A Durable Gas Purification Technology for High-flow Hydrogen in LED, Power Device and Photovoltaic Fabrication

Power + Energy Inc. Ivyland, PA

Summary

The use of ultra high-purity hydrogen for LED, power device and photovoltaic device fabrication has grown rapidly in the past few years. Palladium membrane purification technology has long been recognized as the most effective means to purify various sources of hydrogen in order to achieve parts-per-billion purity. The transition from R&D and limited production to high-volume manufacturing processes has brought new challenges for cost and durability of palladium-based purification systems.

A new palladium membrane technology developed in cooperation with the US Department of Defense offers the most significant innovation in gas purification in over 20 years. This micro-channel palladium membrane technology and associated advanced quality processes and system design innovations have been proven to reduce cost and greatly improve durability. These advancements greatly improve purifier durability while eliminating contamination, yield loss and downtime caused by hydrogen purity variability in compressed, cryogenic and generator sources.

Hydrogen Purification by Palladium Membrane

Purification of hydrogen by palladium (Pd) membrane diffusion is the accepted technology for applications requiring parts-per-trillion gas purity. Palladium is acts as a catalyst, causing hydrogen gas molecules to dissociate into atoms upon contacting the membrane surface. The atoms are small enough to diffuse through the palladium membrane, driven by differential hydrogen pressure across the membrane. The hydrogen atoms recombine into molecules after passing through the membrane. Hydrogen purifiers operate at approximately 400 C. At this temperature, hydrogen atoms readily diffuse through the membranes. No other material can diffuse through palladium and so the permeate is only hydrogen (Figure 1).

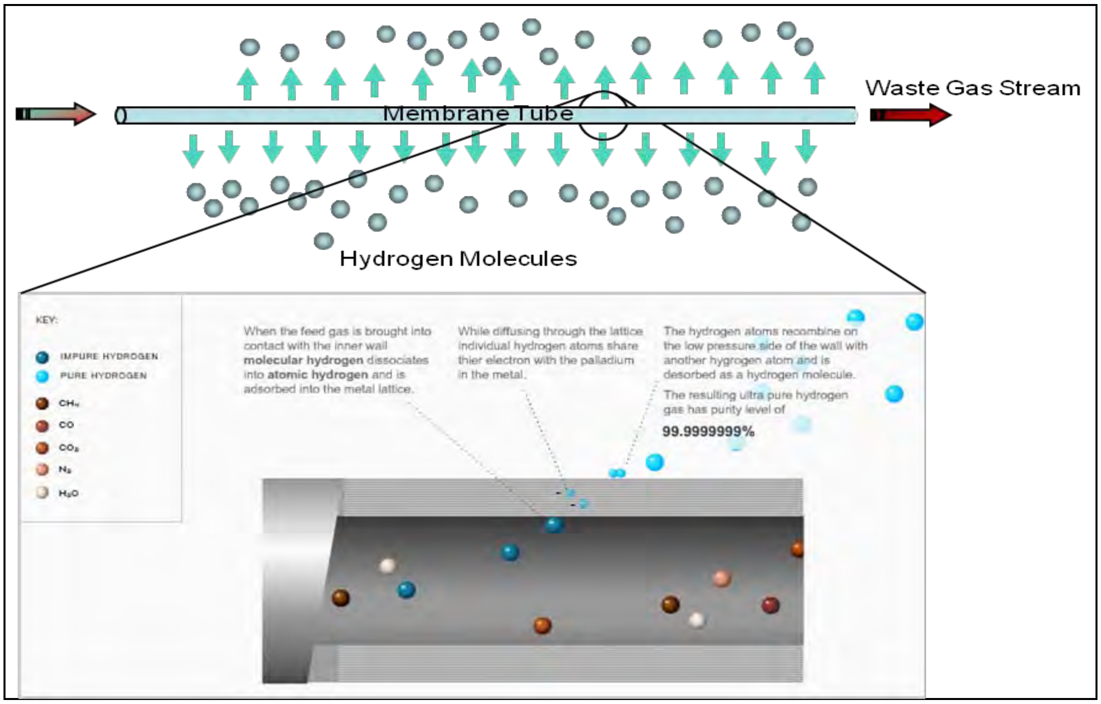

Figure 1: Palladium membrane tubes provide the unique ability to only allow hydrogen molecules to pass through to the pure side

Impurities including H_2O, O_2, N_2, CO_2, CO, hydrocarbons and rare gases remain on the inlet side of the membrane and are continuously purged through a bleed connection. The unique properties of palladium provide a solid barrier with no breakthroughs as compared to catalysts and getters that rely on chemical reactions on reactive surface areas. This solid barrier also provides the benefit of in-situ verification of performance via helium leak detection. Helium on the inlet side will not show on a downstream leak detector. Palladium purifiers are the only technology that can be quickly verified for purity performance. Palladium technology also offers the unique ability to remove high-ppm levels of impurities from cylinder source gas with no effect on purifier lifetime or outlet H_2 purity. Figure 2 shows removal of CO_2 to parts-per-trillion (ppt) levels with incoming levels as high as 94 ppm. Other methods of hydrogen purification, such as regenerable catalysts and heated zirconium getters, are intended for removal of low ppm impurities, and the purifier lifetime is directly dependent on the incoming impurity and flow rate. This robust capability makes it ideal for compressed cylinder and generator sources where the gas quality can vary significantly from day-to-day.

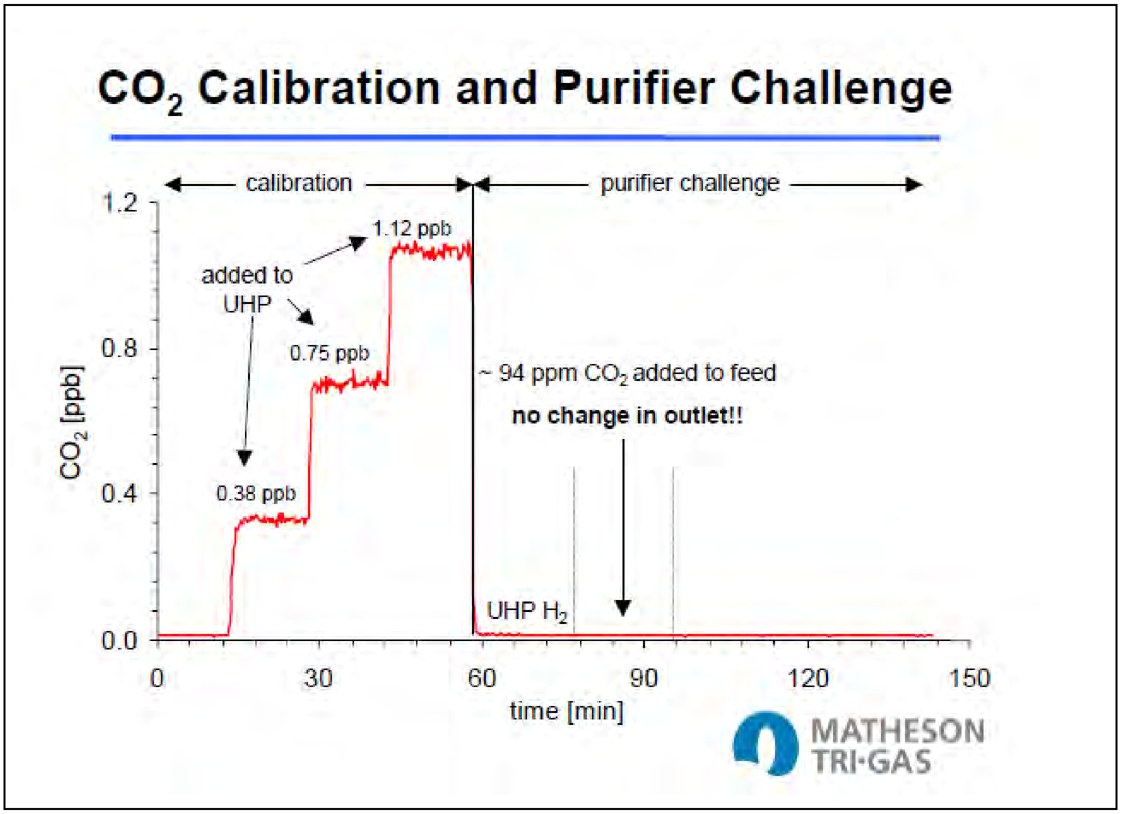

Figure 2: A palladium purifier is challenged with up to 94 ppm of CO_2 with no change in outlet purity. (Data courtesy of Matheson Tri-Gas)

.

The first palladium purification systems (traditional Pd) used coiled tubes housed in a simple stainless steel vessel. In traditional Pd purifiers, the incoming hydrogen flows into a chamber containing tubular membranes closed on one end. The gas flows "outside-in" through the tube and the pure gas is collected on the outlet end of the membranes. There is a supporting spring inserted into the membranes to prevent the hydrogen pressure from collapsing the membranes. This design has remained unchanged for decades even though the new demands for ppt purity and higher flow rates at lower cost have pushed traditional Pd purifiers beyond their original performance capabilities. The outer vessel is heated with simple band heaters and a temperature controller. Units of this type were first used in the 1970's at government and university laboratories for analytical testing and basic research on semiconductor wafer processing. In the 1980's, new applications in MOCVD to purify hydrogen carrier gas for metal-organic precursors and purge gas required very high purity hydrogen to prevent oxygen incorporation in epitaxial wafers. The unstable quality of hydrogen sources used at R&D laboratories, universities and small manufacturing facilities led to widespread adoption of palladium purification by MOCVD equipment manufacturers at compound semiconductor fabrication facilities.

Hydrogen Quality Challenges – Sources, Geographic Limitations and Backup Strategies

Hydrogen can be supplied as a compressed gas, as a liquefied (cryogenic) gas or generated on site. The purity of gas can vary widely depending on the source and specific region. For example, liquid hydrogen, usually the most pure form of hydrogen, is not available in Taiwan, Korea and China where most of the new high volume LED and photovoltaic fabs are located. These fast-growing regions must rely on compressed and generator sources which can include a great deal of variability in the purity of compressed and locally generated hydrogen.

- Compressed Hydrogen- Purity can vary widely depending on source and operating practices.
- Liquid Hydrogen- Generally the highest commercial purity available, liquid hydrogen is typically between 6 and 7 nines purity (1,000-100 ppb total impurities).
- Generators- Available in a wide variety of capacities, typically used for high volume requirements or when local sources are limited. The purity of generated hydrogen can vary greatly depending on design and feedstock.

H_2 Source	Delivery	Typical Purity	Regional Availability	Large Volumes	Hydrogen Cost	Capital Cost
Compressed	Trailers, Cylinders	99.9%-99.999%	▲▲	▼	—	▼
Cryogenic Liquid	Tanker / Storage Tank	99.99999%	▼[1]	▲	—	—
Generator	Steam Methane Reformer (SMR)	99.9%-99.999%	▲▲	▲▲▲	▼[2]	▲▲
	Electrolysis of Water	99.999%	▲▲	▲	▲[3]	▲▲

1. Availability is limited to several regions including North America, Northern Europe and Japan.
2. SMR requires availability of Natural Gas
3. Electrolytic H2 generators consume large quantities of electricity

Regardless of the source, there will be impurities in the hydrogen that vary over time. Variations in impurity levels can result from changes in feedstock, contamination from improper purging, transfills and contaminated distribution equipment as well as from piping and control systems. Microelectronics industry facilities that require high-purity hydrogen must also have a contingency plan in case the primary source is unavailable due to maintenance or unforeseen downtime. In this case, the backup H_2 may be delivered from an industrial or chemical plant with much lower gas purity. For example, a facility with onsite storage of 99.999% hydrogen may be forced to use 99.99% backup hydrogen on rare occasions. The purification systems must be designed for these contingencies so that gas purity is unaffected by changing gas quality sources. Palladium purifiers can ensure that all impurities are removed from the hydrogen, whether typically present or the result of an unusual event.

In order to ensure constant availability of high purity hydrogen, facilities often employ an “N+1” strategy, where a spare purifier is installed and maintained as a backup. The on-line and off-line purifiers can be alternated to ensure even usage This strategy provides for down-time for routine maintenance. Installing three purifiers, two on-line (with the capacity to meet peak demand) and one back up is an example of this strategy. An alternative strategy would be to operate all three purifiers at two-thirds of total capacity. . If one unit should require attention, there is still sufficient capacity available to support full plant operation.

Limited Durability of Traditional Palladium Membrane Purifiers

Applications for palladium purifiers have become more demanding, but traditional palladium membrane technology has changed little for over 20 years. As the compound semiconductor industry has transitioned to more complex, demanding processes with larger chambers and larger 4” and 6” wafers, sensitivity to oxygen and carbon contamination has increased, hydrogen flow rates have tripled for the largest MOCVD reactors, and flow changes during the process recipe runs can surge from 0 to 300 slpm with no transition period. Traditional Pd purifiers were not designed for the parameters of these new process recipes and they have a number of inherent limitations in durability, quality and cost that have led some users to consider alternative purification technologies.

Durability is compromised when purifier operating temperature moves out of optimum range for even short periods of time. Palladium operates most efficiently at temperatures of 390-410C. Hydrogen diffuses into and through the lattice structure and recombines on the permeate (pure) side of the membrane at the highest flux rate when the purifier temperature is stable.. The internal temperature of traditional Pd purifiers has been shown to fluctuate resulting in local hot spots as flows ramp up or down in response to process demands. This variable temperature contributes to stress on the Pd tubes and can lead to pinhole leaks that may allow impurities to pass through to the pure side. Quality of the palladium tubing is another factor contributing to early failures. The alloy melt and tube drawing process can result in imperfections including inclusions and voids in the membranes. For traditional Pd tube with large wall thicknesses, it is difficult to find and eliminate these micro-defects in the inspection process.

Innovative Palladium Membrane Development

Power+Energy is focused on innovations for hydrogen purification and separation via palladium alloy membranes. Through a series of US Department of Defense (Navy, Army and DARPA) Research Contracts, P+E has developed a unique micro-channel Pd Alloy membrane configuration, automated membrane test and inspection methods and advanced manufacturing technologies. Building reliable systems for higher flow rates begins with robust, defect free membranes and low stress purifier cell construction. P+E has configured its purifiers to protect both the membrane and process integrity. Years of research and validation processes have led to the following innovations:

1. Micro-channel membrane structure with “inside-out” flow path
2. Improved quality and durability of palladium tubes via stringent manufacturing and inspection techniques
3. Automated robotic fabrication methods.
4. Improved system design with pressure and thermal uniformity
5. Increased flow capacity to allow smaller systems for higher flow rates
6. Novel manufacturing techniques to achieve impurity specifications of <0.1ppb (100 ppt)
7. Expanded functionality for new applications in energy, military and electronics industries

With higher flow capacity, tighter quality and manufacturing specifications, and robust performance, P+E’s micro-channel purifiers are the optimum choice for compound semiconductor applications where consistent ppt purity must be provided with no variation caused by varying hydrogen sources.

An “inside-out” design has been developed using an entirely unique membrane structure called “micro-channel” in which the hydrogen enters the *inside* of the membrane tube (Figure 3). This palladium tube has an inner “return tube” that is inside and concentric with the membrane. The hydrogen diffuses out into a passivated stainless steel chamber while a small volume of hydrogen continuously sweeps all impurities to a bleed line.

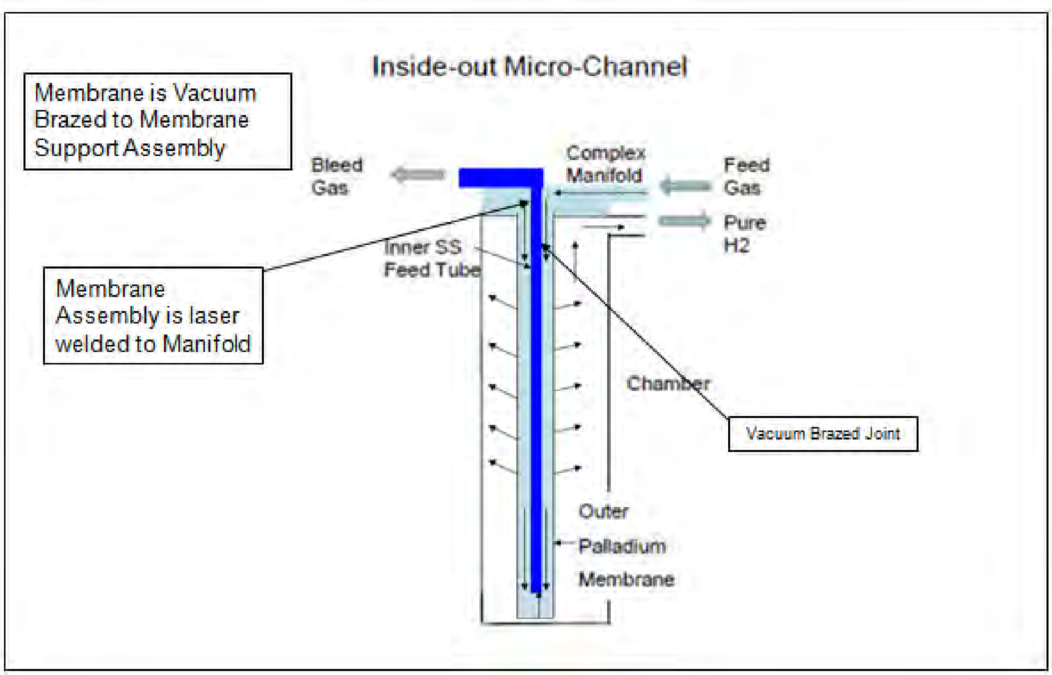

Figure 3: Inside-out micro-channel palladium purifier

The micro-channel design has shown dramatic increases in durability, compared to traditional Pd designs, after improvements in weld and brazing methods, quality inspection, and membrane assembly design. This micro-channel design reduces stress on the membranes and does not require a supporting spring. The micro-channel also enhances hydrogen recovery so that even low concentrations of hydrogen from reformed fuel streams are efficiently recovered by this method. P+E has been working with its vendors to improve alloy and tube drawing processes to reduce impurities and physical defects, inclusions, particles, bubbles and seams. The result is a more uniform alloy with fewer micro-defects, leading to more reliable membranes.

Another key step to improve durability and lifetime has been to implement more stringent quality control to preemptively screen out material defects. P+E developed a proprietary membrane inspection station to identify and eliminate substandard membranes at the earliest possible stage. This process tests each membrane under extreme conditions to look for abnormalities and surface irregularities. Each membrane is also individually subjected to a helium leak test prior to acceptance into inventory

In the micro-channel membrane configuration, the palladium membrane tubes are vacuum brazed to stainless steel fittings to allow connection to welded assemblies. An advanced computer-controlled vacuum braze process provides precise, repeatable brazing to eliminate weak points in the braze joint. The membrane assembly is laser welded into an electropolished and passivated stainless steel manifold. This unique design moves the stress point to the laser weld rather than the palladium membrane, improving the strength and durability of the membrane assembly. The straight Pd tube assembly incorporates a guide that further reduces stress by preventing lateral movement and rubbing. The design allows axial and radial expansion and contraction without restriction, reducing stress on the membrane tubes. The membrane assemblies are laser welded using a robotic system with machine vision, resulting in a consistently reliable system.

To confirm significant improvements, automated, accelerated life testing systems were developed to replicate extreme operating conditions. The membranes were pressure cycled every 25 seconds from 40 to 180 psia at 400C with industrial grade hydrogen to simulate the stresses possible from long term operation. The goal was to confirm a 10,000 minimum cycle lifetime – equivalent to 10 years with 3 on/off cycles per day. Since purifiers generally operate unattended for weeks at a time, this benchmark is well above actual operating conditions. Figure 4 shows that membranes passing incoming inspection always met the 10,000 cycle lifetime, and even some membranes that failed inspection still shows excellent lifetimes. This testing confirmed that the inspection methods may eliminate “good” membranes, but it also assures that no accepted membranes fail the cycle test.

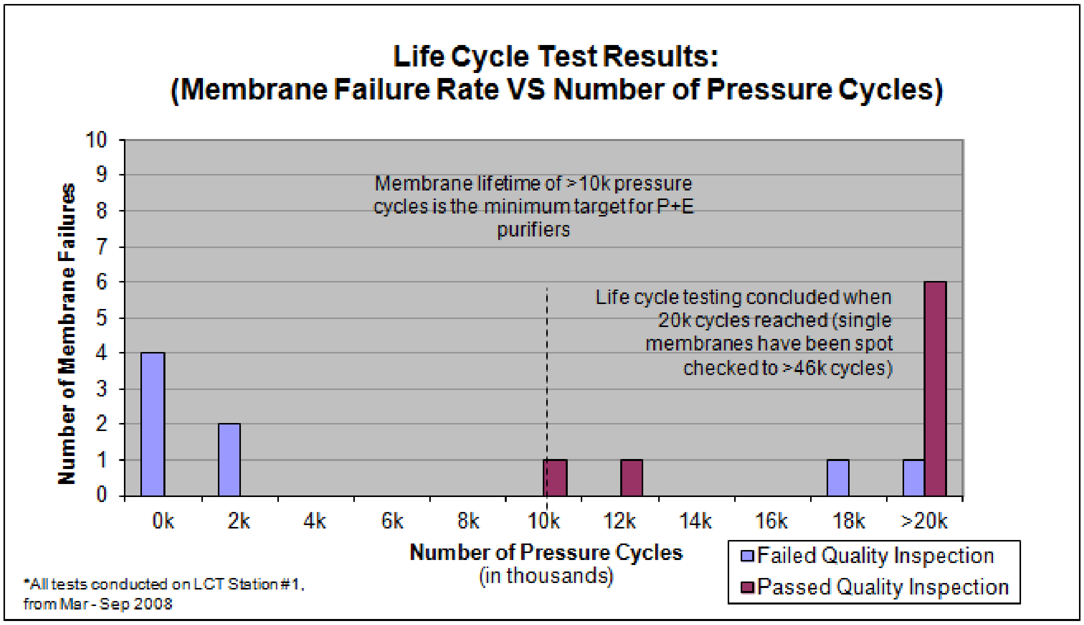

Figure 4: Membrane life cycle test confirms 10,000 cycle minimum lifetime for all membranes that passed new inspection procedures

Sample membranes were also run through thermal cycling to validate flow performance and stability over time. After 150 cycles of temperatures from 50 to 400C, leak integrity was confirmed and there was no loss of flow performance. Both tests have confirmed the effectiveness of P+E's membrane test methods to identify and remove membranes with micro-defects prior to the assembly process. Testing also confirmed that the new micro-channel membranes provide improved durability under the most hostile operating conditions.

The assembled system improvements have also contributed to the improved durability. Palladium purifier lifetime is maximized when the membranes are maintained under stable pressure and temperature. For high pressure systems, small orifices are added on the hydrogen inlet side to protect the Pd tube from pressure surges during system startup. Palladium should be operated at 390-410C regardless of flow, so it is important to provide uniform heating. To reduce exposure to hot spots, the new design includes preheating of the feed hydrogen to maximize thermal stability across the flow path. Finally, the design of the membrane vessel has been engineered to take advantage of advanced robotic manufacturing technology. Each membrane is held in an array where there is no contact with other membranes. Traditional Pd purifiers allow the membranes to move freely against each other, and this contributes to long-term stress of the tubes. Positioning each membrane so that they do not contact each other allows free flow of gas and prevents damage to tubes from unplanned contact.

The compact array of membranes provides a high flow capacity in a very compact package. A single vessel measuring 6" x 24" that previously purified up to 200 slpm can now flow 600 slpm, a 3x improvement in flow capacity. The compact package also reduces power consumption and allows savings in required floor space and HVAC sizing, important considerations in the design of the larger semiconductor fabrication facilities in Asia.

Analysis of raw materials, assembled systems and resulting outlet gas purity has led to the development of improved techniques to lower the outlet gas purity consistently below 0.1 ppb (100 ppt). Proprietary manufacturing processing to prepare and passivate stainless steel have reduced sources of carbon and moisture that can contribute impurities downstream of the palladium membranes. Standard specifications from traditional Pd purifiers offer < 1 ppb impurities after lengthy startup purging and at a minimum 20% of rated flow. With newly-developed P+E procedures, startup purity of < 100 ppt for all impurities is now available.

The micro-channel technology also economically brings the benefits of Pd purification to expanding applications for hydrogen purification and separation in photovoltaic solar cells production, polysilicon manufacturing and fuel cell applications. Special alloys of palladium and copper have been developed to provide improved tolerance to impurities such as sulfur. Sulfur is a common impurity in low-grade hydrogen sources, so it was useful to find an alloy that could tolerate higher levels. The micro-channel enables recovery of hydrogen from a mixed stream because the inside out path allows recovery for as low as 20% hydrogen. Micro-channel membrane separators will extract hydrogen from reformed fuels such as natural gas and diesel, supplying hydrogen with no trace sulfur or carbon monoxide purity is critical for long fuel cell lifetime.

Conclusion

Extremely pure hydrogen is essential to meet the growing capacity demands of the LED, Power and Photovoltaic industries. Variations in hydrogen source quality are particularly challenging in Asia where liquid source is not available, so semiconductor fabs must specify redundant and robust gas purification systems to operate under 'worst-case' scenarios. Palladium purification offers the best purity results for this application because it offers an absolute barrier regardless of flow rate or inlet gas quality.

Power + Energy has developed an advanced micro-channel palladium membrane technology specifically designed to provide high capacity, energy efficient hydrogen purification for high-volume production facilities with stringent requirements for continuous uptime. The micro-channel membranes offer improved durability through better raw material processing and quality inspection methods. Automated fabrication techniques and improved system design provides a purification system that will deliver consistent purity over time independent of feed gas contamination. The advanced membrane and cell construction results in higher capacity systems in small footprints with the lowest cost of ownership. These innovative improvements have provided significant increases in durability to tolerate the demanding conditions of high flows and varying hydrogen gas quality common in volume manufacturing processes.