BILIWG Meeting: DOE Hydrogen Quality Working Group Update and Recent Progress

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DOE Hydrogen Quality Working Group (H2QWG) Objectives

- Develop a process to determine hydrogen quality requirements for fuel cell vehicles based on life-cycle costs
  - evaluate impact of fuel quality requirements on hydrogen production and purification costs
  - evaluate impact of contaminants on fuel cell performance, durability, and related life-cycle costs

- Identify information gaps and the R&D needed to fill those gaps
  - recommend approaches to funding and conducting the needed R&D

H2QWG has prepared a draft Roadmap and submitted it to DOE for review and comment

The H2QWG focus is on the near- to mid-term (to 2015)

- Production: distributed (forecourt) production
  - reforming of natural gas (autothermal & steam reforming)
  - reforming of renewable fuels, e.g., ethanol (i.e., E-95 & E-85)
  - electrolysis (alkaline and PEM electrolyzers)
- Purification:
  - pressure-swing adsorption, PSA (may be aided by TSA)
  - hydrogen-permeable membrane separators
- Use in fuel cell systems (no storage effects):
  - performance / cost / durability impact of
    - electrochemically active contaminants
    - inert contaminants
- Analysis and quality verification
  - available analytical technologies (mostly research laboratory)
  - standardized (commercially accepted) technologies

Draft Roadmap
Summary findings (preliminary)

- PSA can achieve most of the H_2 impurity limits proposed by SAE / ISO, but it may add 5-20% to the cost of H_2
- PSA is ineffective for removing helium
- There are some contaminants for which PSA's effectiveness has not been reported (e.g., formic acid)
- The proposed levels for CO_2, O_2, and inert gases may be overly restrictive (based only on their effects on fuel cell performance)
- Testing and analysis may be a very significant cost factor, both for certification and for control of hydrogen quality

Draft Roadmap Recommendations (preliminary)

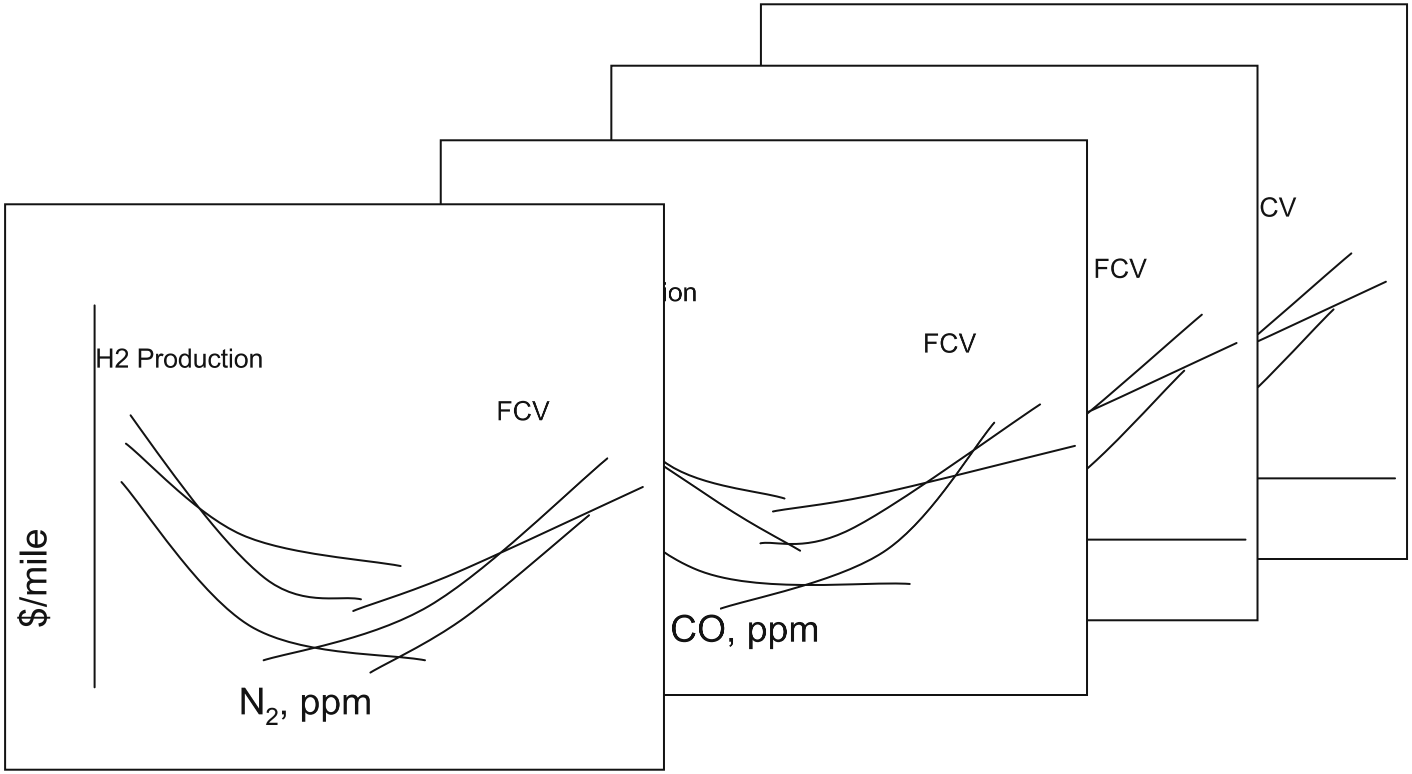
- Quantify the cost and performance of PSA vs. H_2 quality to determine life-cycle costs

- Quantify the effects of specific contaminants on cost and performance of fuel cells, and the costs of overcoming performance degradation

- Develop low-cost methods for gas sampling and analysis for certification and on-line quality control (and fuel quality regulation enforcement)

Modeling and experimental data are being used to assess the impact of specific fuel impurities on life-cycle costs

- Study individual contaminants
- Evaluate potentially different effects for different production / purification and fuel cell operating conditions



The H2A model is the basis for the cost of hydrogen

- Based on options / assumptions available in H2A

- The current H2A model does not reflect sensitivity to hydrogen quality
  - Add effects of hydrogen recovery and process efficiencies

- Component models are being developed to support the H2A
  - Argonne is modeling a steam reformer + PSA process
  - Results will be incorporated into H2A
    - *Look-up tables*
    - *Interface with component module*

- End Result
  - Cost of hydrogen (trend) = f (Process pathway, conditions, efficiency, contaminant level, etc.)

Typical reformate compositions from natural gas and ethanol are similar

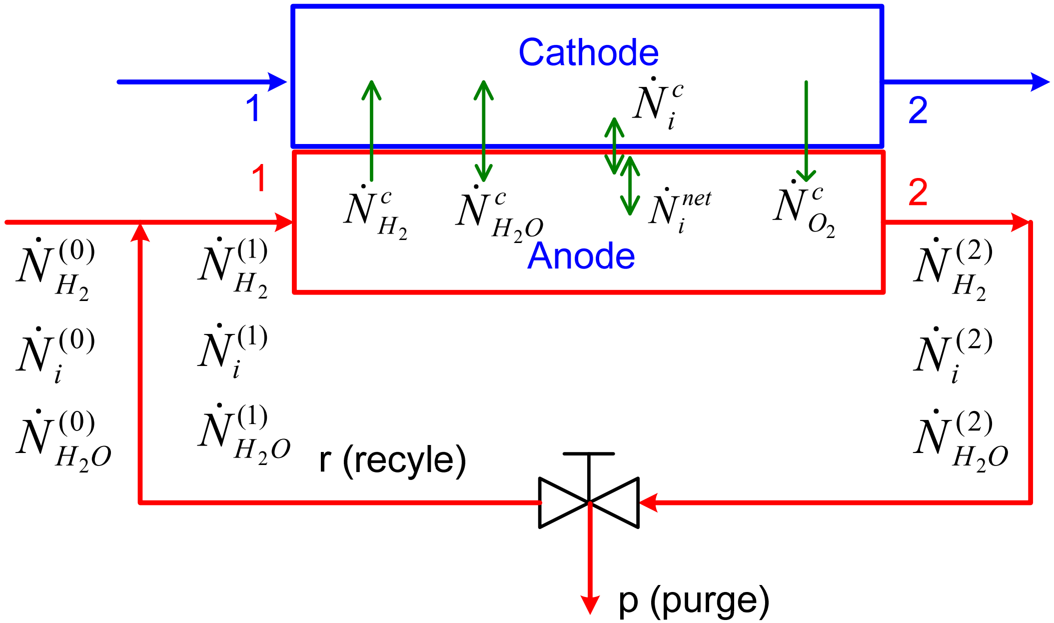
Product gas composition from steam reforming

Species	Natural Gas	Ethanol
H_2	75–80%	70–75%
CO_2	15–18%	22–25%
CO	0.1–4%	0.1–4%
CH_4	0.5–3%	0.5–3%
Non-CH_4 HCs	0.5%	0.5%
He	$\leq$500 ppm	trace
N_2	100 ppm	100 ppm
Ar	5 ppm	5 ppm
H_2S	5 ppm	1 ppm
O_2	trace	trace
NH_3	trace	trace

Reformate from ethanol may also have traces of organic acids and aldehydes

Fuel cell stack model:
Effects of fuel impurities on fuel cell performance

- Current generation and transport in catalyst layers
- Transport of ions across PFSA membrane
- Kinetics of HOR and ORR over Pt catalyst
- Multi-species diffusion in porous media
- Water transport across PFSA membranes
- Capillary transport of water across GDL and catalyst
- 2-phase flow in gas channels



- Once-through cathode stream
- Anode gas recirculation

$$R = \dot{N}_r / \dot{N}_p$$

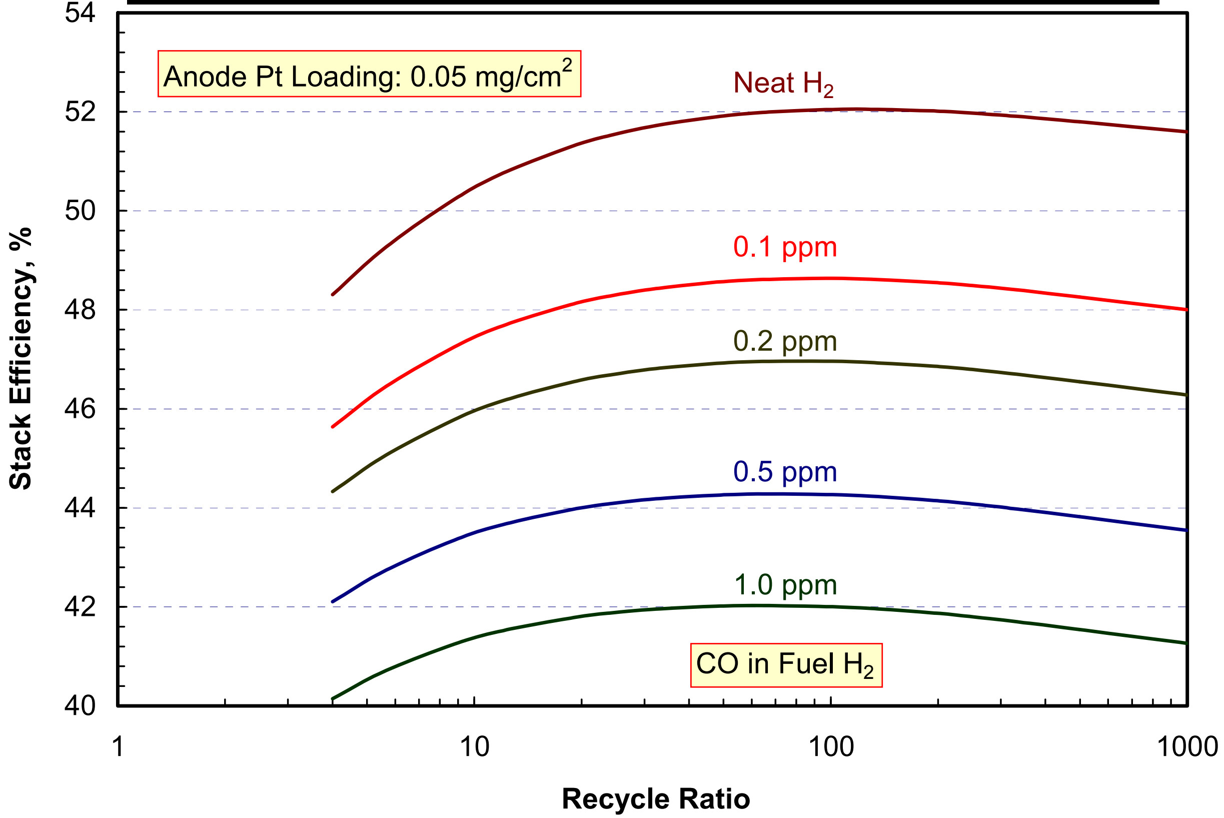
- Crossover of H_2, O_2, N_2, H_2O and NH_3

Mechanistic models of electrocatalyst poisoning

- Hydrogen Oxidation Reaction
  - $H_2 + 2M \Leftrightarrow$ (Dissociative Adsorption)
  - $M\text{-}H \Rightarrow M + H^+ + e^-$ 2M-H (Electrochemical Oxidation)
- CO Poisoning of Pt
  - $CO + 2M \Leftrightarrow M_2\text{-}CO$ (Associative Adsorption on Bridge Sites)
  - $CO_2 + 2M\text{-}H \Rightarrow M_2\text{-}CO + H_2O$ (Reverse Water-Gas Shift)
  - $M_2\text{-}CO + H_2O \Rightarrow 2M + CO_2 + 2H^+ + 2e^-$ (Electrochemical Oxidation)
- Reactions with Oxygen
  - $M_2\text{-}CO + ½ O_2 \Rightarrow 2M + CO_2$ (CO Oxidation)
  - $2M\text{-}H + ½ O_2 \Rightarrow 2M + H_2O$ (H_2 Oxidation)
- H_2S Poisoning of Pt
  - $M + H_2S \Leftrightarrow M\text{-}H_2S$ (Reversible Associative Adsorption)
  - $M\text{-}H_2S + M\text{-}H \Rightarrow M_2S + 3/2H_2$ (Irreversible Dissociation)
  - $M_2S + 2H_2O \Rightarrow 2M + SO_2 + 4H^+ + 4e^-$ (Electrochemical Oxidation)

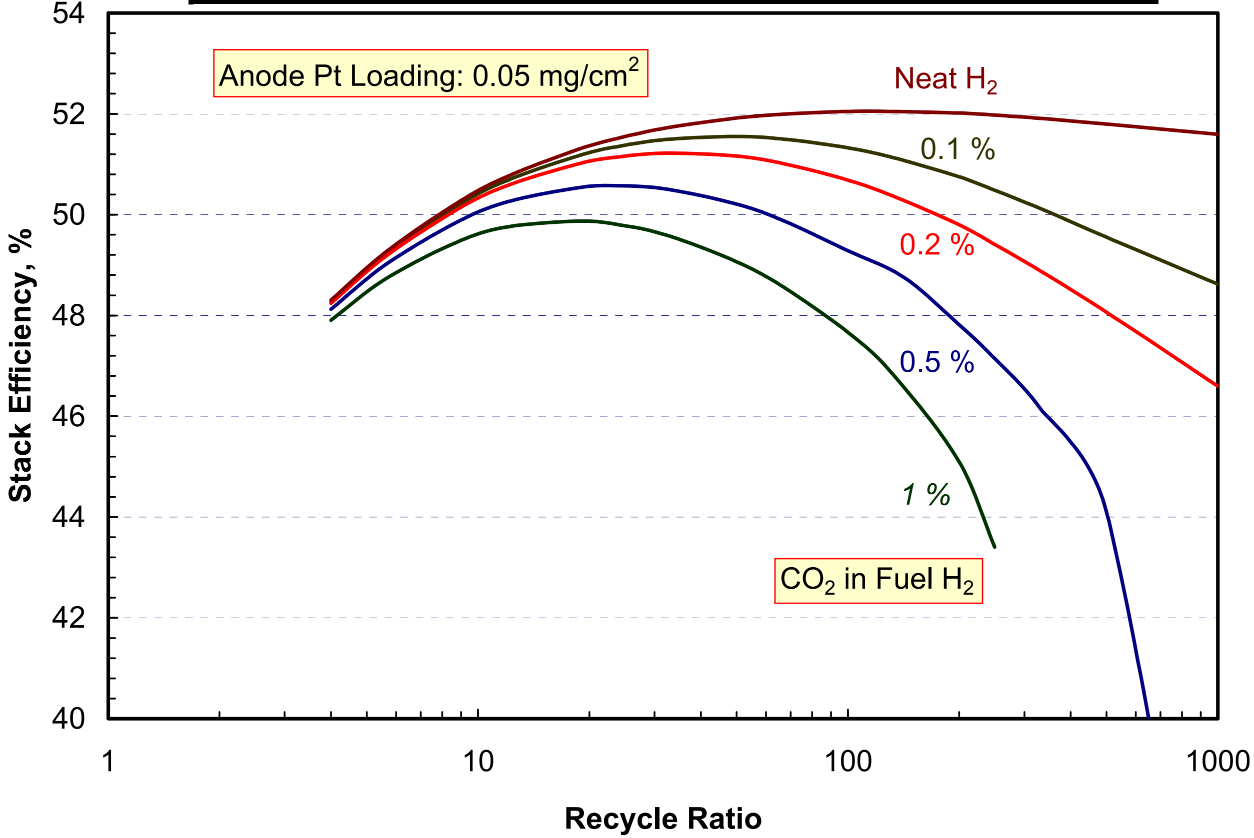
CO poisoning:
Effect of Pt loading on fuel cell performance degradation

Pt Loading	0.4 mg/cm^2		0.05 mg/cm^2	
CO, ppm	ΔV	$\Delta\eta$	ΔV	$\Delta\eta$
0.1	18.4	1.5	42.3	3.4
0.2	28.1	2.2	63.3	5.1
0.5	44.1	3.6	95.9	7.8
1.0	60.5	4.9	124.3	10.0



CO_2 poisoning:
Effect of Pt loading on fuel cell performance degradation

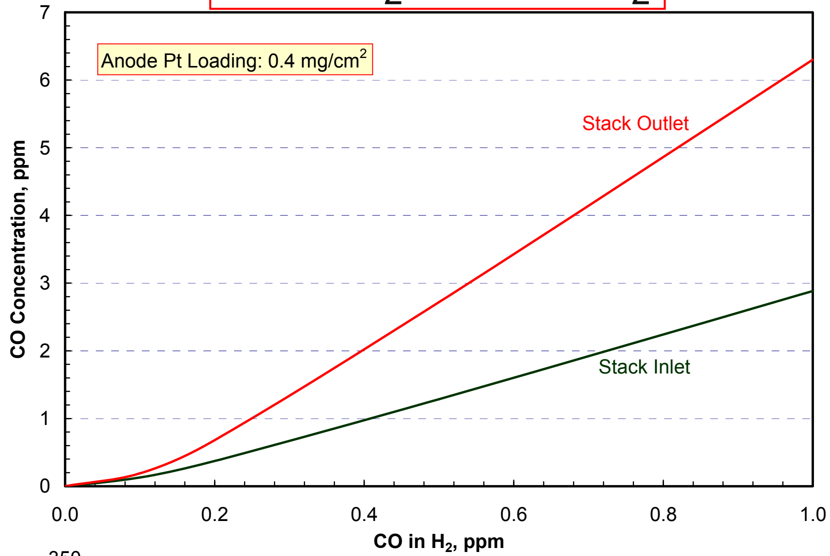
Pt Loading	0.4 mg/cm^2		0.05 mg/cm^2	
CO_2, %	ΔV	Δη	ΔV	Δη
0.1	5.7	0.7	4.2	0.4
0.2	7.8	1.1	5.6	0.8
0.5	14.3	1.8	11.1	1.4
1.0	20.5	2.5	17.4	2.1



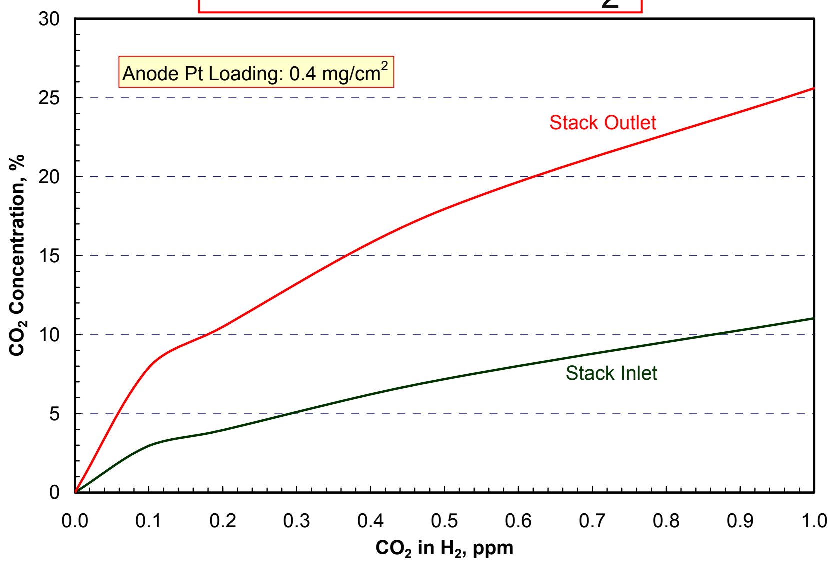
Buildup of CO and CO_2 in the recirculating anode gas

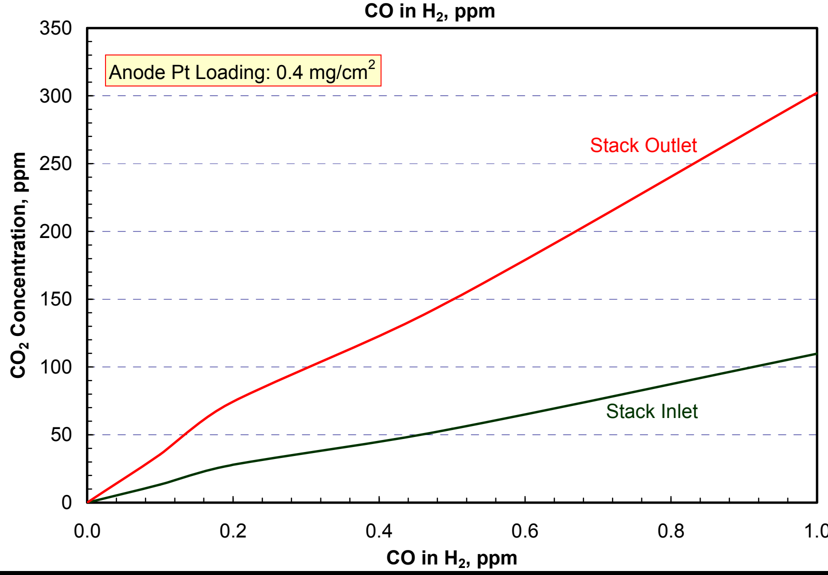
- Fraction of CO at stack inlet that is converted to CO_2 by O_2 crossing over from cathode (internal air bleed, 50-μm membrane)
  - <50% for 0.1-ppm CO in fuel H_2
  - ~20% for 1-ppm CO in fuel H_2

No CO_2 in Fuel H_2



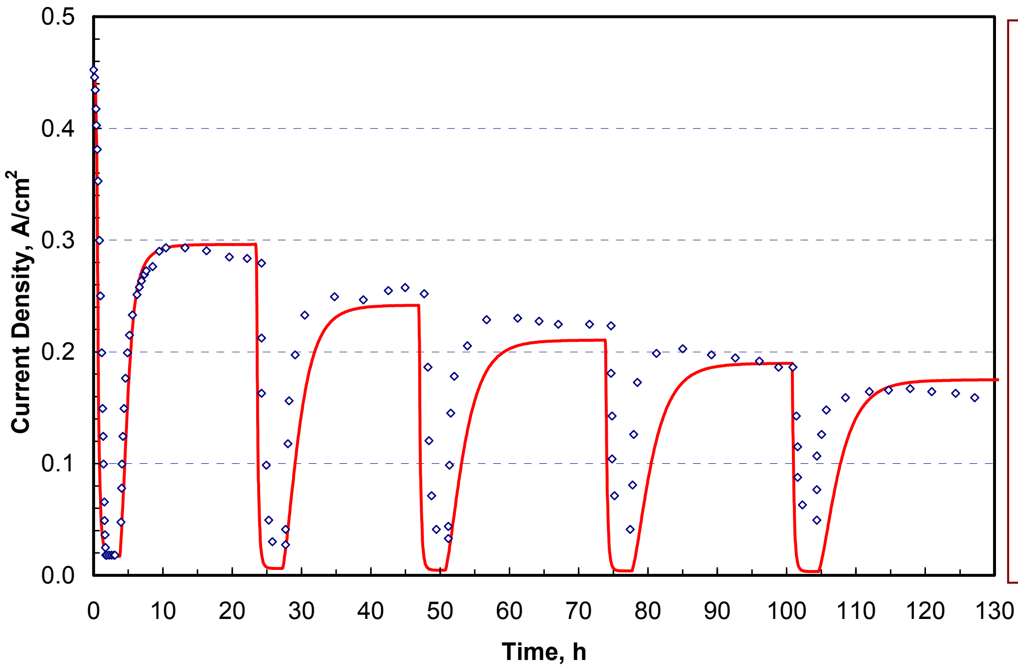
No CO in Fuel H_2





H_2S poisoning: Transient poisoning and recovery

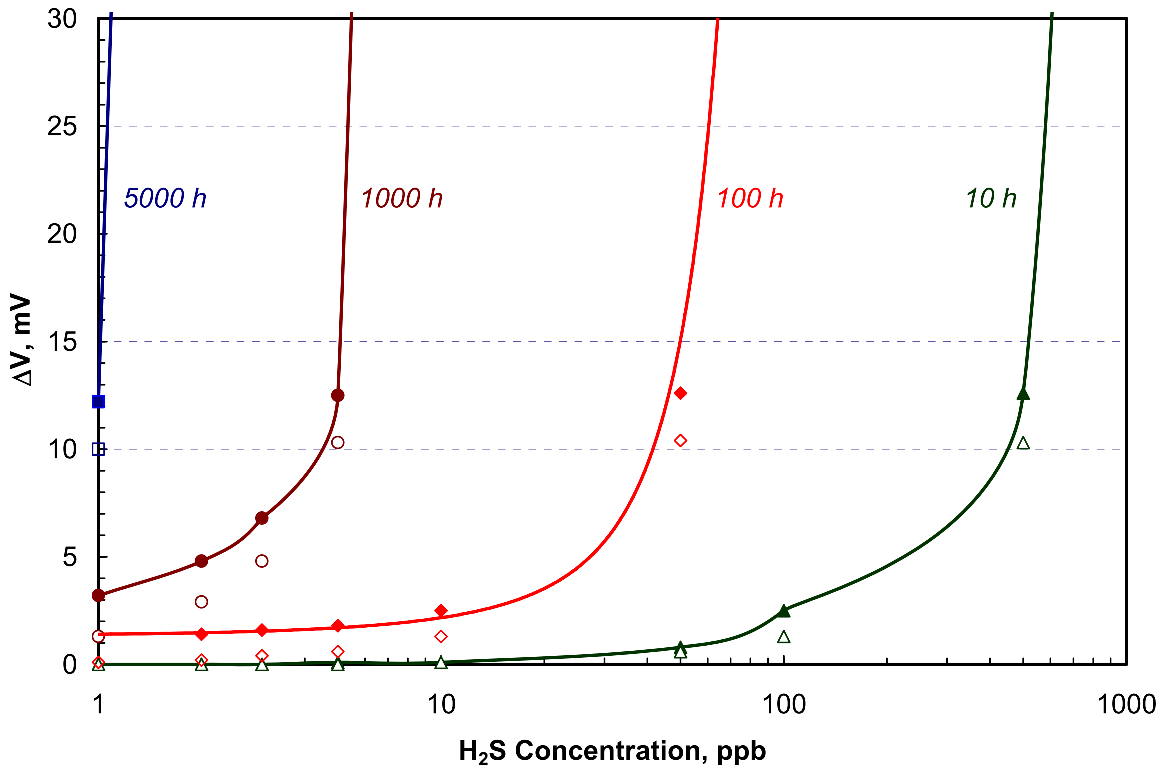
- Data from Mohtadi, PhD thesis, USC (2004)
- Kinetic constants for H_2S reactions derived from measured transient poisoning and recovery response of current density
- Partial recovery in neat H_2, progressive degradation over five cycles



- Gore PRIMEA MEA Series 5510
- 25 μm membrane
- 0.4 mg/cm² Pt on anode
- 0.4 mg/cm² Pt on cathode
- Poisoned by 50-ppm H_2S for 3.8 h
- Recovery in neat H_2 for 24 h
- Constant cell voltage: 0.69 V
- 70°C, 101 kPa

Effect of H_2S dosage on cell voltage decline

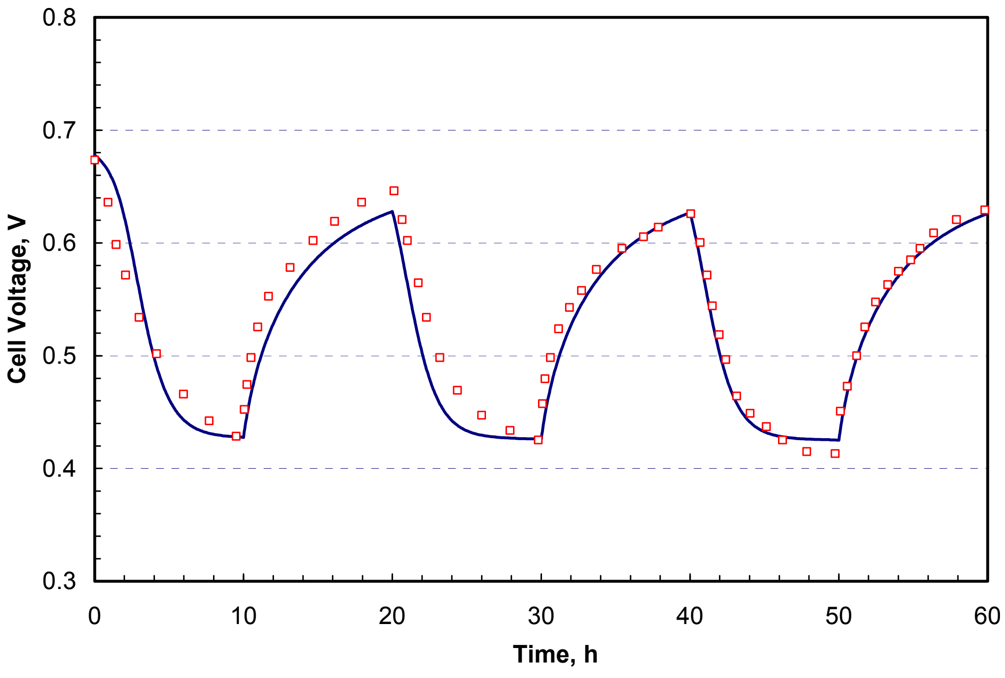
- H_2S concentration needs to be <1 ppb to limit decrease in cell voltage at 1.05 A/cm² to 10 mV after 5000 h



- 1.05 A/cm² current density
- 70% H_2 utilization per pass
- 50% O_2 utilization
- Open Symbols (R=10)
- Closed Symbols (R=100)

NH_3 poisoning: Transient poisoning and recovery

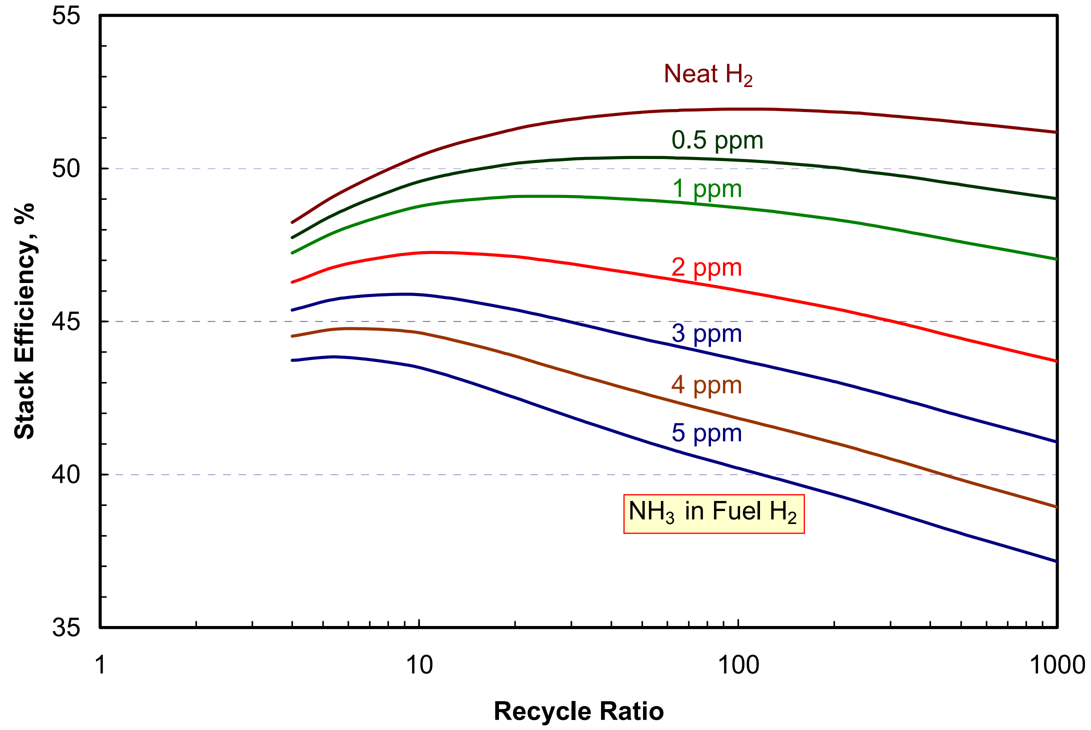
- Data from Soto et. al., Electrochemical and Solid-State Letters, 6 (7) A133-A135, 2003
- Kinetic constants for NH_3 uptake reactions derived from measured transient poisoning and recovery response of cell voltage



- Gore PRIMEA MEA Series 5621
- 35 μm membrane
- 0.45 mg/cm^2 Pt-Ru alloy on anode
- 0.6 mg/cm^2 Pt on cathode
- Poisoned by 200-ppm NH_3 for 10 h
- Recovery with neat H_2 for 10 h
- Constant current density: 0.6 A/cm^2
- 70^{o}C, 101 kPa

Effect of NH_3 buildup on stack efficiency

NH_3 in Fuel H_2	Recycle Ratio	Purge	$\Delta\eta$
0.5 ppm	50	~2%	1.6%
1 ppm	25	~4%	2.9%
2 ppm	12	~7%	4.7%
5 ppm	6	~15%	8.1%



- Results at constant 1.05 A/cm²

Held a hydrogen quality modeling workshop at Argonne on August 30-31, 2007

- Purpose: to describe models being developed to assess impurity effects on fuel cell performance and durability (and hydrogen purification by PSA)
  - Describe the significant components and processes in the models
  - Provide details of input parameters
    - *Sensitivity of output results to input parameters*
  - Define data needed to validate / refine models
  - Develop mutual understanding between modelers and experimentalists on what is achievable
  - Identify limitations / capabilities of modeling and experimentation
    - *How to reduce limitations, increase capabilities*
  - Develop specific means for maintaining continuing interactions among this research community

Status of impurities effects modeling and future work

- We have developed a framework for modeling the effects of impurities (site blockage, ion exchange, HOR and ORR reaction kinetics for hydrogen oxidation and oxygen reduction, etc.)
  - Quantitatively predict effects of impurities, not just to explain experimental observations
  - Assess effects of simultaneous presence of multiple impurities
  - Simulate steady-state and dynamic effects
  - Modify / update mechanisms as additional data become available
  - Extend models to other fuel impurities
  - Extend models to air impurities

Summary

- The H2QWG has prepared and submitted to DOE a draft roadmap for continuing activities to address issues of hydrogen quality for automotive fuel cell systems

- DOE contaminant effects projects are being complemented by the fuel cell system modeling work at Argonne

- There is close interaction between these activities and the related work of SAE and ISO by participation in Working Group meetings and workshops