ODORIZATION OF HYDROGEN FOR FUEL LEAK DETECTION

Enersol Inc. NA, LP
Michael J. Sprague and Patrick J. Flynn

The Pennsylvania State University
André L. Boehman, Serguei N. Lvov, Steven Kirby and Jeong Lee

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Outline

1. Introduction and Background
2. Hydrogen Odorization
3. Fuel Cell Compatibility Results
4. Summary of Results and Future Work

Introduction and Background

- Enersol was formed in 2003 to investigate the potential of using odorants as a means of hydrogen leak detection

- Limited available literature in the public domain which demonstrates the compatibility and utility of odorants with hydrogen. Sufficient research has not been performed to the degree of detail to support the technical merit of hydrogen odorants

- Our work is focused on gathering information for the hydrogen community to help understand the viability of odorization

- Enersol is working to evaluate the compatibility of odorization technology with infrastructure (i.e. fuel cells)

Introduction to Odorization Technology

- Odorization is emerging as one of two possible leak detection technologies available to satisfy regulatory requirements for leak detection

- Odorants offer the promise of a low-cost detection solution for hydrogen delivery infrastructure, fueling stations, and for end use hydrogen applications

- The general public can relate to the concept of odorization, providing enhanced public confidence and sense of security. Among other things odorization is expected to enhance overall safety in tandem to sensors

- Sensors and odorants should be considered complementary technologies working collectively to provide the highest level of redundancy as an integrated safety system

Odorant Selection Criteria

"**Odorant Selection Criteria**" → describes minimum characteristic requirements of an odorant used for hydrogen leak detection:

- An odorant must have a distinctive and alarming smell
- An odorant must possess sufficient olfactory power to be in the vapor phase at detectable concentrations at high pressure (pOI-P_{vap} relationship)
- In a strictly diffusive environment the odorant must possess sufficient diffusivity and olfactory power to be detectable before hydrogen reaches 20% LFL (diffusivity - pOI relationship)
- ***A hydrogen-odorant mixture must not impact fuel cell performance***

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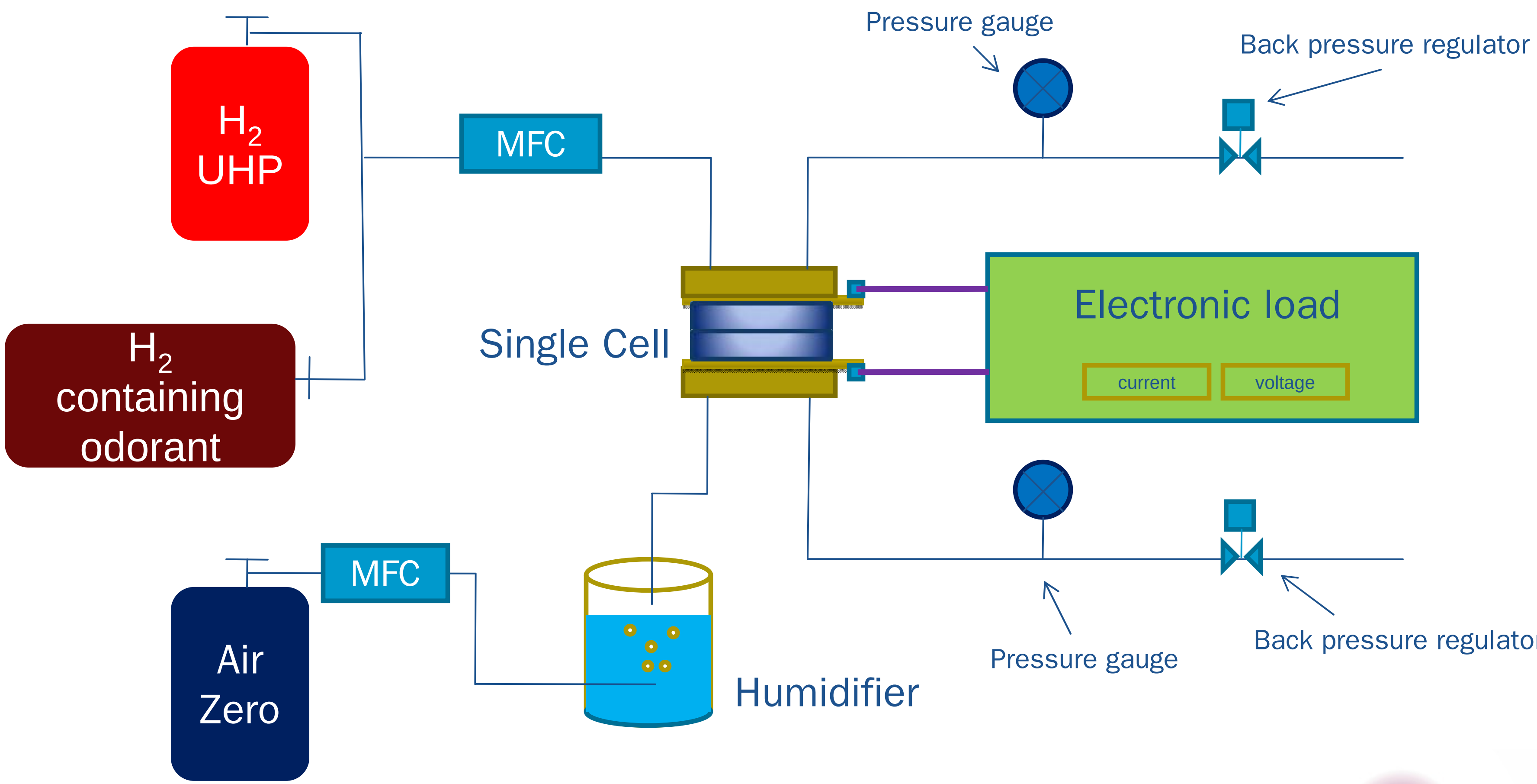
Fuel Cell Compatibility Testing

- Assess whether certain odorant compositions merit further development by evaluating whether odorants adversely affect fuel cell performance:
  - examine impact of different odorant compositions
  - examine impact of odorant concentration in hydrogen

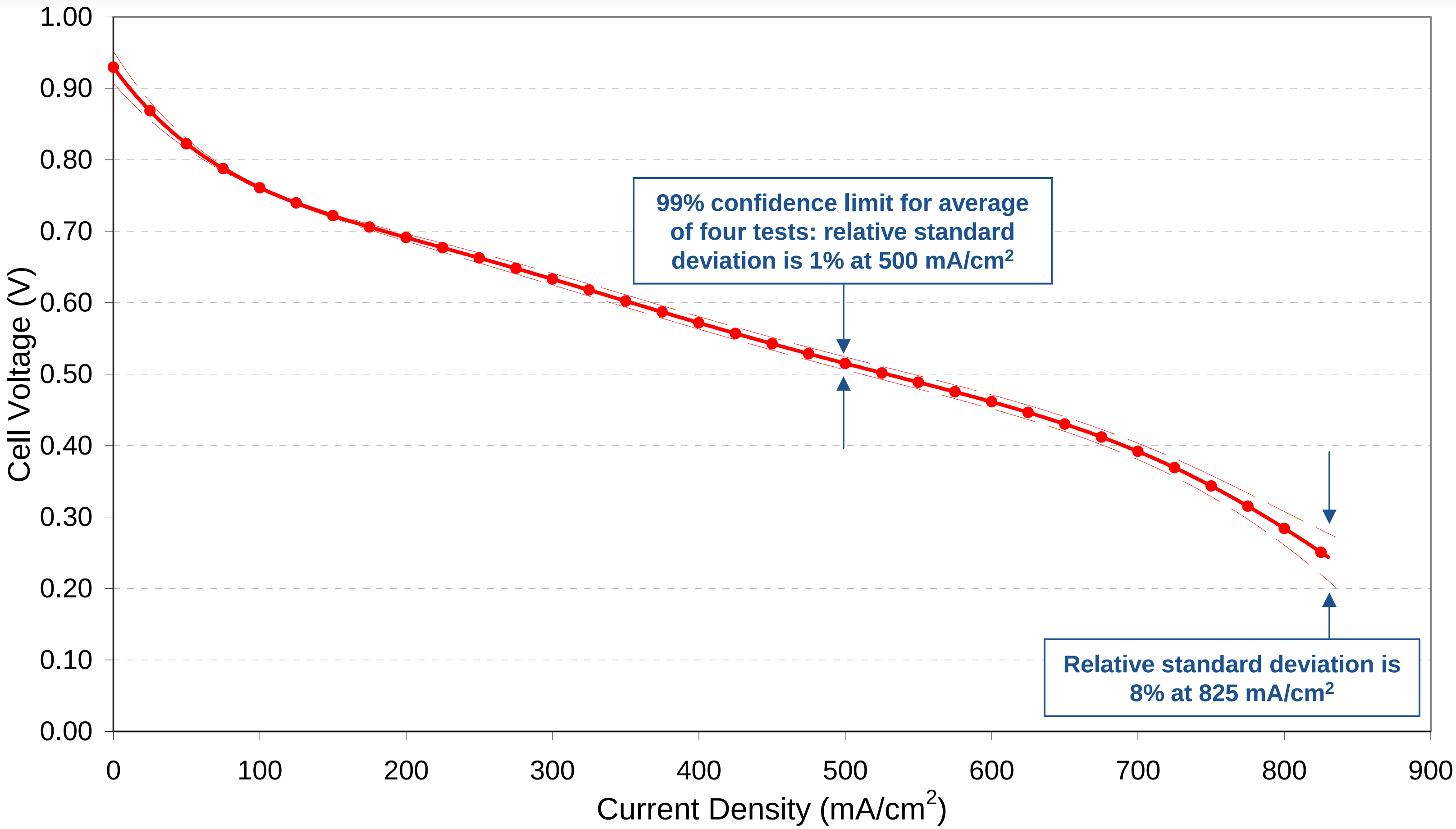
- Single cell fuel cell test parameters:

	Enersol / PSU
Electrode Assembly	Electrochem / Std. Gas Diffusion Electrodes
Membrane/Electrolyte	Nafion 115
Electrode Catalyst (anode/cathode)	Pt/Pt
Catalyst Loading (anode/cathode) [mg/cm^2]	0.5/0.5
Nafion Ionomer Loading [mg/cm^2]	0.8
Electrode Area [cm^2]	5.0
Temperature (°C)	70
Anode Gas	UHP H2 + odorant
Cathode Gas	Air
Odorant Loading	3, 30, 300 ppm

Schematic of Fuel Cell Test System



Polarization Curve - Hydrogen



Polarization curves with commercial Nafion 115 MEA. Pt loading of the anode and cathode: 0.5 mg/cm². Cell temperature: 70°C, pure hydrogen/air used (50 and 200 ml/min), for the anode and cathode, respectively. Cathode humidification.

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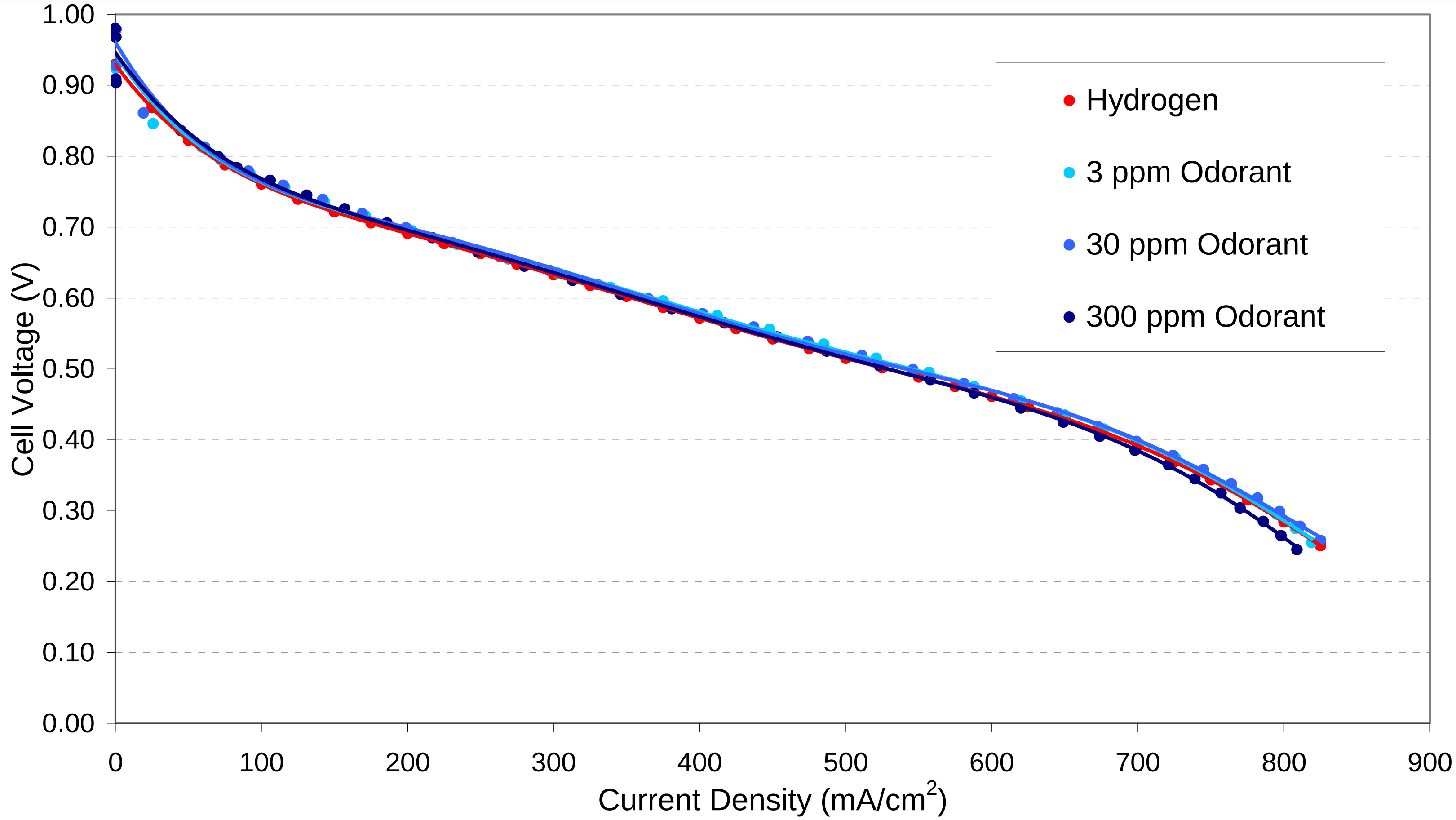
Polarization Curves: Odorized Hydrogen



Polarization curves with commercial Nafion 115 MEA. Pt loading of the anode and cathode: 0.5 mg/cm². Cell temperature: 70°C, odorized hydrogen/air used (50 and 200 ml/min), for the anode and cathode, respectively. Cathode humidification.

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Fuel Utilization and Odorant Accumulation

$$\text{Fuel Utilization (\%)} = \frac{I_{cell}}{I_{fuel}} \times 100$$

I_{cell} = Current drawing from the cell

$$I_{fuel} = \frac{n \bullet F \bullet (\text{Flow rate of gas}) \bullet (\text{Density of gas})}{(\text{Molecular weight of gas})}$$

<u>Odorant Accumulation</u>

This concept of odorant accumulation becomes critical at high fuel utilization. Necessitates the need to test high odorant concentrations in hydrogen.

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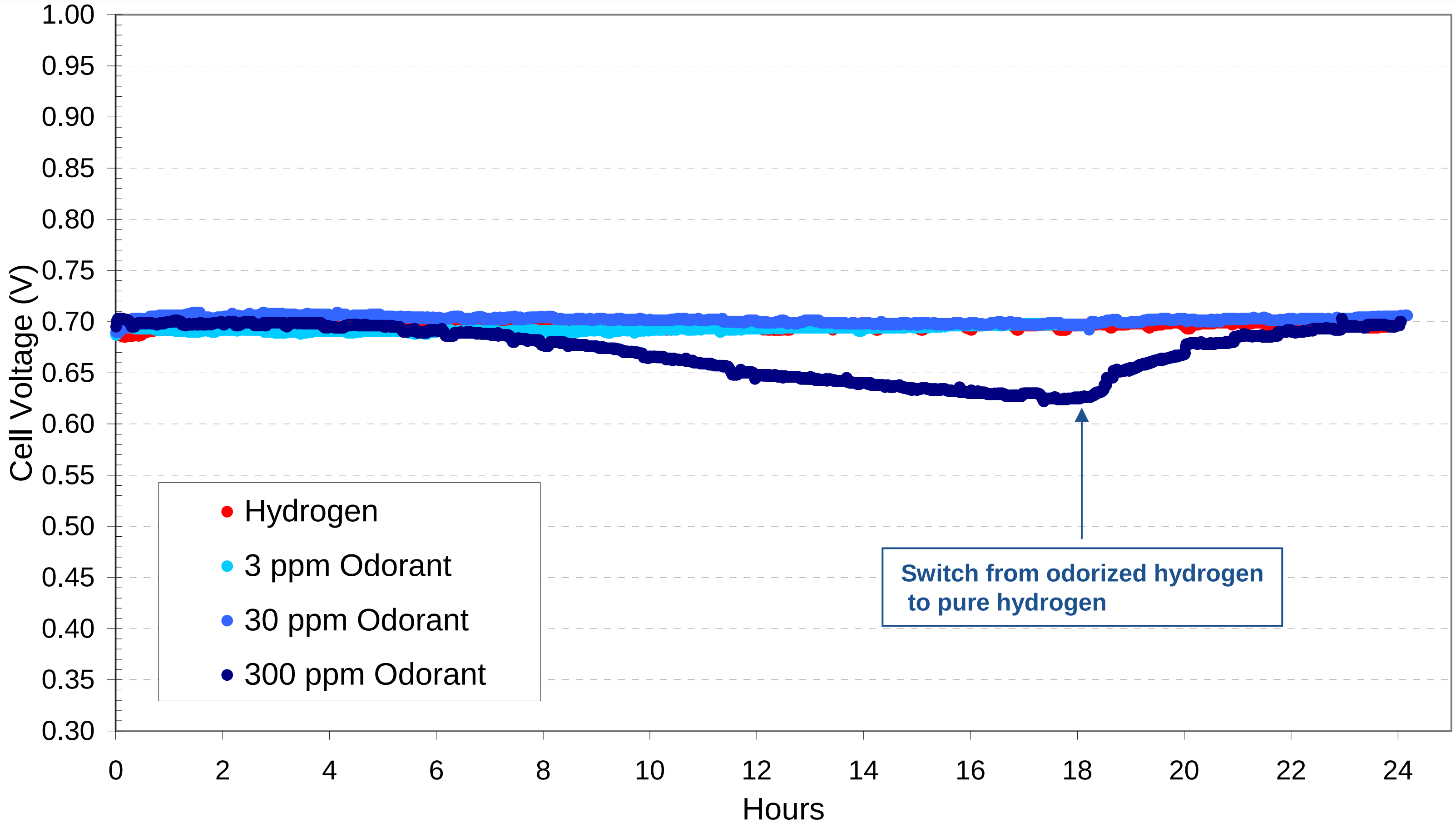
Degradation Test: Odorized Hydrogen



Long term fuel cell performance of commercial Nafion 115 MEA (under current density of 200 mA/cm^2). Pt loading of the anode and cathode: 0.5 mg/cm^2. Cell temperature: 70°C, pure hydrogen/air with cathode humidification.

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Summary and Conclusions

- Impact of odorization on fuel cell performance was tested over a range of odorant concentrations
- No adverse effects on fuel cell performance (IV-curves or long-term degradation) for concentrations up to 30 ppm loading in hydrogen
- This work provides a basis for addition of odorants to hydrogen at concentrations well above the odorant detection threshold, but below the critical concentration where fuel cell performance is impacted
- At elevated odorant concentrations where deterioration in fuel cell performance occurs, complete recovery in the cell voltage can be attained upon supplying pure hydrogen to the fuel cell

Future Work

- Facilitate further PEM fuel cell compatibility testing at lower catalyst loading and using thinner membrane materials
- Fuel cell degradation tests over longer time period
- Characterize odorant stability under high pressure
- Demonstrate / validate minimum odorant loading requirements in high pressure to deliver sufficient sensory detection
- Demonstrate hydrogen odorization within pipeline and fueling infrastructure

Acknowledgments

- DOE Hydrogen Fuel Cells Technologies & Infrastructure Program, Safety Codes and Standards
- FreedomCAR and Fuel Partnership, Safety Codes and Standards Tech Team
- Sandia National Laboratories

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Contact Information

Enersol Incorporated
North America, L.P.
10363-B Democracy Lane
Fairfax, VA 22030

Enersol
Hydrogen Odorization Technology

Michael Sprague, M.S.
General Partner
Ph: 403.481.1241
Email: michael.sprague@shaw.ca

Patrick Flynn, M.S.
General Partner
Ph: 610.724.9411
Email: enersol_pjf@comcast.net

Why is Odorization Important?

- *There is a need for fully redundant safety systems, & contingency:*
  - *Sensors enable mechanical detection and have ability to mechanically shut systems down;*
  - *Odorization allows sensory detection by humans;*
  - *The probability of both systems failing at the same time is exceedingly low.*
  - *Odorants provide contingency in case leakage occurs in conjunction with a power loss or function loss in the sensor/actuator system.*

Note: It is absolutely true that some redundancy is achieved through the combination of H2 gas detectors with pressure and temperature sensors.

- *Odorization becomes an essential redundant safety feature because it becomes difficult for sensors to be distributed with sufficient density to detect all leak situations.*
  - *Not all environments where a vehicle may be present, in real world operation, could be instrumented, particularly in the near term and at reasonable cost;*
  - *Portable hydrogen applications will require independent verification of a leak.*
  - *Consider the natural gas case → Leak sensors are only distributed in certain specialized environments, such as central refueling & maintenance facilities for CNG vehicles.*
- *Odorization offers unique detection → Sensory (human sence) vs. Mechanical*
  - *Odorants are fail safe, in that they provide independent verification of a leak*
- *Odorization provides enhanced public confidence*

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Why is Odorization Important?

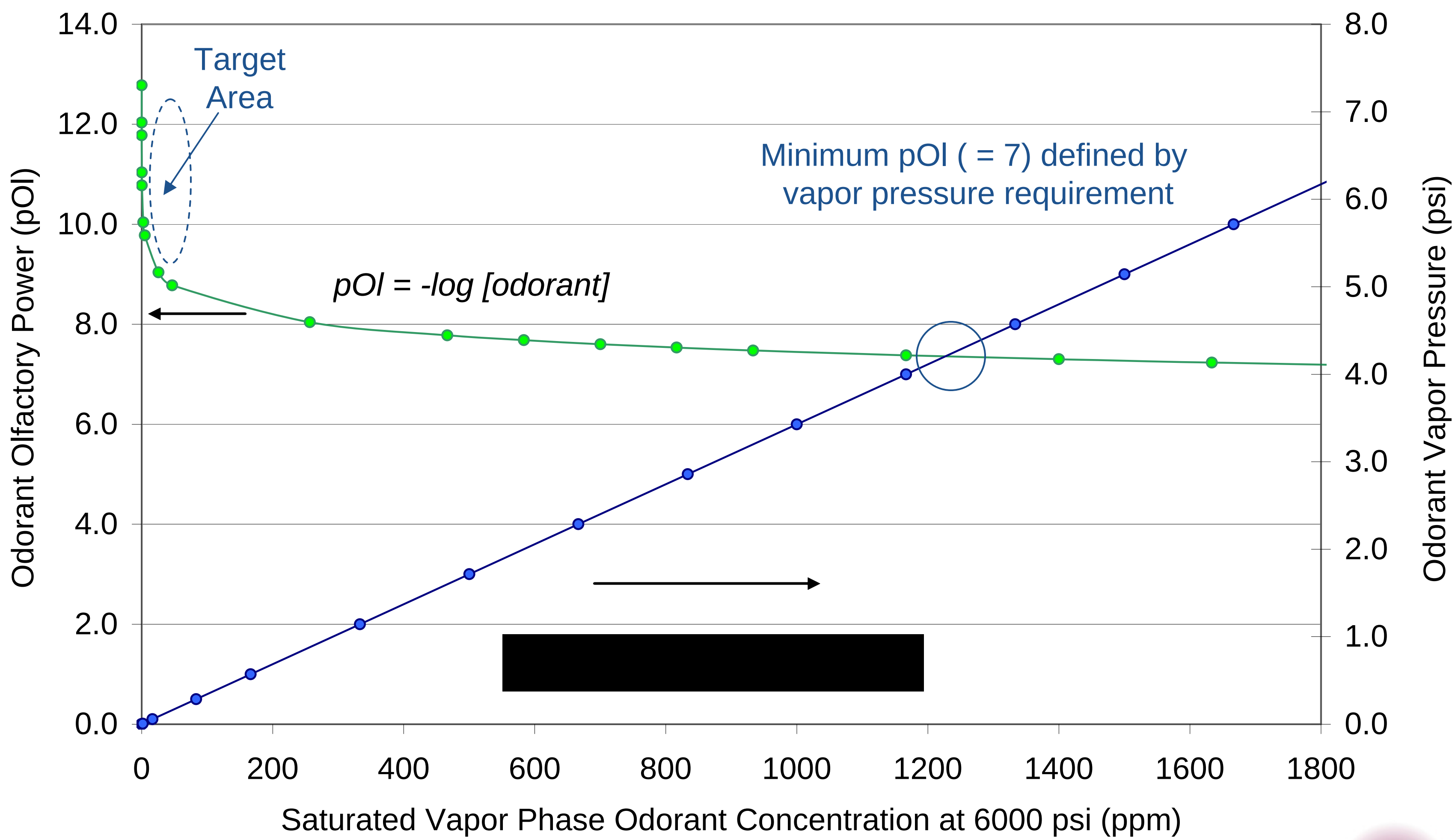
- *A Safety system comprised of Sensors & Odorants are required:*
  - *Mechanical sensors mainly abate or minimize financial risks (infrastructure, Insurance, liability)*
  - *Odorization mainly abate or minimize safety risk posed to humans (loss of life, injury)*
  - *An odorant/sensor combination inherently provides redundancy across many incident scenarios at insignificant additional cost.*
  - *Natural Gas Industry has a good track record with regards to Safety, once odorants were implemented*

Note: Consider the most simple of detectors used for Human Safety → Smoke Detector

- *Good news → 90% of Homes in the U.S. have at least 1 smoke detector*
- *Bad news → A substantial proportion of the smoke detectors installed do not work*
- *Home Site Surveys demonstrate that between 25-30% of installed detectors do not function when tested*
- *Failures are due to malfunction of the alarm itself, others due to a dead battery, and some do not function because the battery has been removed (false detection due to cooking, ect)*

- *Odorant Cost → Odorization proves to be a cost effective safety system for users in real world application*
  - *Cost varies depending on type of odorant and odorant loading;*
  - *Odorization costs per fill depend on size of fuel tank etc. → Many variables, however cost is small compared to the cost of hydrogen;*
  - *Cost of odorants is estimated (back of-the-envelope) to be → $1-2 per 5-10 Kg of hydrogen dispensed.*

pOI – Pvap Relationship



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H2 Dispersion

- Hydrogen's use as a fuel is a greater safety risk in confined spaces where there are enclosures or boundaries to contain the volume of leaking H_2
- Containment allows H_2 to collect or accumulate over a short period of time creating flammable or explosive hazards.
- It is identified in Enersol's odorant selection criteria that odorants must perform successfully even in the most extreme environmental conditions → within a stagnant air enclosure, an environment which poses the worst-case risk during a H_2 leak event

Dispersion = *Convection / Advection* + *Diffusion*

Convection / Advection ↓

Dominant in Open Air Environment
(Turbulent Mixing)

Diffusion ↓

Dominant in Stagnant Air Environment
Or Confined Space
(Mixing by Molecular Diffusion)

H2 Dispersion con't...

- Because of molecular weight and dispersion properties of H_2 relative to general classes of odorant compounds, it becomes obvious that no odorant composition leaking in a diffusion limited (Stagnant) environment will track in a like manner as H_2

D_{H2} = 0.76 cm^2/s (at ambient temperature)

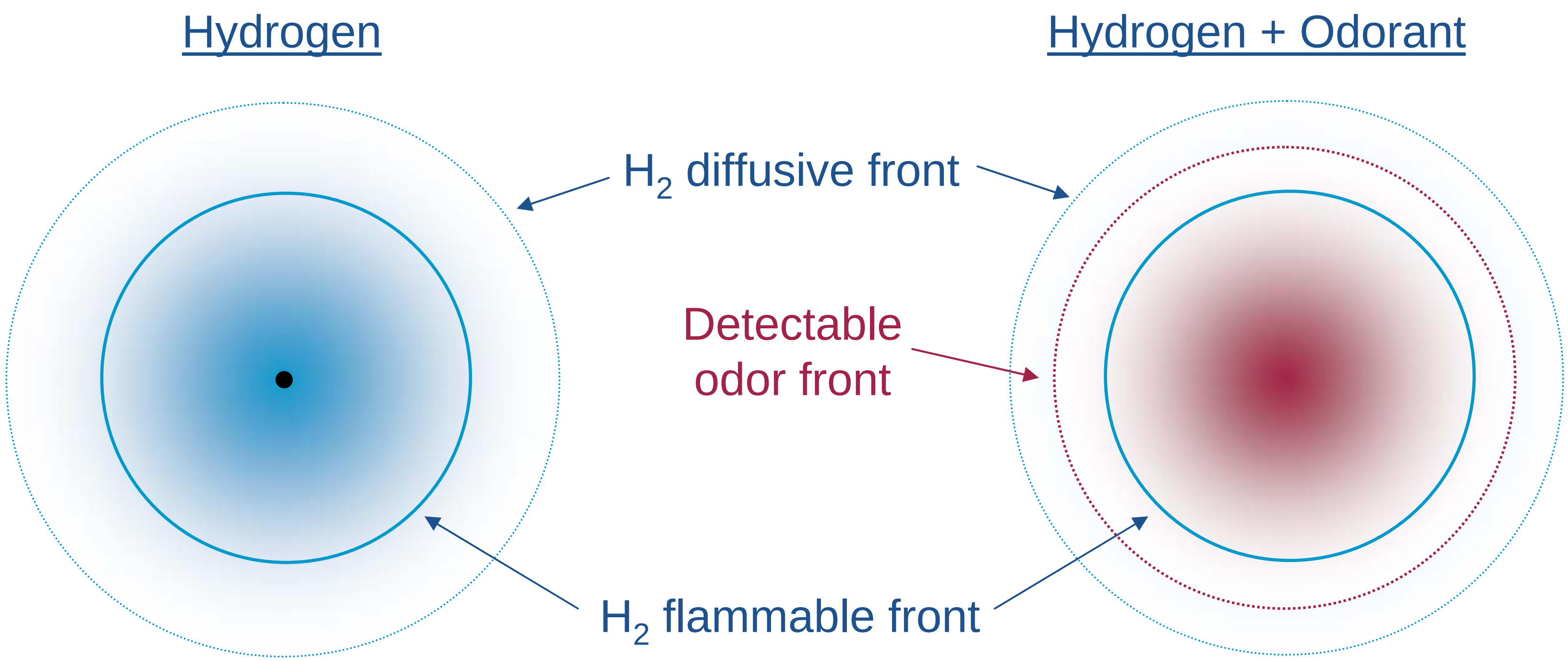
$D_{odorant, average}$ = 0.12 cm^2/s

- Enersol devoted significant effort toward finding odorant compositions that ensure detection prior to H_2 accumulating to a flammable concentration, a known performance based criteria required by the Department of Transportation (**49 CFR 192.625**)

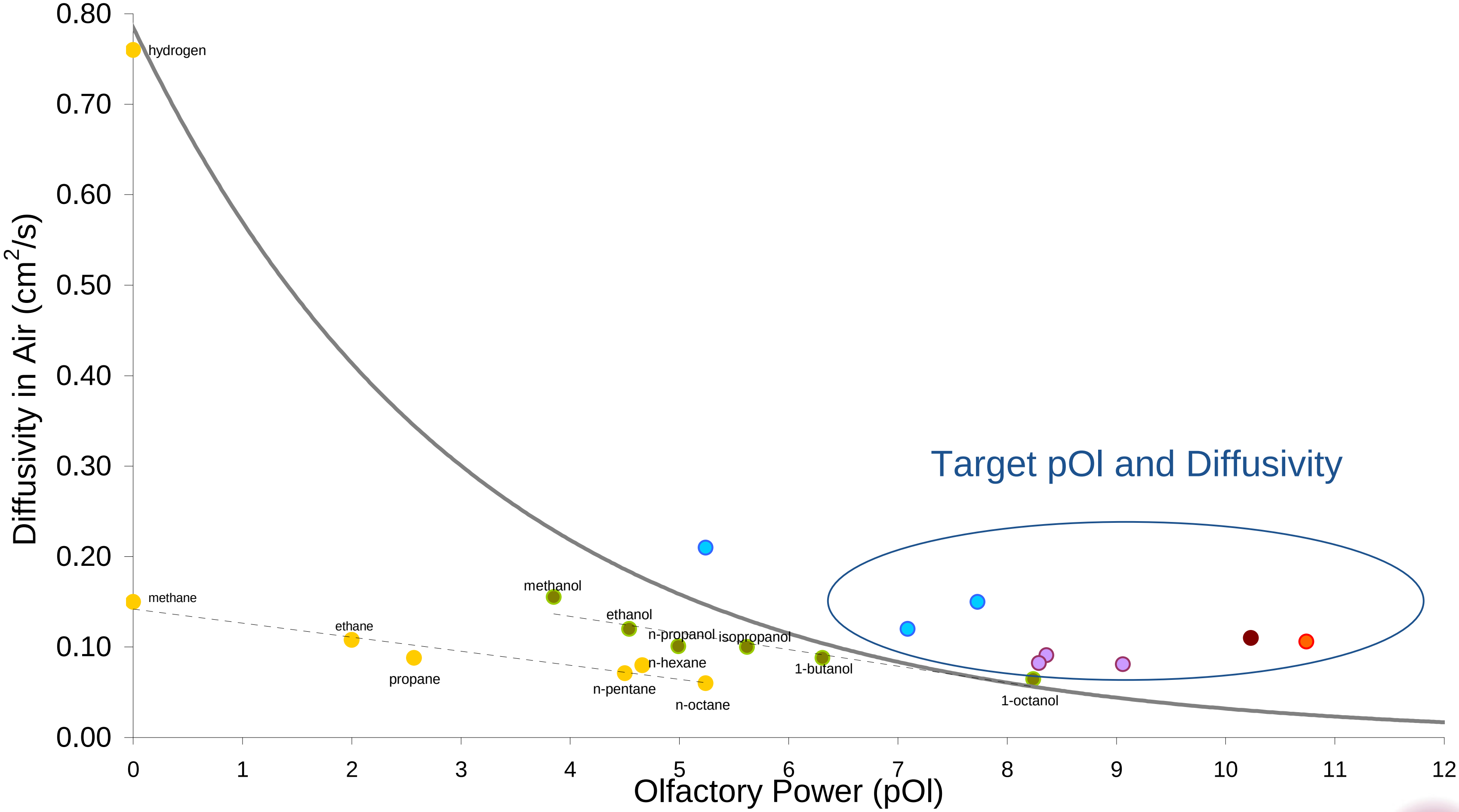
- Enersol has identified classes of odorants which deliver sufficient sensory detection prior to H_2 accumulating to both the LFL and 20% of the LFL, proving for sufficient performance even at the most extreme and dangerous conditions

Note: Even though a diffusion limited leak scenario is the scenario of most concern, actual H2 Dispersion by molecular diffusion is highly unlikely. Any indoor environment would have some form of ventilation and or some external advective force driving dispersion (whether it be wind or air temperature variations) , enabling any odorant to track very well with Hydrogen.

2D Diffusion: Odorant vs Hydrogen



Diffusivity - pOI Relationship



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Hydrogen Odoization: Conceptual Cost-Benefit Analysis

Hydrogen Odorization
Cost - Benefit

Cost: Catastrophic system failure / mechanical sensor loss / *undetected* release of hydrogen.

Major Incident: loss of life, property, infrastructure.

Risk: loss of public confidence in hydrogen technology; impedance of hydrogen technology market penetration.

Benefit: Odorization is a non-instrumented redundant safety system. Both systems may be needed (sensors and odorants).

Reduces incident frequency: Not all environments can be instrumented. Contingency in case leakage occurs in conjunction with power loss or system/sensor loss. Odorants are fail-safe giving independent verification of a leak.

Reward: Increases consumer and public confidence in hydrogen technology.

Proactive vs. Reactive
Odorization as a safety system is expected to reduce the number of incidents.

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