PdAgAu alloy with high resistance to corrosion by H₂S

Fernando Braun, James B. Miller, Andrew J. Gellman, Ana M. Tarditi, Benoit Fleutot, Petro Kondratyuk, Laura M. Cornaglia

1. Introduction

Hydrogen has received significant attention as an energy carrier because it can be used for electricity generation in fuel cells without emission of CO₂. H₂ production from fossil fuels will continue for many decades to come because of the relatively low cost and high availability of coal and, to an increasing extent, natural gas. Conventional H₂ production from fossil-derived syngas requires multiple stages of purification to completely remove impurities such as CO and H₂S, which can deactivate the platinum electrodes of polymer electrolyte membrane fuel cells.

One strategy for reducing production costs and increasing the yield of ultrapure hydrogen is to use membrane type reactors for reforming and/or water-gas shift. In a single unit operation, membrane reactors deliver high purity hydrogen

Copyright © 2012, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.
(by permeation of product hydrogen through reactor walls) and a separate concentrated CO₂ stream that can be sequestered. Pd-based membranes have been extensively studied for the H₂ separation application. The Pd surface is active for dissociation of molecular hydrogen and H-atoms readily diffuse through bulk Pd, enabling high selectivity for hydrogen permeation. However, exposure to H₂S, a common minor component of methane and fossil-derived syngas, can compromise membrane permeability by formation of surface or bulk sulfides.

Exposure of pure Pd to H₂S is well known to cause formation of a bulk sulfide corrosion product over a wide range of H₂S concentrations (3.5–1000 ppm) and exposure temperatures (623–1100 K). The corrosion product, Pd₄S₈, has a hydrogen permeability about an order of magnitude lower than Pd. To improve its tolerance to sulfur, Pd has been alloyed with various minor components. PdCu has been extensively studied for its sulfur tolerance over a range of temperatures and H₂S concentrations. The potential for bulk corrosion of a PdCu alloy by H₂S exposure depends not only on the alloy composition, but also on the temperature of exposure and the composition of the exposure gas; PdCu alloys will not corrode at conditions at which the sulfide corrosion product is unstable. Thus, at high temperatures (generally > 900 K), PdCu alloys with 30–50% Cu are completely inert to H₂S, even at concentrations of H₂S as high as 1000 ppm. At lower temperatures, which are preferred for H₂ production, surface sulfides are formed, which make the surface inactive for the dissociation step.

PdAu has also been studied for its sulfur tolerance, but not to the same extent as PdCu. Sulfide formation has been reported in low-Au composition alloys (4–7%) at mild exposure conditions (673 K and 20 ppm H₂S), while PdAu alloys with higher Au composition have displayed high sulfur tolerance at 623 K, even upon exposure to 66,000 ppm of H₂S. In addition, several authors have reported that the PdAu alloy has a higher permeability than PdCu alloy membranes. PdAg alloys have been found to be as inert to H₂S as pure Pd, even in the presence of H₂S, PdAg corrodes as quickly as Pd.

With the aim of combining the H₂S tolerance of the PdAu binary with the high permeance of the PdAg binary, we prepared ternary PdAgAu alloys by sequential electroless plating and characterized their resistance to bulk corrosion by H₂S. We exposed a pair of ternary alloys and a reference Pd sample to 1000 ppm of H₂S for periods of 3 and 30 h at 623 K. We show that, unlike the Pd reference sample, the ternary alloys do not react with H₂S to form bulk sulfide under these conditions.

### Table 1 – Chemical composition of Pd, Ag and Au electroless plating solutions, activation and plating conditions.

<table>
<thead>
<tr>
<th>Activation/pH modifier</th>
<th>Plating bath</th>
<th>Pd</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl₂ (g/l)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PdCl₂ (g/l)</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl (M)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrazine (mM)</td>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄OH (M)</td>
<td>9.8</td>
<td>9.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂EDTA (g/l)</td>
<td>180</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PdCl₂ (mM)</td>
<td>20.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgNO₃ (mM)</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SO₃·5H₂O (mM)</td>
<td>149.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄ (mM)</td>
<td>169.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆H₈O₆ (mM)</td>
<td>339.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AuCl₃·HCl·4H₂O (mM)</td>
<td>6.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>11.5</td>
<td>11.5</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>50</td>
<td>50</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 1 – Scheme of the H₂S treatment system.](image-url)
Resistance to bulk corrosion may be linked to co-segregation of Ag and especially Au to the top surface of the alloy.

2. Experimental

2.1. PdAgAu membrane preparation

Two PdAgAu films were deposited by sequential electroless plating onto porous, 0.1 μm grade (PSSD), stainless steel 316L discs, 1.27 cm diameter × 2 mm thick. Before metal deposition, discs were washed with an alkaline solution consisting of 0.12 M Na3PO4, 0.6 M Na2CO3 and 1.12 M NaOH using the procedure reported by Ma and coworkers [22], and then annealed in air for 12 h at 773 K. To avoid intermetallic diffusion between the stainless steel substrate and the PdAgAu alloy components, the supports were modified with alumina by a vacuum assisted dip coating method [23]. Before the electroless plating step, the discs were activated. The sensitizing-activation of the substrate was performed at room temperature, first in an acidic SnCl2 (1 g/l) solution, and then in an acidic PdCl2 solution (0.1 g/l). The sensitizing-activation process was repeated six times. Palladium, silver and gold were deposited by sequential electroless deposition using the bath compositions shown in Table 1. For the sample with the lower Ag content, palladium was deposited in two steps of 60 min each, followed by a short Ag deposition of 5 min. In the case of the sample with the higher Ag content, palladium was deposited in two steps of 60 min and 40 min each, followed by Ag deposition for 15 min. For both samples, the Au deposition on top of the PdAg layers was performed for 20 min. After the metal depositions, the samples were rinsed with water and dried at 393 K overnight. The three-metal deposition cycle was repeated for both samples to achieve a target thickness of ~ 10 μm.

The ternary samples were annealed at 773 K in H2 to promote metallic inter-diffusion and alloy formation. The samples were mounted in a tube furnace as shown in Fig. 1 and heated from room temperature to 773 K at 0.5 K min⁻¹ in flowing nitrogen. The flow was then changed to hydrogen and the samples were held at 773 K in H2 for 120 h. X-ray diffraction experiments revealed that FCC ternary alloy formation was incomplete at 773 K, so both samples were incrementally annealed at 873 K in H2 for 48 h.

2.2. PdAgAu membrane H2S treatment

For the study of the sulfur tolerance of the PdAgAu alloy, two ternary alloys and a 25 μm thick Pd foil were exposed to a H2S/H2 gas mixture. The pure Pd foil was used as a reference because it is well known that it corrodes upon exposure to H2S, even at low concentrations [10]. Samples of the ternary alloys and a Pd foil were mounted horizontally in a tube furnace. Then, they were heated from room temperature to 623 K at 1 K min⁻¹ in a flow of high purity argon (40 ml/min). Next, the samples were treated in flowing hydrogen (10 ml/min, high purity) at 623 K for 30 min, followed by a mixture of 1000 ppm H2S/H2 (10 ml/min) for 3 h. Immediately after the H2S treatment, the reactor feed gas was switched back to Ar (90 ml/min) for 25 min to sweep all the H2S trapped in the reactor volume. After characterization, the 3-h samples were exposed to H2S for another 27 h (for a total of 30 h of exposure).

**Fig. 2** – X-ray diffraction patterns of the Pd film before and after H2S exposure (a) and both PdAgAu ternary alloys as prepared, after annealing and after H2S exposure (b, c). Ternary samples annealing conditions: 1st cycle; 120 h at 773 K in H2, 2nd cycle; 48 h at 873 K in H2. H2S treatment conditions: T = 623 K, [H2S] = 1000 ppm, time = 3 and 30 h.
Table 2 – Summary of literature results involving the effect of H₂S exposure to Pd, PdAg and PdAu alloys at several temperatures.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Membrane composition (Mol %)</th>
<th>Temperature (K)/time of exposure (h)</th>
<th>Feed composition</th>
<th>Experiment result</th>
</tr>
</thead>
<tbody>
<tr>
<td>McKinley [10]</td>
<td>Pd</td>
<td>623/144</td>
<td>4.5 ppm H₂S in H₂</td>
<td>Dull and etched surface.</td>
</tr>
<tr>
<td>This work</td>
<td>Pd</td>
<td>623/3</td>
<td>1000 ppm H₂S in H₂</td>
<td>Pd₄S formation.</td>
</tr>
<tr>
<td>McKinley [10]</td>
<td>Pd₇₃Ag₂₇</td>
<td>623/48</td>
<td>3.5 ppm H₂S in H₂</td>
<td>Dull and etched surface.</td>
</tr>
<tr>
<td>McKinley [10]</td>
<td>Pd₃Au₂₆</td>
<td>623/144</td>
<td>4.3 ppm H₂S in H₂</td>
<td>Retained original luster.</td>
</tr>
<tr>
<td>McKinley [10]</td>
<td>Pd₇₄Au₁₂</td>
<td>623/6</td>
<td>60000 ppm H₂S in H₂</td>
<td>Retained original luster.</td>
</tr>
<tr>
<td>Gade [15]</td>
<td>Pd₄₄Au₇₅ (Cold-worked)</td>
<td>673/80</td>
<td>20 ppm H₂S/50%H₂/29%H₂O/19%CO₂/1%CO</td>
<td>Pd₄S and Pd₂₈S formation.</td>
</tr>
<tr>
<td>Ma [14]</td>
<td>Pd₆₄Au₁₅</td>
<td>673/24</td>
<td>54.8 ppm H₂S in H₂</td>
<td>No bulk sulfide formation.</td>
</tr>
<tr>
<td>Coulter [28]</td>
<td>Pd₈₆Au₁₇Pt₇</td>
<td>673/100</td>
<td>20 ppmv H₂S/50%H₂/29%H₂O/19%CO₂/1%CO</td>
<td>Pd₄S formation.</td>
</tr>
<tr>
<td>This work</td>
<td>Pd₇₄Ag₁₄Au₁₂</td>
<td>623/30</td>
<td>1000 ppm H₂S in H₂</td>
<td>No bulk sulfide formation.</td>
</tr>
<tr>
<td>This work</td>
<td>Pd₆₄Ag₁₅Au₁₅</td>
<td>623/30</td>
<td>1000 ppm H₂S in H₂</td>
<td>No bulk sulfide formation.</td>
</tr>
</tbody>
</table>

Fig. 3 – Effect of time of exposure on the morphology of Pd foil (a, b and c), Pd₆₄Ag₁₅Au₁₅ (d, e and f) and Pd₇₄Ag₁₄Au₁₂ (g, h and i). H₂S treatment conditions: T = 623 K, [H₂S] = 1000 ppm, time = 3 and 30 h.
2.3. Film characterization

2.3.1. X-ray diffraction
The phase structure of the samples was determined by X-ray Diffraction. The XRD patterns of the films were obtained using a PANalytical X’Pert Pro instrument, having a theta–theta configuration, a Cu X-ray source operated at 45 kV and 40 mA and an X’Celerator detector equipped with a monochromator. Patterns were recorded over a 2\( \theta \) range of 20–100° at a step size of 0.02°.

2.3.2. Scanning electron microscopy, mapping and energy-dispersive X-ray analysis
The outer surface of the samples was imaged using a Tescan Vega-3 SEM instrument, operated at 20 kV in high-vacuum mode. The instrument was equipped with an Oxford INCA energy dispersive X-ray detection system for composition mapping; compositions were quantified using software provided by the manufacturer.

2.3.3. Elemental depth profiles by X-ray photoelectron spectroscopy (XPS)
XPS depth profiles were performed using a ThermoFisher Theta Probe instrument. The instrument has a base working pressure of 1.0 \( \times \) 10^{-10} kPa; it is equipped with a monochromatic Al K\( \alpha \) X-ray source. The instrument’s hemispherical analyzer was operated in Constant Analyzer Energy (CAE) mode with a pass energy of 200 eV. Depth profiles were performed using argon ion sputtering. A differentially pumped ion gun was operated at 1 \( \times \) 10^{-8} kPa, 3 kV and 500 nA, conditions which delivered a sputtering rate of approximately 1 nm min\(^{-1}\). Sputtering was performed in 10 steps of 60 s, followed by 10 steps of 180 s to examine the top ~50 nm of the sample surfaces. Before sputtering and then at each sputtering step, photoemission spectra for Pd 3d, Pd 3p, O1s, C 1s, Au 4f, S 1s, S 2p core levels were recorded; peak areas were determined by integration employing a Shirley-type background. Sensitivity factors provided by the instrument’s manufacturer were used for the quantification of the elements.

3. Results and discussion

3.1. PdAgAu alloy formation and phase analysis after exposure to H\(_2\)S

X-ray diffraction patterns of the Pd foil and the two alloys, before and after exposure to H\(_2\)S, are displayed in Fig. 2. The XRD patterns of the as-deposited alloy samples (bottom patterns, Fig. 2a and b) contain diffraction features of a pure Pd phase (2\( \theta \) = 40.12°, 46.62°, 68.12°) and pure phases of Ag and Au (2\( \theta \) = ~38.15°, ~44.33°, ~64.50°). After the first annealing cycle performed at 773 K during 120 h, formation of the FCC ternary alloy phase was incomplete, as illustrated by the continued appearance of small features at 2\( \theta \) = 40.12°, 46.62° and 68.12°. For both samples, formation of the alloy FCC phase was complete after a second annealing cycle performed at 773 K during 120 h, formation of the FCC ternary alloy phase was incomplete, as illustrated by the continued appearance of small features at 2\( \theta \) = 40.12°, 46.62° and 68.12°. For both samples, formation of the alloy FCC phase was complete after a second annealing cycle performed at 873 K for 48 h.

Several investigations of PdAg and PdAu alloy formation have been reported in the literature and provide context for our results [14,24–26]. Complete formation of a Pd\(_{56}\)Ag\(_{24}\)FCC alloy has been observed upon annealing at 773 K in H\(_2\) for 110 h [25]. Pd\(_{53}\)Au\(_7\) alloy formation, in contrast, is a slower...
process requiring more than 500 h in H₂ at 773 K [26]. The difference reflects the low solid-phase mobility of Au (Tammann temperature = 669 K) relative to Ag (Tammann temperature = 618 K). The aggressive anneal conditions that our PdAgAu alloys require for complete alloy formation suggest that the Au component dominates the alloying process.

After alloy formation, both ternary samples and a Pd foil were treated in 1000 ppm H₂S/H₂ at 623 K for 3, and then 30 h. The H₂S-exposed samples were characterized by XRD in the 30°–80° range to study the phases formed during the treatment. The Pd foil shows clear evidence of bulk sulfide growth upon H₂S exposure. A Pd₄S phase starts to form at 3 h and grows with increasing exposure time. The XRD pattern of the Pd foil exposed for 30 h (Fig. 2c) reveals an almost complete Pd₄S phase in the XRD analysis depth. In contrast, PdAgAu alloys show the same FCC phase before and after 30 h of exposure, as shown in Fig. 2a and b, with no evidence of formation of a crystalline sulfide phase.

Table 2 is a summary of results published in the literature involving the effect of H₂S exposure to Pd, PdAg and PdAu alloys at several temperatures. Several authors have used XRD to identify bulk sulfide phases in Pd and PdAg alloys upon exposure to relatively low H₂S concentrations [5,10,11,13,17,18,27]. Consistent with the results of our Pd reference sample, O’Brien et al. [16] reported complete conversion of a Pd foil to Pd₄S upon exposure to 1000 ppm H₂S at 623 K for 6 h. Mundschau et al. also observed the Pd₄S XRD pattern for a Pd foil treated with 20 ppm H₂S at 593 K for 115 h [5]. These authors also reported formation of mixed Ag₅Pd₁₀S₅ sulfide phase upon exposure of a Pd₇₅Ag₂₅ alloy membrane to 10 ppm H₂S at 593 K for 65 h.

While not studied as thoroughly as Cu, an Au minor component has also been reported to improve Pd’s resistance to H₂S corrosion. Ma and co-workers [14] did not observe sulfide formation upon exposure of a Pd₉₄Au₄ alloy to 54.8 ppm H₂S in H₂ at 673 K for 24 h. McKinley reported that a Pd₇₄Au₂₆ alloy did not tarnish (visual inspection) upon exposure to H₂S (in H₂) concentrations as high as 6.6% at 623 K [10]. In a counter-example, formation of Pd-sulfide phases, detected by XRD, was observed in low-Au content (6–7 at%) binary and ternary alloys that were exposed to 20 ppm H₂S in a complex background of H₂, H₂O, CO₂, and CO at 673 K [15,28]; these components might have an influence on the sulfide formation. Our ternary membranes did not react to form bulk sulfides at exposure conditions more severe than those that cause corrosion of PdAg alloys, providing clear evidence of Au’s role in imparting sulfur tolerance to the PdAg binary.

Fig. 5 – X-ray photoelectron spectroscopy depth profiles of the Pd foil (a), Pd₆₅Ag₂₅Au₁₅ (b) and Pd₇₄Ag₁₄Au₁₂ (c) Samples after 3 h of H₂S exposure. Elemental concentrations shown for Pd (black), Ag (blue), Au (green) and S (red). Analysis conditions: 1st 10 sputtering cycles of 60 s each. 2nd 10 sputtering cycles of 180 s each. H₂S treatment conditions: T = 623 K, [H₂S] = 1000 ppm, time = 3 h. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The Pd foil and the ternary samples were characterized by SEM both before and after exposure to H₂S. Fig. 3 displays micrographs for the three non-exposed samples, and the same samples after 3, and then 30 h of exposure to 1000 ppm H₂S. After 3 h of exposure, the Pd foil micrograph (Fig. 3b) reveals the appearance of discrete surface aggregates, evidence of partial conversion of the foil to Pd₄S. After 30 h of treatment (Fig. 3c) the micrograph shows that the Pd₄S layer has grown to cover the entire surface. The H₂S-exposed Pd foils were also characterized by X-ray mapping, as shown in Fig. 4. The sulfur maps confirm the presence of S in the aggregates formed at 3 h, and demonstrate complete sulfur coverage after 30 h. Bulk composition characterization of the
30-h sample by EDS revealed Pd₄S stoichiometry, confirming that the reference foil had been completely converted to the sulfide.

In contrast to the Pd foil, neither PdAgAu ternary sample exhibited a morphology change upon H₂S exposure (Fig. 2d–i). The micrograph of the Pd₇₄Ag₁₄Au₁₂ sample reveals pinhole pores on its surface, which is likely related to the relatively high Ag content of that sample; the dendritic morphology of the silver deposits has been reported by many authors [29,30]. EDS-mapping of the alloys after 3 and 30 h of exposure (not shown) did not reveal the presence of S. Thus, in agreement with XRD results, SEM and mapping analyses of the H₂S-exposed PdAgAu alloys did not uncover evidence of bulk sulfide formation upon aggressive treatment with H₂S.

3.3. XPS depth profile analysis after 3 h of H₂S exposure

To assess local sulfur contamination at the surfaces of the materials, which may be undetectable by EDS and XRD, XPS composition depth profiles were performed on the Pd foil and the ternary alloys after 3 h of H₂S exposure. The atomic compositions of Pd, Ag, Au and S as a function of etching time/depth are plotted in Fig. 5. The Pd foil has a significant sulfur content (S > 10 at.%% throughout the ~40 nm profiling experiment, as shown in Fig. 5a. In contrast, the depth profiles of both alloys display only very weak S signals at the top-surface (etch time = 0), which disappear before the etch depth reaches ~ 10 nm. At the same depth, the relative Pd, Ag and Au contents of the surface region reach steady state values that are the same as bulk compositions measured by EDS. Our sulfur profiles are similar to those reported by O’Brien et al. [16], who used XPS depth profiling to study the surface compositions of Pd and Pd₄₇Cu₅₃ foils after exposure to 1000 ppm H₂S at 623 K for 6 h. These authors observed constant sulfur content of 20 at % (i.e., Pd₄S stoichiometry) throughout the depth profile of their Pd sample. S appeared only at the very top-surface of their Pd₄₇Cu₅₃ alloy.

Metals composition profiles (Pd, Ag and Au only; S not included in the calculation) of the PdAgAu alloys samples after 30 h of H₂S exposure are displayed in Fig. 6. Clearly, Ag and Au co-segregate to the top surfaces (etch time = 0) of both alloys. The extent of Au segregation to the surface of Pd₈₃Ag₂₅Au₁₅...
annealing the (1 1 1) and (1 1 0) surfaces of a Pd70Au30 alloy
concentrations of 75% and 85% in the top layers after
Au content of 52% (at.) for a Pd80Au20 alloy prepared by melting
sulfides formation at 623 K: Au2S (PdAgAu alloys is consistent with the Au enrichment at the
¼ 
compared to that of a similarly prepared pure Pd membrane. At
[34] studied the surface segregation of a Au to the surface of
(1 1 1) alloy by LEED and LEIS. Au and Ag enrichment at
[33] using 1:1 Pd-Au/Mo (110) alloy annealed at 800 K. Li et al.
above 723 K. Similar surface enrichment, attributed to surface segregation of Au was observed by Goodman and co-workers
[33] using 1:1 Pd-Au/Mo (110) alloy annealed at 800 K. Li et al.
found that Au also imparts corrosion resistance to the PdAg
binary. Au preferentially segregates to the surfaces of both the
PdAu binary and the PdAgAu ternary alloys; high surface
concentrations of Au are likely linked to the lack of reactivity
of the alloy surfaces toward H2S. The high H2S tolerance of the
PdAgAu alloys is consistent with the Au enrichment at the surface and the pure-component standard free energies of sulfides formation at 623 K: Au2S (−8901 J/mol), Ag2S (−63,427 J/mol) and Pd4S (−132,005 J/mol) [37–39].

3.4. PdAgAu alloy permeation properties: preliminary results
Using an apparatus and procedure that have been described previously [40], the permeability of a 14 μm thick Pd35Ag15Au55/0.1 μm PSS disc (modified with ZrO2) ternary alloy membrane was compared to that of a similarly prepared pure Pd membrane. At T = 673 K and P = 50 kPa, the alloy membrane displayed pure H2 permeability of 1.3 × 10−8 mol m−1 s−1 Pa−0.5, slightly higher than that of the pure Pd sample, 1.2 × 10−8 mol m−1 s−1 Pa−0.5. Both membranes had H2/N2 ideal selectivity >10,000. After 24 h of exposure to 100 ppm H2S/H2 at 673 K, the alloy membrane retained 32% of its initial permeability, while the pure Pd membrane retained only 15%. These preliminary results provide a link between improved permeability performance in the presence of H2S and the resistance to bulk sulfide formation imparted by the minor alloy components.

4. Conclusions
Pd35Ag15Au55 and Pd74Ag14Au12 alloys, synthesized by sequential electroless plating, and a Pd foil reference were treated with 1000 ppm H2S in H2 at 623 K for 3 and 30 h. As expected, the Pd foil reacted with H2S to form a bulk PdS corrosion product within the first 3 h of H2S exposure. In contrast, neither PdAgAu alloy displayed evidence of bulk sulfide development upon post-exposure examination by XRD, EDX, SEM and X-ray mapping. Local sulfur contamination at the surfaces of the ternary alloys and Pd foil was studied by XPS depth profiling. Consistent with the results of bulk characterization, depth profiles of the H2S-exposed Pd reference samples show significant concentrations of S (~10 at% in the 3-h sample) throughout the 40 nm etch depth. In contrast, the PdAgAu alloys’ sulfur profiles displayed only small S signals at the top-surface (etch time = 0), which disappeared before the etch depth reached ~10 nm, even after 30 h of H2S exposure. The depth profile experiments also revealed significant co-segregation of Ag and Au to the H2S-exposed alloy surfaces. Preferential location of Au at the alloy surface is likely related to its resistance to bulk sulfidation by H2S. In a preliminary permeation test, a Pd35Ag15Au55 alloy delivered H2 fluxes comparable to those of pure Pd, and a residual permeability of 32% in 100 ppm H2S/H2 mixed gas experiments at 673 K after 24 h of exposure.

Our work illustrates the resistance of PdAgAu alloys to bulk corrosion by H2S. It suggests that fabrication of a ternary alloy membrane based on the high-permeability PdAg binary, but with an Au component specifically for H2S tolerance, could be an effective strategy for improving the membrane performance in extreme environments.

Acknowledgments
The authors wish to acknowledge the financial support received from UNL, ANPCyT, and the NSF-CONICET Program. Thanks are given to Elsa Grimaldi for the English language editing. The authors also wish to acknowledge the National Science Foundation for its support of research on Pd- alloys for hydrogen separation at Carnegie Mellon (CBET 1033804).

References