MATERIALS SOLUTIONS | TECHNICAL NOTE

Assessment of Different Methods for Hydrogen Delivery to Improve Ion Implant Tool Productivity

Joseph Despres, Luke Kinard, Kaitlin Lawrence, Brianna Mancuso, Ying Tang – Entegris, Inc.

INTRODUCTION

The purpose of this study was to provide an experimental and technical analysis of considerations that should be reviewed prior to selecting the hydrogen delivery method. The addition of hydrogen when using a fluoride gas (BF_3, GeF_4) helps to reduce the effects of the halogen cycle. There are multiple delivery options available for hydrogen and we explored the impact on material quality, long-term reliability, and safety.

HYDROGEN DELIVERY OPTIONS FOR ION IMPLANTATION

Option 1: Pre-mixed fluoride and hydrogen in a single cylinder

The fluoride gas and hydrogen are mixed in the cylinder by the gas supplier.

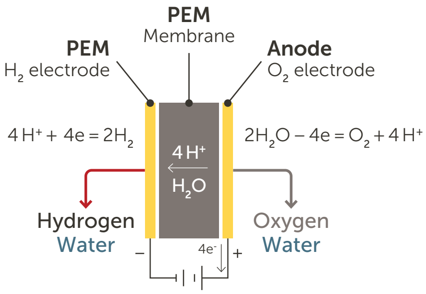
- Multiple concentrations available
- Stable mixtures over cylinder lifetime
- Material quality is monitored and controlled via a certificate of analysis (CoA)
- Safe cylinder package with sub-atmospheric delivery pressure

Option 2: Cylinder with 100% fluoride gas and cylinder with 100% hydrogen, mixed on-board the tool

The fluoride gas and hydrogen are co-flowed from separate cylinders and mixed on the tool.

- Mixture concentration flexibility via MFC control
- Material quality is monitored and controlled with a CoA
- Safe cylinder packaging available with subatmospheric delivery pressure
- 100% H_2 is the highest flammability risk
- Additional gas slot needed for H_2 cylinder
- Additional H_2 monitoring required

Option 3: Hydrogen generation on-board the implant tool



Hydrogen is made *in-situ* through the electrolysis of DI water and then co-flowed with the fluoride gas.

- Mixture concentration flexibility via MFC control
- Non-cylinder option
- Hydrogen quality is not known and controlled
- Generators result in entrained moisture in the hydrogen stream
- Maintenance requirements at even 1-month intervals for DI water replenishment, purifier replacement, and moisture desiccant replacement
- Oxygen must be vented safely as to not mix with other flammable gases that are in use
- Water leaks need to be prevented given the elevated voltage of the gas box relative to ground
- Gas slots are converted to house the generator
- Additional H_2 monitoring required

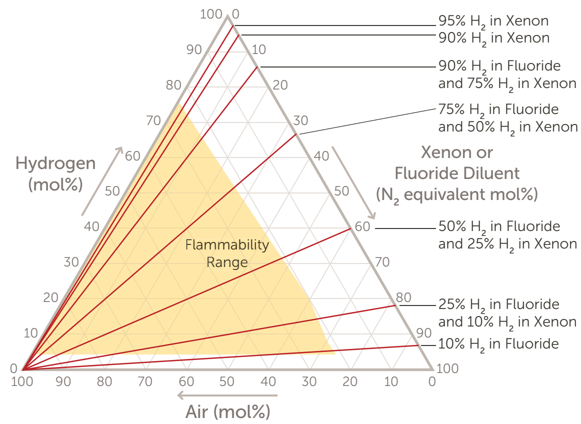
EXPERIMENTAL AND TECHNICAL RESULTS

Several experiments were performed to quantify the purity of the different delivery options and measure moisture and nitrogen. A commercially available hydrogen generator was used. The generator was set up to constantly generate hydrogen for one year and periodic purity measurements were made using gas chromatography (GC) and cavity ring down spectrometer (CRDS).

FLAMMABILITY RISKS

All sources of hydrogen above a certain percentage have flammability risks, however the risks are not all equal. Calculations were done to assess the relative flammability in air for different mixtures.

- 100% hydrogen sources have the highest risk.
- Dilution with a fluoride gas reduces the risk more when compared to dilution with xenon. 50% H_2 in BF_3 is the same as 25% H_2 in xenon.
- If a leak were to occur, a pre-mixed cylinder can be detected with existing HF toxic gas monitors, however new H_2 monitors need to be purchased and installed for other sources.



GAS PURITY AND MOISTURE LEVELS IN HYDROGEN

Pre-mixed fluoride and hydrogen cylinder

Moisture content is controlled and quantified by measuring the HF concentration. Any water that may be present from the source gases, cylinder preparation, or mixture process undergoes full hydrolysis via the following mechanism:

$$BF_3 + nH_2O \leftrightarrow BF_3 \bullet nH_2O \leftrightarrow BF_2(OH) + \mathbf{HF}$$

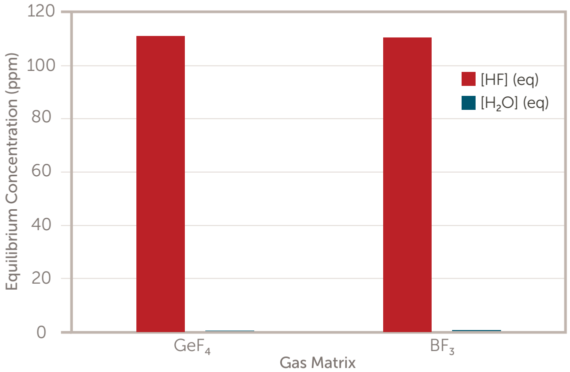
$$MF_4 + H_2O \leftrightarrow MF_3OH + \mathbf{HF}$$

(where M = C, Si, or Ge)

For a starting concentration of 100 ppm of water, thermodynamic calculations confirm nearly complete hydrolysis to HF.

- Water at even trace amounts is not present in fluoride gas mixtures.
- HF is easily measurable, and specifications are set such that HF amounts that result from even trace amounts of water will be rejected.

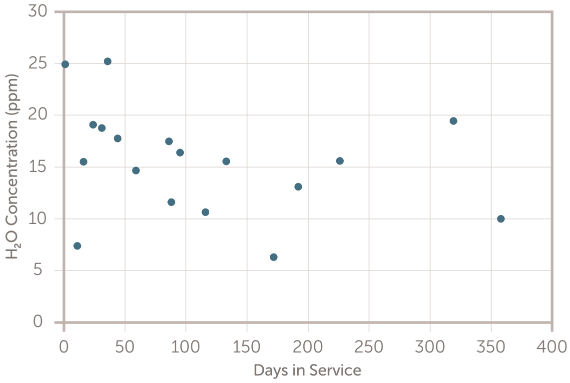
Thermodynamic Calculations of Water and HF Initial $[H_2O]$ = 100 ppm



Hydrogen generator

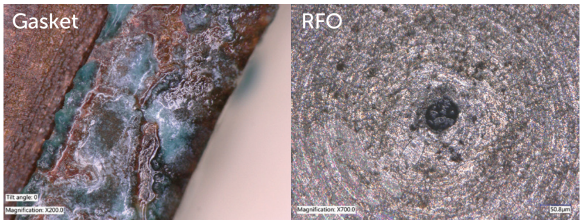
- DI water is the source and conversion efficiency is typically 60 – 90%, so moisture will inherently be entrained in the hydrogen stream.
- H_2 from the generator had H_2O concentrations >25 ppm during the one-year test. Average over this time was 16 ppm.
- Moisture was able to be transported from the unit through the delivery lines and to the analytical instrument.

Measured H_2O Levels from a Hydrogen Generator



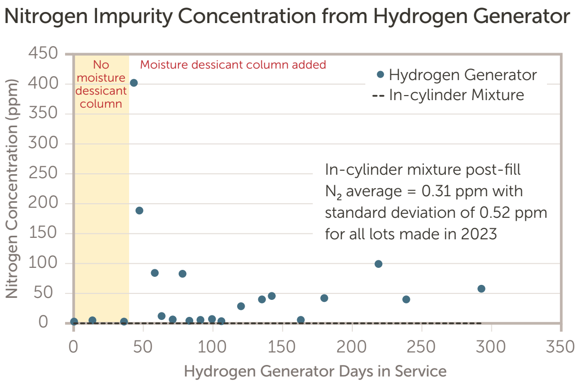
Why does moisture matter?

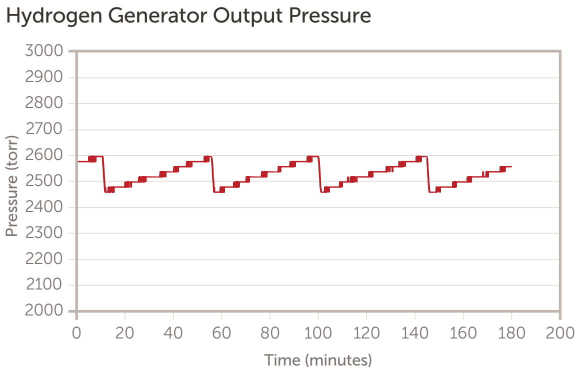
- A second experiment was completed where we exposed common gas line components to a BF_3 and moisture mixture.
- An accelerated aging test was completed to simulate 150 days at room temperature.
- Gasket showed significant signs of corrosion, which could lead to a compromised seal and a gas leak.



Hydrogen generator removal of moisture

- A third experiment was completed where a desiccant column was added to the hydrogen generator to remove moisture.
- Moisture dropped to ~5 ppm, however other impurities such as nitrogen increased ~60× to 400 ppm.
- The desiccant will desorb impurities as pressure and temperature changes.
- It is difficult to predict when the desiccant will reach breakthrough, at which time moisture and other impurities will spike considerably.
- Impurities can be orders of magnitude lower in a pre-mixed cylinder compared to a generator.





CONCLUSIONS

Pre-mixed cylinders provide the highest quality and the least maintenance of all the options evaluated

- Pre-mixed cylinders do not have moisture due to hydrolysis. The resulting HF concentration is easily measured and controlled.
- H_2 generators by design have entrained moisture which can be >25 ppm in our experimentation.
- In these experiments, moisture led to corrosion of gas line components such as gaskets, which could lead to a sudden failure and loss of gas line integrity.
- Addition of a desiccant can reduce moisture, however the desiccant can desorb other impurities such as nitrogen. In our testing we saw a 60× increase in nitrogen concentration with the desiccant. Pre-mixed cylinders typically have less than 0.2 ppm of nitrogen.
- The flammability risk needs to be considered, and calculations indicate 100% H_2 is the highest risk, followed by dilution with a fluoride gas and then dilution with xenon.
- Monitoring needs to be added for 100% hydrogen sources.
- Maintenance cost for generators can be substantial, with PM intervals as short as every 2 weeks.

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Corporate Headquarters
129 Concord Road
Billerica, MA 01821
USA

Customer Service
Tel +1 952 556 4181
Fax +1 952 556 8022
Toll Free 800 394 4083