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Performance of Palladium Diffusers for Reliable Purification of Hydrogen

H. H. Funke and M.W. Raynor
Matheson Tri-Gas, Inc., Advanced Technology Center, 1861 Lefthand Circle, Longmont, CO 80501, USA

Abstract: Stress tests including large flow fluctuations and power outages demonstrate that a Palladium-diffuser designed for improved reliability was able to sustain 'real-life' operating conditions without premature failure from membrane cracking. Additionally, gas purity measurements were performed to confirm the efficiency for impurity removal. Even percent-level challenges did not result in any detectable changes in outlet gas quality as shown by atmospheric pressure ionisation mass spectrometry (APIMS).

1. Introduction

Palladium (Pd) diffusers are widely used for hydrogen purification in MOCVD processes (to 99.9999999%) because only hydrogen can diffuse through the Pd membranes at the operating temperatures of ~400°C, whereas impurities such as H_2O, CO_2, or CO remain on the inlet side of the membrane and can be purged from the cell through a bleed port [1]. Although, Pd-cells can last up to 3-5 years, failure can occur much sooner and is often very unpredictable. Shortcomings of currently available commercial designs include cracking of the membrane or brazing, due to mechanical stress from pressure pulses, changing flow conditions, and high impurity challenges, or from embrittlement by dissolved hydrogen in the membranes during power outages. Additionally, thorough cleaning and appropriate choice of cell materials is essential to minimize outgassing of contaminants such as methane at operation temperatures during initial operation.

2. Experimental

2.1.Palladium Cell

All experiments were performed with a PerfectH2™ PE6130 unit (max. flow: 130 slpm at 200 psig feed pressure and 0 psig UHP H_2 pressure) maintained at 400°C. The feed hydrogen was supplied through the inside of a set of coiled ~4 mm O.D. Pd/Ag alloy tubes. To minimise pressure pulsing of the membranes, the high purity hydrogen exited via a collection tube, running down the center of the membrane coils (Figure 1).

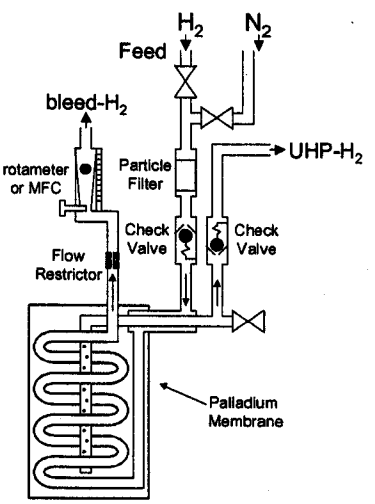

Figure 1: Schematic of the purifier design and flow setup

2.2. *Set-up*

The set-up used for the efficiency measurements comprised an ABB-Extrel atmospheric pressure ionization mass spectrometer equipped with a dilution manifold for analysis of the purified hydrogen stream. The feed H_2 (ULSI quality) was supplied from cylinder source and purified cryogenic house N_2 was used for purge. Flow rate measurements were made with a set of mass flow controllers connected to a data acquisition system. The purifier integrity was evaluated with a Veeco MS 40 helium leak detector (detection limit: $4*10^{-11}$ cc/sec).

3. Results

3.1 High/Low Flow Rates

The purifier was exposed to a series of rapid changes between full flow (<100 slpm at 200 psig feed pressure) and no flow (Figure 2). No ramp-up was required and the system reached the maximum flow rate within a few seconds. Temperature overshoots were within acceptable range (~10-15°C) indicating that heater dimensioning and heat dissipation was sufficient. The integrity of the membranes was verified with the helium leak detector after each test and no leaks were found within the accuracy of the instrument. Flow-rates as function of pressure gradients followed basic laws of diffusion for palladium membranes, ruling out external mass-transfer limitations and pressure drops inside the cell for maximum flow-ratings [2], [3].

3.2. Power Outages

Power outages are one of the potential failure modes for palladium purifiers due to cooling of the membrane in the presence of hydrogen. Large amounts of trapped hydrogen inside the metal matrix at lower temperatures might weaken the membranes and cause defects. A series of power outage tests at full flow and no flow verified, that cooling of the purifier after power loss is slow enough to remove residual hydrogen from the system through a vent, while diffusion of dissolved hydrogen out of the metal matrix is still sufficiently fast (>200 °C) to prevent damage. Cooling from 400 °C to about 200 °C requires about 1 hour for the model tested and residual hydrogen pressure on the high purity side of the membrane was <10 psia at that time. Helium leak tests after all tests confirmed defect free membranes.

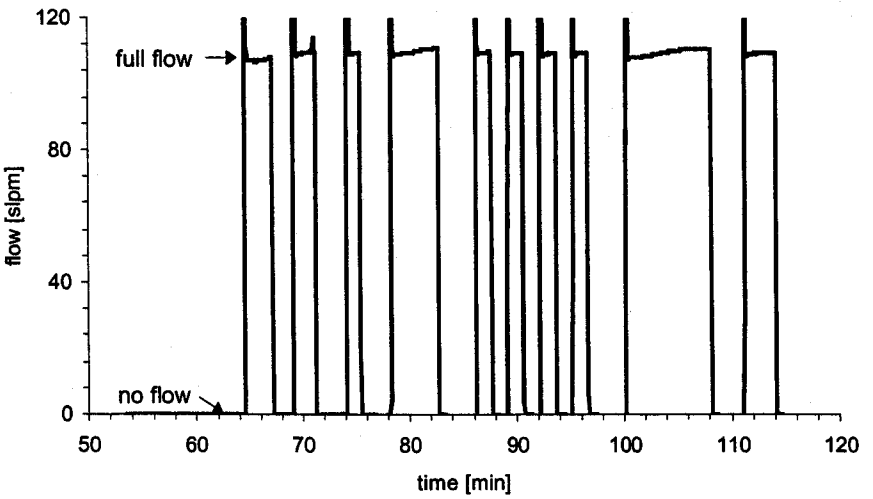

Figure 2: Rapid changes between full flow and no flow

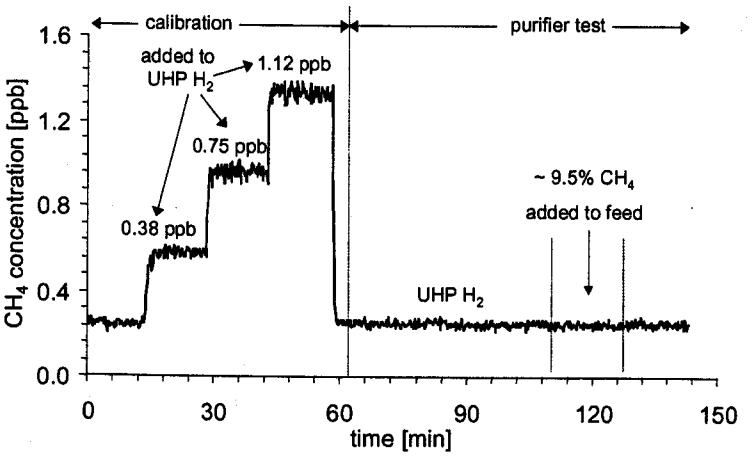

Figure 3: Methane calibration and purifier challenge with 9.5%

3.3. *Gas Purity*

After the flow and power outage tests were completed, APIMS measurements with several different impurity challenges were performed. None of the typical contaminants such as CO, CO_2, CH_4, O_2, N_2 were able to penetrate the membrane within the detection limit of APIMS, even at percent-level challenges, indicating a defect-free system. Background-methane levels, often of concern for Palladium diffusers due to high-temperature reaction of hydrogen with carbon components from the steel housing or from residual hydrocarbon contamination were in the sub-ppb range (Figure 3). Calibration data in the first half of Figure 3 demonstrate the sensitivity of APIMS in hydrogen matrix. Similar data were obtained for the other impurities listed above.

4. Conclusions

The thermal design of the PerfectH2 palladium cell, use of a central collection tube for the exiting purified hydrogen stream, and optimised brazing procedures allow for rapid flow-changes on demand without the risk of premature membrane failure due to mechanical stress. The wide-bore tubular membranes that are easily cleaned prior to assembly provide improved gas purity as demonstrated by APIMS.

5. References

[1] Newey J, 2001 *Compound Semiconductor* **12** 51-54.
[2] Buxbaum R E and Kinney A B 1996 *Ind. & Eng. Chem. Res.* **35** 530-537.
[3] Funke H H, Raynor, M W, Houlding V H, Bossard P., Fabiano P and Stuckey D, *J. Cryst. Growth,* accepted for publication.