be sealed or the surface is dipped in sealant. Other methods, such as spraying, are also feasible. In the described embodiment, the ends of the tubular substrate are each dipped into the sealant. With the ends sealed and assuming that the Pd alloy film is going to be applied to the inner wall of the substrate,  $H_2$  and other materials that are in a stream that is passing through the tubular substrate are constrained to traveling through the Pd alloy film on the inner wall and then from the inner wall of the substrate to the outer wall of the substrate, which leads, in many applications, to some kind of collection manifold. Because of the sealant, the  $H_2$  and other materials are prevented from exiting the substrate via the end walls, which do not, in many applications, lead to a collection manifold. It is also feasible to performing sealing operations at a different point in the process. For instance, in the case of a metal substrate, sealing by brazing, silver soldering or welding are feasible at any point in the process.

[0048] After pre-processing of the substrate, the surface of the substrate where the Pd—Cu film is to be deposited is “seeded” with Pd crystallites. This process can be performed using a variety of methods including impregnation with an organic solution of Pd acetate or Pd acetylacetonate. In one embodiment, the substrate is dip-coated for 3 minutes in a 0.05-0.2 M solution of Pd acetate in chloroform, dried, calcined at  $400^\circ\text{C}$ . and hydrotreated at  $450^\circ\text{C}$ . for 2 hours, followed by cooling under hydrogen. This particular embodiment is described in greater detail in a paper entitled, “A New Preparation Technique for Pd/Alumina Membranes with Enhanced High-Temperature Stability,” Industrial & Chemical Engineering Research, 1999, 38, 1925-1936, which is incorporated herein by reference. Other Pd solutions can be applied to the substrate to “seed” the surface of the substrate. Further, following the application of whatever Pd solution is utilized, other processing steps and/or different sequences of steps are feasible for “seeding” the surface of the substrate on which the PdCu alloy film is to be deposited. Further, other methods, such as ion exchange are feasible for seeding the substrate. Regardless of the method employed, good adhesion of the “seeds” to the substrate is achieved by employing “seeds” that are smaller than the grains on the surface of the substrate that is being plated.

[0049] In the case of a metal substrate, the seeding of the surface with Pd crystallites is accomplished using an organic Pd solution in which the solvent is a light, polar, oxygenated organic solvent, such as tetrahydrofuran (THF), ethyl acetate, acetonitrile, diethyl ether, methyl ethyl keton (MEK), or acetone.

[0050] After the portion of the surface that is to bear the PdCu film has been seeded, Pd film is deposited on the surface of the portion of the substrate that is to bear the PdCu film. In one embodiment, the Pd film is deposited using a flow system with an osmotic pressure gradient. A more detailed description of this plating procedure is in the paper entitled “Preparation and Characterization of Pd—Cu composite Membranes for Hydrogen Separation,” substantially incorporated herein as an appendix. Other electroless plating systems, such as batch plating and vacuum pump plating, are also feasible. Further, electro-plating is also feasible.

[0051] After the portion of the substrate that is to bear the PdCu film has been plated with Pd, the portion of the substrate is plated with Cu. The Cu is plated onto the substrate using an electroless method, such as a dip or flow method. It is also feasible to use an osmotic plating method. Maximum hydrogen flux is achieved when the alloy is at or about 40 wt. % Cu. Given the densities of Pd and Cu, which are respectively about  $12\text{ g/cm}^3$  and  $9\text{ g/cm}^3$ , an approximately 40 wt. % Cu alloy is achieved with layers of Pd and Cu that are approximately equal in thickness. One way to achieve Pd and Cu layers of approximately equal thickness is by performing the Pd and Cu plating operations under substantially the same thermodynamic conditions and for appropriate periods of time. It is also possible to perform the plating operations under different thermodynamic conditions and/or over different periods of time and achieve layers of substantially equal thickness. The maximum hydrogen flux for other Pd alloys is achieved with different weight percentages of constituents. Consequently, the conditions under which weight percentages are achieved that are at or near the weight percentages for maximum hydrogen flux are typically different than those for the PdCu alloy.

[0052] After the Pd and Cu have been plated onto the substrate, the structure is subjected to an annealing operation that is sufficient to achieve at least some intermetallic diffusion of the Cu layer into the Pd layer. In one embodiment, annealing is accomplished by slowly heating up the structure to at least  $350^\circ\text{C}$ . but less than  $600^\circ\text{C}$ . in inert gas atmosphere, such as He, Ar, or  $N_2$ , over a period of 12 hours and then switching the atmosphere to  $H_2$ . The annealing step permits intermetallic diffusion of the Cu layer into the Pd layer forming the alloy. Pd and Cu are miscible over the entire composition range. Annealing progress can be observed by measurement of the  $H_2$  flux. When the flux reaches a steady-state value, the annealing process is complete. For thin,  $1\text{ }\mu\text{m}$  films, this process will require about 24 hours at the lowest temperature.

[0053] At this point, the PdCu composite membrane is complete and useable in hydrogen separation applications that involve stream of hydrocarbons that include sulfur or sulfur compounds. Moreover, the PdCu film is  $1\text{ }\mu\text{m}$  or less in thickness. Hydrogen flux data are shown in FIG. 2, for a nominal  $3\text{ }\mu\text{m Pd}_{60}\text{Cu}_{40}$  composite membrane. From FIG. 1, one obtains an  $H_2$  flux of  $240\text{ ml/cm}^2\text{ min}$ . expected for a feed pressure of 100 psig. The data points in FIG. 2 are at a temperature of  $350^\circ\text{C}$ .

[0054] A further step has been found to increase the hydrogen flux of the membrane. Namely, the composite membrane is subjected to air oxidation and reduction to activate the metal surface. This step is believed to “roughen” the surface of the film, and thereby increase the surface area



of the film. The increased surface area is believed to provide the greater hydrogen flux. The increased surface is believed to be responsible for the greater hydrogen flux. In one embodiment, a short duration (5 to 30 minutes) air oxidation at temperatures above 350° C. followed by exposure to H<sub>2</sub> and subsequent reduction. With reference to **FIG. 3**, an “air purge” at 3.5 days caused a sharp increase in hydrogen flux from 0.81 mol/m<sup>2</sup> s to 1.32 mol/m<sup>2</sup> s. The flux decreased to a new steady-state value of 1.07 mol/m<sup>2</sup> s, 32% higher than the flux before the air purge treatment. Rather than air reduction and oxidation, the composite membrane can be subjected to O<sub>2</sub>, O<sub>3</sub>, acids, steam, SO<sub>2</sub>, or a combination of H<sub>2</sub>S/steam to disturb the surface of the palladium alloy film.

**[0055]** Typical applications are high temperature hydrogen separations, fuel cell power systems, hydrogen fueling stations, hydrocarbon reforming, and use in membrane reactors, devices that can simultaneously form a product and separate the reaction products. For example, in the case of a fuel cell, the membrane is part of the fuel processor reformer. In membrane reactors, the membrane forms at least a wall of the reactor. In the case of a hydrogen fueling station, the membrane is part of the fuel processor or reformer.

#### **[0056]** Appendix

**[0057]** Pd—Cu composite membranes were made by successive electroless deposition of Pd and then Cu onto various tubular porous ceramic supports. Ceramic filters used as supports included symmetric  $\alpha$ -alumina (nominal 200 nm in pore size), asymmetric zirconia on  $\alpha$ -alumina (nominal 50 nm pore size), and asymmetric  $\gamma$ -alumina on  $\alpha$ -alumina (nominal 5 nm pore size). The resulting metal/ceramic composite membranes were heat-treated between 350° C. and 700° C. for times ranging from 6 to 25 days to induce intermetallic diffusion and obtain homogeneous metal films. Pure gas permeability tests were conducted using hydrogen and nitrogen. For a 11  $\mu$ m thick, 10 wt. % Cu film on a nominal 50 nm pore size asymmetric ultrafilter with zirconia top layer, the flux at 450° C. and 345 kPa H<sub>2</sub> feed pressure was 0.8 mol/m<sup>2</sup> s. The ideal hydrogen/nitrogen separation factor was 1150 at the same conditions. The thickness of the metallic film was progressively decreased from 28  $\mu$ m down to 1-2  $\mu$ m and the alloy concentration was increased to 30 wt. % Cu.

**[0058]** Structural factors related to the ceramic support and the metallic film chemical composition are shown to be responsible for the differences in membrane performance. Among the former are the support pore size, which controls the required metal film thickness to insure a leak free membrane and the internal structure of the support (symmetric or asymmetric) which changes the mass transfer resistance. The support with the 200 nm pores required more Pd to plug the pores than the asymmetric membranes with smaller pore sizes, as was expected. However, leak free films could not be deposited on the support with the smallest pore size (5 nm  $\gamma$ -alumina), presumably due to surface defects and/or a lack of adhesion between the metal film and the membrane surface.

#### **[0059]** Introduction

**[0060]** The hydrogen separating capability of Pd alloy membranes is well known. Applications include hydrogenation and dehydrogenation reactions [1] and recovery of

hydrogen from petrochemical plant streams [2]. Recently there has been interest in utilization of Pd membranes to separate hydrogen produced in hydrocarbon reforming and coal gasification for power generation in fuel cells. Such applications have the potential to reduce energy consumption, capital costs or the number of unit operations compared to conventional systems. To consume less Pd, thin films or foils of Pd on the order of microns in thickness are applied to porous substrates for mechanical strength. Porous glass, ceramic, stainless steel, and polymers are common supports [3]. Hydrogen permeable metals such as tantalum (Ta) with a Pd coating also function as effective hydrogen separators [2, 4].

**[0061]** Some very thin, permeable and permselective Pd composite membranes have been prepared by various research groups, although several hurdles inhibit commercial implementation of Pd membrane technology [5-7]. These problems include embrittlement and cracking due to the  $\alpha \rightarrow \beta$  Pd hydride phase transition, which occurs during temperature cycling [8] and poisoning or fouling due to the presence of sulfur or unsaturated carbon compounds in the operating stream [9-11]. Also, in order to be accepted by industry, membranes must have a lifecycle on the order of years under process conditions [12].

**[0062]** Alloys of Pd possess properties that may alleviate some of the shortcomings of pure Pd [13]. To begin with, the critical temperature for existence of the  $\beta$  phase hydride is lowered in alloys. This helps eliminate membrane rupture due to warping or cracking, a failure associated with temperature cycling. Many alloys are also more permeable to hydrogen than pure Pd including PdAg<sub>23</sub> [14] (compositions in wt. %), PdCu<sub>40</sub> [15], PdY<sub>7</sub> [16, 17] and PdRu<sub>7</sub> [18]. Alloys containing Au or Cu are more resistant to sulfur compounds [19, 20]. Ternary and higher alloys of Pd have been developed to impart high temperature operating capability [21].

**[0063]** The hydrogen permeability of Pd—Cu passes through a maximum around 40 wt. % Cu significantly reducing membrane cost (relative to pure Pd), and this alloy exhibits increased resistance to H<sub>2</sub>S [19, 22-27]. Additionally, a bcc alloy phase formed below 600° C. is credited with the increased permeability compared to pure Pd [26, 28, 29]. Like PdAg<sub>23</sub>, PdCu<sub>40</sub> can withstand repeated temperature cycling with less distortion than pure Pd since at 40 wt. % Cu, the critical temperature for  $\beta$ -hydride phase formation is below room temperature [15, 30-32].

**[0064]** Preparation of Pd alloys has been accomplished in the past by casting and rolling or induction melting followed by cold working into a foil or tube [33-35]. Composite Pd alloy membranes have been fabricated by sputtering, CVD, electroplating, and electroless plating. Much recent work has involved the use of electroless plating to make Pd—Ag [36-39], Pd—Ni [40] and Pd—Au alloy membranes [41].

**[0065]** Pd—Ag alloy films have been fabricated by several research groups using sequential metal deposition followed by annealing [39, 42, 43]. To obtain a homogeneous alloy film from two distinct metal layers in a reasonable amount of time, a high enough temperature must be utilized to promote complete intermetallic diffusion [38]. Shu et al. annealed a codeposited Pd—Ag film for 150 minutes at 400° C. and a sequentially deposited Pd—Ag film for 5 hours at 700° C. [37], while Kikuchi annealed a sequentially depos-



ited Pd—Cu film between 300 and 540° C. [39]. Kikuchi and Uemiya deposited Pd—Ag alloy films by sequential electroless plating, followed by heat treatment at temperatures of 800-1300° C. [44]. Uemiya et al. found that Pd—Ag films deposited by sequential electroless deposition require high temperatures (>800° C.) to produce a homogeneous film [38]. Sakai et al., and Kawae et al. annealed Pd—Ag at 900° C. for 2, and 12 hours respectively [43, 45].

[0066] Lin and coworkers have deposited Pd—Ag films onto asymmetric  $\gamma$ -alumina supports (3 nm pores) using magnetron sputtering [46-48]. A membrane with a 177 nm PdAg<sub>18</sub> film exhibited hydrogen/helium perm-selectivity of 3845 at 300° C. [48]. An observation they made was that the beginning surface roughness of the support was a critical parameter in obtaining a defect free and adherent membrane [46].

[0067] Deposition under an osmotic pressure gradient by conducting electroless plating with a more concentrated solution on the opposite side of the porous support has been found to produce thinner Pd films that are more impenetrable to permeation of gases other than hydrogen [49, 50]. Several desirable features of applying this technique to the manufacture of the Pd/Cu membranes include smaller grain-size, reduction in porosity, surface homogeneity and densification of the plated film.

[0068] Most Pd—Cu alloy membrane work has been carried out using foils [15, 17, 26, 51]. Apparently, the only group to previously fabricate Pd—Cu alloy films on porous supports by electroless deposition of Pd and then Cu with subsequent annealing (500° C. for 12 hours) was Kikuchi and coworkers [38, 39]. The objective of the present work was to fabricate a thin and hydrogen selective Pd—Cu composite membrane in a similar fashion while reducing the thickness of the metal film. Three different types of tubular, porous ceramic membranes with progressively smaller pore sizes were used as supports for the thin Pd—Cu films. The effect of film thickness and composition on annealing conditions and hydrogen permeability was also investigated.

## [0069] EXPERIMENTAL SECTION

### [0070] Support Specifications

[0071] Tubular, porous alumina microfilters with nominal 0.2  $\mu$ m pore size, were procured from Golden Technologies Company (GTC, Golden, Colo. now Coors Tech Oak Ridge, Oak Ridge, Tenn.). Designated GTC998, these tubes have an OD of 9 mm, an ID of 6.1 mm, and are fabricated from 99.8% pure  $\alpha$ -alumina. FIG. 4 is a Scanning Electron Microscope (SEM) image of the GTC998 cross section. Asymmetric ceramic membranes consisting of a sol-gel zirconia selective layer on top of several porous support layers composed of  $\alpha$ -alumina particles were also used. The other asymmetric membranes used in this work had nominal 5 nm pore size with a  $\gamma$ -alumina selective layer coated on top of the two layers with pore sizes of 0.4 and 0.2  $\mu$ m ( $\alpha$ -alumina) on the same type of macroporous support. A scanning electron micrograph of the cross-section of a typical asymmetric alumina membrane is shown in FIG. 5.

### [0072] Substrate Preparation

[0073] The detailed procedure for substrate preparation has been given elsewhere [52, 53]. Selected support tubes were cut to length with a diamond saw, sequentially cleaned

and rinsed ultrasonically in solutions of Alconox detergent, acetic acid, hot water, and 2-propanol [52]. After cleaning, the ends of the ceramic tubes were sealed with a high temperature glaze.

### [0074] Surface Activation

[0075] The surface activation step has been described in detail by Paglieri et al. [53]. Briefly, the support tube was dip-coated for 3 minutes in a 0.05-0.2 M solution of Pd acetate in chloroform, dried, calcined at 400° C. and hydrotreated at 450° C. for 2 h, followed by cooling under hydrogen.

### [0076] Metal Film Deposition

[0077] The plating methodology to produce a Pd—Cu alloy film has been described in detail by Paglieri [54]. In summary, the preparation of a Pd—Cu alloy membrane film can be divided into two distinct steps, electroless plating of Pd and Cu followed by high temperature annealing in flowing H<sub>2</sub>. First, layers of Pd and Cu were sequentially deposited by electroless plating on activated porous substrates. The plating time and gravimetric analysis were used to approximately determine the final alloy composition. The electroless palladium and copper plating bath recipes are reported in FIG. 15. It was found that electroless plating of Cu onto a Pd/alumina composite membrane was necessary because otherwise the electroless Pd solution replaced Cu by displacement plating. The plating bath temperature was controlled to 65 $\pm$ 5° C. in a water bath. Plating cycle time was adjusted to achieve the desired Pd-layer thickness. After plating, the membranes were rinsed, soaked for several hours to overnight in 70° C. water (to remove plating solution and other impurities), rinsed, dried in air at 80° C., and weighed. The Pd film thickness was estimated by dividing the weight difference between the plated and unplated membrane by the plated surface area and density of Pd (11.96 g/cm<sup>3</sup>). Scanning electron microscopy was also used to determine film thickness following permeation measurements. Finally, the composite membrane was annealed above 350° C. in hydrogen to form a homogeneous alloy.

### [0078] High Temperature Testing Procedures

[0079] Gas permeation experiments began with a room temperature leak test conducted with nitrogen, followed by high temperature gas permeation experiments conducted with hydrogen and nitrogen. The room temperature leak test was conducted in the following manner: the membranes were sealed into stainless steel compression fittings with graphite ferrules, the lumen was pressurized with nitrogen at 896 kPa and submerged in an alcohol/water mixture. The time for the pressure to drop to 827 kPa was measured and an unsteady state mass balance was solved to yield the room temperature nitrogen flux through the membrane:

$$J_{N_2} = \frac{D_m x_{Pd-Cu}}{4RTt} \ln \left[ \frac{P_1 - P_0}{P_2 - P_0} \right] \quad (1)$$

[0080] Where  $J_{N_2}$  is the nitrogen leak flux,  $D_m$  is the internal tube diameter,  $x_{Pd-Cu}$  is the thickness of the metal film,  $R$  the universal gas constant,  $T$  the temperature,  $P_1$  the initial pressure,  $P_2$  the final pressure,  $P_0$  the atmospheric pressure and  $t$  the time for the pressure to drop from  $P_1$  to  $P_2$ . Calculated N<sub>2</sub> fluxes are reported in FIG. 16.



[0081] Following the leak test, permeation tests were performed at high temperature. The membrane was loaded into a stainless steel shell and centered in a tube furnace. The permeation module design is described in detail in a prior publication [52]. Single gas permeability tests were conducted at transmembrane pressure differentials of either 345 kPa or 690 kPa using either hydrogen or nitrogen up to 650° C. Brooks mass flow controllers metered gas flow or it was controlled manually with a needle valve. All gases were nominally 99.999% pure (UHP grade) and were used without further purification. Permeate pressure (shell side) was local atmospheric pressure (−83 kPa). No sweep gas was used on the permeate side during the single-gas permeation experiments. Gas flow rates were measured using bubble flowmeters. These values were converted to STP and pure gas fluxes were calculated. The sweep side was purged with helium after testing with hydrogen, otherwise back-permeation of hydrogen to the tube side through the membrane resulted in a negative flux for a period of time.

[0082] The membrane was heated (and cooled) at 1° C./min. under helium purge. To avoid embrittlement of the pure Pd films hydrogen was not introduced until 350° C., well above the critical temperature for the  $\alpha \rightarrow \beta$  phase transition [13] for pure Pd. In some instances, while conducting the permeability tests, the membranes were exposed to flowing air at 275 kPa for 30 minutes. This procedure seems to enhance the hydrogen permeation through rearrangement of the metal surface [55].

[0083] Upon completion of high temperature permeability tests, the membrane was cooled at 1° C./min. under inert gas. Final measurements of inert gas flux through the membrane were then made at room temperature. After removal of the membrane from the permeation apparatus, it was visually inspected to determine if leaks originated from the membrane or the fittings by performing another ambient temperature leak test under isopropanol/water.

#### [0084] Membrane Characterization

[0085] The tested membranes were frozen in liquid nitrogen and then fractured into small pieces, acceptable for instrumental analysis. Scanning electron microscopy (SEM-JOEL 840) was used to study film morphology and estimate Pd film thickness. Specimens were prepared by attaching pieces of broken membrane to metal buttons with carbon paint or tape. The samples were coated with gold (thickness of gold coating −500 pm) to make them more conductive. Then the film morphology was observed by scanning over large portions of the film surface and cross-section at both low and high magnifications. Metal film thicknesses were obtained by averaging measurements made from several micrographs taken at different locations perpendicular to the cross section.

[0086] Pd—Cu alloy structure and domain orientation were examined by X-ray diffraction (XRD-Rigaku RU-200). Metal films were first peeled off from the ceramic substrate and then mounted on glass slides using double-sided tape. Scanning was typically conducted over the angular range from 20 to 90° 2  $\theta$ . Energy-dispersive X-ray analysis (EDAX-Noran 5500) was used for elemental analysis. Samples were prepared the same as those for SEM but coated with carbon instead of gold for elemental analysis.

## [0087] RESULTS AND DISCUSSION

### [0088] Annealing

[0089] The objective of this part of the work was to prove that alloys of Pd and Cu could be prepared in-situ by heating successively electrolessly deposited layers of each metal. The literature provides wide support to this hypothesis [27, 38, 39]. From the Pd—Cu phase diagram, Pd and Cu are miscible over the entire range of compositions, so their intermixing should take place with relative ease [56].

[0090] Small pieces of GTC Pd/Cu Membrane were heated to 600° C. for 12 hours under helium and analyzed afterwards with XRD to determine if a homogeneous film was created. The XRD analysis of the metal films (FIG. 6) demonstrated that an alloy membrane was formed upon heat treatment at 600° C. in comparison to the unheated sample. Small amounts of non-annealed copper are still observed; however, additional annealing is accomplished during H<sub>2</sub> permeation testing. EDAX analysis of membranes after testing has always shown uniform Cu and Pd concentration profiles as shown in FIGS. 9b and 11b below. Those results demonstrated the potential for Pd—Cu membranes to be prepared by sequential electroless deposition followed by “in-situ” annealing at high temperature. Subsequent membranes were all heat-treated while carrying out the hydrogen transport measurements at the same time.

### [0091] Influence of Supports

[0092] Two important structural factors were considered in selecting the supports: pore size and symmetry. Their influence on the membrane performance is fundamental in establishing an understanding of how the support affects membrane fabrication and performance. These include the minimum thickness of a leak free metal film and the overall mass transfer resistance. Regarding the former, our conjecture was that a support having a smoother surface (small pore size) would require a thinner film of metal to be leak free. For the second, our proposition was that asymmetric supports when combined with the metal film should present less resistance to the hydrogen flux than symmetric tubes.

[0093] In order to address these hypotheses, different types of supports with varied structural features were used to make the Pd—Cu composite membranes, which were later annealed and tested according to the procedure described before. FIG. 17 presents the high temperature gas permeation results for all the membranes tested.

### [0094] Symmetric Supports

[0095] Initial experiments were performed using symmetric  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> tubes, 200 nm in pore size. Early trials using these supports suggested that palladium deposition alone was sufficient to plug the pores. For instance, when a leaking Pd-coated tube was plated with copper, it routinely continued leaking. In general, palladium plating times of several hours were required for these symmetric tubes before leak-free membranes were obtained. Consequently, thicker layers of metal were deposited in comparison with the asymmetric tubes as shown in FIG. 16. This behavior indicates that the pore size basically controls how thick the metal film has to be to guarantee a low leakage rate.

[0096] FIG. 7 presents the high temperature permeation test results for membrane 1. With a thickness close to 30  $\mu$ m, this membrane produced a maximum ideal separation factor



H<sub>2</sub>/N<sub>2</sub> of 14 and a hydrogen flux of roughly 0.05 mol/m<sup>2</sup> s. An XRD analysis on that membrane revealed the formation of a Pd—Cu alloy containing 24 wt. % copper [54].

[0097] Using the same kind of support, three more membranes were fabricated reducing the palladium plating time to determine the minimum metal film thickness required. In FIG. 17, details for membranes 2, 3 and 4 are presented. Membrane 3 was chosen as most representative for those three. FIG. 8 represents the high temperature permeation test for this membrane; FIG. 9 shows a detailed SEM section of the metal layer upon which EDAX elemental analysis was carried out.

[0098] Clearly, improvements in the separation factor and the hydrogen flux through the membrane were achieved. As seen in FIG. 17, an average separation factor of 170 and a H<sub>2</sub> flux of over 8 an a half times that for membrane 1 were obtained using just one third of the thickness in the latter. The EDAX concentration plot indicates the presence of copper throughout the palladium film but at slightly higher concentration close to the gas-metal interface. Similar EDAX patterns were obtained for membranes 2 and 4, proving that alloying 'in situ' had worked as proposed and the Cu composition profile was essentially uniform.

[0099] The increase in the separation factor can be attributed to the fine tuning of plating parameters including bath temperature, flow rates and overall hydrodynamics of the plating set up. These allowed more stable and homogeneous plating, which in turn created a more impervious film. On the other hand, smaller metal film thicknesses, a result of less plating time, were the cause of higher hydrogen fluxes since the metal layer provides the major mass transfer resistance [7, 57]. However, an acceptably low nitrogen leakage rate could not be obtained for any of these membranes if the thickness was less than about 11 microns. As pointed out before, to further decrease the thickness of the metal film, a support having smaller pore size in the top layer (less surface roughness) had to be used.

#### [0100] Asymmetric Supports

[0101] Membranes 5 and 6 were made using an asymmetric support, whose selective porous top layer was 50 nm in pore size. We hypothesized that the thickness of metal layer needed to make a leak free membrane on these supports should be greatly diminished. In general, this strategy was confirmed and successful in achieving better membrane performance as seen in FIG. 17.

[0102] Membrane 5, in particular, exhibited very high separation factor and hydrogen flux in spite of having about the same thickness as membranes 3 and 4. FIG. 10 shows the high temperature permeation experiments and FIG. 11 the membrane's EDAX quantitative elemental analysis with respective SEM detail. A very homogeneous Pd—Cu film can be observed, containing about 10%Cu.

[0103] The improved performance of membrane 5 relative to membrane 3 could be due to the change in support structure or the difference in Cu composition of the metal film. The support structure changes include both a reduction in particle size cut-off (0.2  $\mu$ m to 0.05  $\mu$ m) and the use of an asymmetric support having lower resistance to flow. Both the support internal structure and the top layer pore size play fundamental roles in the membrane performance.

[0104] The asymmetric supports concentrate the mass transfer resistance in the top selective layer upon which the metal layer is deposited. This selective layer is very thin (less than 1% of the total wall thickness) as can be observed in FIG. 5. The inner layers are formed of increasingly larger particles of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> that offer small resistance to the flow. In contrast, the symmetric tubes used exhibit the same pore size all the way across the wall thickness. This type of support should present a considerably higher resistance to flow than asymmetric supports do as a consequence of that configuration. Thus, if a similar thickness of metal is deposited, greater fluxes can be achieved with the asymmetric support.

[0105] Regarding the large difference in separation factor, it is important to note the sizable differences in support pore size shown in FIG. 16. The asymmetric support used for membranes 5 and 6 had a pore size of 50 nm while the analogous value for the symmetric tubes used for membranes 1 through 4 is 200 nm. The pore size is clearly related to surface roughness; a surface having small pores is smoother as a whole than another bearing large pores. On the smoother support a more continuous metal film with fewer defects through which N<sub>2</sub> can diffuse is likely to result.

[0106] The above reasoning provides support for the hypothesis that a thinner film is required to make a leak free membrane when a support with small pores is used. This is because it is relatively easier to cap small pores by plugging them with metal. Visible evidence that this occurs was observed in the SEM micrographs of membrane 5 as shown in FIG. 11. The metal penetrated into the pores of the support, filling them and then growing into a continuous thick layer of metal. This layer thickness appears to be more than adequate to produce a continuous film, suggesting that the thickness can be reduced even further. The next step was then to reduce the amount of metal deposited to verify this hypothesis.

[0107] Membrane 6 was made using the same asymmetric support used in membrane 5, but the total metal film thickness was only 1.5 microns. FIG. 12 shows the high temperature permeation behavior of this membrane and FIG. 13 is an SEM image of the metal layer. In observing the latter it is important to highlight that even though the metal film was very thin in comparison with what has been reported in the literature to date, it appears that a continuous film could be obtained with an even thinner film. However, the transport chart (FIG. 17 and FIG. 12) indicated an ideal H<sub>2</sub>/N<sub>2</sub> separation was measured that was below the value for membrane 5. Still, membrane 5 compared well against all of the symmetric supported membranes in terms of both flux and separation factor. An EDAX for this membrane showed a homogeneous composition of 30 wt. % Cu.

[0108] A reasonable explanation for the lower separation factor can be found comparing the room temperature leak test results for membranes 5 and 6. According to the data in FIG. 16, the leakage rate for membrane 5 was almost twice that for membrane 6 at room temperature. At high temperature however, membrane 6 leaked 18 times more nitrogen than did number 5 as inferred from the data in FIG. 17. Evidently, the thin metal film was enough to prevent leaking at low temperature but when heated the metal crystallites may have sintered or otherwise rearranged, opening slightly covered pores in the ceramic support.



[0109] Membrane 7 was prepared on an even smoother asymmetric support having an  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> top layer, 5 nm in pore size. Several of these tubes were plated under the conditions outlined before, yet it was impossible to produce a leak free membrane, even at thickness as high as 10 microns. As Lin and coworkers [46-48] have found, initial surface roughness is a critical factor for producing leak-free membranes. The supports used present large particles and other imperfections on the surface which the metal films could not cover up, as shown in FIG. 14. Also, we suspect the pores on this support to be so small as to not provide the "interlocking" required for the electrolessly deposited metal film to adhere strongly to the ceramic wall. Future work will include supports with an intermediate pore size between 5 and 50 nm that may exhibit sufficient surface roughness to provide adhesion between the support and the Pd—Cu film.

#### [0110] Economics

[0111] The driving force towards thinner palladium-copper layers is twofold in nature. First, from a mass transport standpoint, thin metal films present less resistance to the flow, giving higher flux as a result, therefore enhancing productivity. Second, less palladium is needed to produce the same amount of hydrogen per unit length. This last point is also addressed with the alloying of palladium with inexpensive copper. Both of these factors contribute enormously to the overall economics of the membrane manufacture. Employing supports with small pore size reduces the amount of expensive material needed to fabricate very selective leak-free membranes. Also, the use of asymmetric supports should reduce the overall mass transfer resistance, allowing more permeate production per unit area per unit time.

[0112] For better illustrating an application of these membranes, the following information, collected for design purposes, could be considered [58, 59]. Several manufacturers are proposing to produce fuel cell power systems to produce 1 kW of electricity for residential use in Japan [59]. Production of 1 kW of electricity would require approximately 10 standard liters per minute (SLPM) of high purity hydrogen. Using membrane 5 as an example, 1.5 SLPM were produced using 5 cm of active length. Consequently, if the same type of Pd—Cu composite membrane were to be used, 30 cm of 1 cm OD membrane would be needed. The material costs to make the membrane are summarized in FIG. 18.

[0113] The bulk of the retail costs are associated with the support and not with the Pd film. A further decrease in the thickness would allow higher flux and would significantly lower the area requirements and length of support tubing needed. Several economical analyses have been carried out recently [60, 61] indicating that the high cost of metal membrane devices for hydrogen separation is due mainly to palladium. Future economic analyses of this nature may need to consider the fabrication of micron-thick Pd films, which would significantly reduce the sensitivity of the economics to the cost of the Pd metal.

#### [0114] Conclusions

[0115] The objective of this work was to make ceramic-supported Pd—Cu metal membranes for high temperature hydrogen separation. It was shown that the deposition of Pd and Cu using electroless plating followed by annealing to alloy the metals is a viable way of forming a thin homogeneous defect free metal film capable to selectively separate hydrogen at temperatures between 350° C. and 700° C.

[0116] Controlling the deposition time during the sequential electroless plating was found to be important to tailor the thickness and composition of the film. EDAX and XRD were used to analyze the alloy composition and the metal distribution throughout the metal film.

[0117] Two support structural factors were found to have an important impact on the overall performance of the membrane. The top layer pore size determines the minimum value the metal film thickness must be in order to prevent leaking and inert gas slippage. The larger the pore size the thicker the metal layer has to be to insure an impervious membrane. However, there is a limit in how small the film can be. Although our synthetic procedures were successful for 200 nm and 50 nm substrates, we were unable to deposit a free leak film on the 5 nm cut-off  $\gamma$ -alumina support.

[0118] The other important factor is the internal structure of the ceramic support. An asymmetric support, made of increasingly coarser layers, presents lower resistance to the flow, therefore yielding a higher hydrogen flux if compared with a symmetric one. The latter is homogeneous all the way across its thickness.

[0119] Using the electroless plating technique it was possible to produce a palladium/copper composite membrane with average metal film thickness as small as 1.5  $\mu$ m. The hydrogen flux of an 11  $\mu$ m thick Pd—Cu film was 0.8 mol/m<sup>2</sup> s at 450° C. with a hydrogen/nitrogen ideal separation factor of 1150 at a  $\Delta$  P of 345 kPa.

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1. A method for making a palladium alloy composite membrane comprising:
- providing a porous substrate with a support surface for supporting a palladium alloy film, wherein said porous



substrate has a pore size adjacent to said support surface of less than about 200 nm;

seeding said support surface with palladium crystallites to produce an activated surface;

first plating, over said activated surface, a palladium film;

second plating, over said palladium film, an alloying material other than silver; and

annealing said porous substrate, palladium film, and alloying material so that there is intermetallic diffusion of said alloying material into said palladium film to produce a palladium alloy film over said porous substrate.

**2.** A method, as claimed in claim 1, wherein:

said pore size is less than about 100 nm.

**3.** A method, as claimed in claim 1, wherein:

said pore size is less than about 50 nm.

**4.** A method, as claimed in claim 1, wherein:

said pore size is less than about 20 nm.

**5.** A method, as claimed in claim 1, wherein:

said pore size is greater than about 5 nm.

**6.** A method, as claimed in claim 1, wherein:

said substrate comprises an asymmetric porous substrate with a pore size gradient.

**7.** A method, as claimed in claim 1, wherein:

said step of first plating having a duration that is chosen based on said pore size and a desired palladium alloy film thickness.

**8.** A method, as claimed in claim 1, wherein:

said step of second plating having a duration that is chosen based on said pore size and a desired palladium alloy film thickness.

**9.** A method, as claimed in claim 1, wherein:

said steps of first plating and second plating are performed so as to produce a desired weight percentage for at least one of said palladium and said alloying material.

**10.** A method, as claimed in claim 9, wherein:

said desired weight percentage is chosen based on a desired hydrogen flux for said palladium alloy film.

**11.** A method, as claimed in claim 1, wherein:

said alloying material is copper; and

said steps of first plating and second plating are performed so that said palladium alloy film is about 40% by weight copper.

**12.** A method, as claimed in claim 1, further comprising:

subjecting, after said step of annealing, said porous substrate and said palladium alloy film to an oxidation and reduction.

**13.** A method for making a palladium alloy composite membrane comprising:

providing a porous substrate with a support surface for supporting a palladium alloy film, wherein said porous substrate has a pore size adjacent to said support surface;

seeding said support surface with palladium crystallites to produce an activated surface;

first plating, over said activated surface, a palladium film;

second plating, over said palladium film, an alloying material other than silver; and

annealing said porous substrate, palladium film, and alloying material so that there is intermetallic diffusion of said alloying material and said palladium film to produce a palladium alloy film over said porous substrate;

wherein said pore size is determinative of a minimum thickness for said palladium alloy film that is substantially free of leaks;

wherein said steps of first plating, second plating and annealing are performed so as to produce a palladium alloy film with a film thickness that is equal or greater than said minimum thickness.

**14.** A method, as claimed in claim 13, wherein:

said palladium alloy film thickness is less than about 10 microns.

**15.** A method, as claimed in claim 13, wherein:

said palladium alloy film thickness is less than about 5 microns.

**16.** A method, as claimed in claim 13, wherein:

said palladium alloy film thickness is less than about 2 microns.

**17.** A method, as claimed in claim 13, wherein:

said palladium alloy film thickness equal to or less than about 1 micron.

**18.** A method, as claimed in claim 13, wherein:

said steps of first plating and second plating are performed so as to produce a desired weight percentage for at least one of said palladium and said alloying material.

**19.** A method, as claimed in claim 18, wherein:

said desired weight percentage is chosen based on a desired hydrogen flux for said palladium alloy film.

**20.** A method, as claimed in claim 13, further comprising:

subjecting, after said step of annealing, said porous substrate and said palladium alloy film to an oxidation and reduction.

**21.** A method, as claimed in claim 13, wherein:

said step of providing comprises providing an oxide ceramic substrate.

**22.** A method, as claimed in claim 13, wherein:

said step of providing comprises providing a non-oxide ceramic substrate.

**23.** A method, as claimed in claim 13, wherein:

said step of providing comprises providing a sintered/porous metal substrate.

**24.** A method, as claimed in claim 13, wherein:

said step of providing comprises providing a multi-layer substrate with a sintered/porous metal layer and a ceramic layer, wherein said support layer comprises said ceramic layer.

**25.** A method, as claimed in claim 13, wherein:

said step of providing comprises providing an asymmetric porous substrate with a pore size gradient.



**26.** A method, as claimed in claim 13, wherein:

said alloying material is selected from Groups VIII and IB.

**27.** A method for making a palladium alloy composite membrane comprising:

providing a porous substrate with a support surface for supporting a palladium alloy film;

seeding said support surface with palladium crystallites to produce an activated surface;

first plating, over said activated surface, a palladium film;

second plating, over said palladium film, an alloying material;

annealing said porous substrate, palladium film, and alloying material so that there is intermetallic diffusion of said alloying material and said palladium film to produce a palladium alloy film over said porous substrate; and

subjecting, after said step of annealing, said porous substrate and said palladium alloy film to an oxidation and reduction.

**28.** A method, as claimed in claim 27, wherein:

said step of providing comprises providing a porous substrate that has a pore size adjacent to said support surface of less than about 200 nm.

**29.** A method, as claimed in claim 27, wherein:

said step of providing comprises providing an asymmetric porous substrate with a pore size gradient.

**30.** A method, as claimed in claim 27, wherein:

said porous substrate has a pore size adjacent to said support surface and said pore size is determinative of a minimum thickness for said palladium alloy film that is substantially free of leaks; and

said steps of first plating, second plating and annealing are performed so as to produce a palladium alloy film with a film thickness that is equal to or greater than said minimum thickness.

**31.** A method, as claimed in claim 27, wherein:

said step of providing comprises cleaning said surface prior to said step of seeding.

**32.** A method, as claimed in claim 27, wherein:

said step of providing comprises shaping said porous substrate.

**33.** A method, as claimed in claim 27, wherein:

said step of providing comprises sealing a surface of said porous substrate other than said support surface.

**34.** A palladium alloy composite membrane comprising:

a porous substrate having a support surface; and

a palladium alloy film, other than a palladium-silver alloy film, bonded to said support surface of said porous substrate;

wherein said palladium alloy film has a thickness of less than about 10 microns.

**35.** A palladium alloy composite membrane, as claimed in claim 34, wherein:

said thickness is less than about 5 microns.

**36.** A palladium alloy composite membrane, as claimed in claim 34, wherein:

said thickness is less than about 2 microns.

**37.** A palladium alloy composite membrane, as claimed in claim 34, wherein:

said thickness is less than about 1.5 microns.

**38.** A palladium alloy composite membrane, as claimed in claim 34, wherein:

said porous substrate comprises an asymmetric porous substrate with a pore size gradient.

**39.** A palladium alloy composite membrane, as claimed in claim 34, wherein:

said palladium alloy film having a desired weight percentage for at least one of said palladium and an alloy material, said weight percentage being chosen based upon a desired hydrogen flux.

\* \* \* \* \*