Low Cost Sensors for Hydrogen and CO in Fuel Cells

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Project Structure

• Illinois Institute of Technology
  – administration, scientific leadership, sensor R&D, prototype production, and delivery

• SensorTek, Inc., J&N Enterprises
  – industrial partner, production scale-up, in-service testing, parts, molds and use thereof, application reviews
Chemical Sensors Are Essential in FCVs as feedback elements in power system, and for safety.

* = highly simplified
Goals Updated for 2001

<table>
<thead>
<tr>
<th>Hydrogen Process Sensor</th>
<th>Hydrogen Safety Sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 0 to 100% in reformate matrix</td>
<td>• 0 to 10% in air</td>
</tr>
<tr>
<td>• 10 – 30 mol % water</td>
<td>• 10 – 98 % RH</td>
</tr>
<tr>
<td>• 3 atm total pressure</td>
<td>• 1.0 s response time</td>
</tr>
<tr>
<td>• 0.1 – 1.0 s response time</td>
<td>• -30 to 80°C</td>
</tr>
<tr>
<td>• 70 to 150°C</td>
<td>• Lifetime 5 yr</td>
</tr>
</tbody>
</table>

Hydrogen Sulfide Sensor

• 0.05 – 0.5 ppm in reformate
• Up to 400°C
• Response time < 1 min
Goals Updated for 2001 (Cont’d)

<table>
<thead>
<tr>
<th>CO Lo-Range Sensor</th>
<th>CO High-Range Sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Pre-stack protects catalyst</td>
<td>• Raw reformate: controls reformer operation</td>
</tr>
<tr>
<td>• 1 to 100 ppm in reformate matrix</td>
<td>• 0.1 to 2.0% CO in reformate matrix</td>
</tr>
<tr>
<td>• 10 – 30 mol % water</td>
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</tr>
<tr>
<td>• 3 atm total pressure</td>
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<tr>
<td>• 70 to 150°C</td>
<td>• 250-800°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CO Mid-Range Sensor</th>
<th>CO Safety Sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 100-1000 ppm in reformate matrix</td>
<td>• 0-1000 ppm</td>
</tr>
<tr>
<td>• 250°C</td>
<td>• Ambient conditions</td>
</tr>
</tbody>
</table>
Achievements

• Ag/AgCl reference electrode in liquid-electrolyte cell:
  – eliminates long-term drift due to hydrogen
  – reduces response time by 5-fold

• Polymer barrier limits access to cell
  – increases range of hydrogen sensor to > 1 atm.
  – eliminates CO interference in hydrogen measurements
  – barrier good to 300 °C, can be used with any sensor

• Response times reduced using dynamic response
  – Using Rate of change of signal gives $T_R$ of ~3 sec

• Stable signal for CO in presence of high hydrogen
Achievements (cont’d)

• Solid-state sensors based on NASICON sodium conductor
  – Very fast response times to nitrogen oxides, hydrogen
  – Extremely pure NASICON phase by proprietary method
  – Tunable selectivity by varying electrode materials and doping with inorganic salts
  – Potentiometric mode
  – Operating range of 50 to 700 °C
Achievements (cont’d)

• Data collection system for reformate gases at Argonne
  – long-term logger for testing sensor responses in 24/7 system

• Sensor Technology User Facility
  – Tests sensors in gases of arbitrary composition
  – Temp range 25 to 400 °C
  – Pressure range ambient to 3 atm
  – Flow rates 0 to 800 cc/min
  – Script-driven experiments permits totally flexibility in experimental protocol
  – Available for use by non-IIT personnel as user facility
Achievements (cont’d)

• Low surface area gold electrode gives much higher signal-to-noise ratio than conventional hydrogen-sulfide sensor electrodes
  – slightly reduced response times not considered important for H₂S
  – electrode made in mass numbers by sputtering and fits into standard low-cost sensor housing
  – high-purity gold eliminates CO interference
  – ppb detection limits achieved

• Targets for low cost have been maintained by using uniform parts originally designed for low cost for all sensor types.
Approach

- Understand the basis of selectivity in sensor catalysts
- Build and test the catalysts in sensor bodies
- Implement, building a product in conjunction with commercial partner
Status Re: Specifications

- Low cost sensor design – COMMERCIAL TEST
- Sensor stability – STABLE IN HIGH HYDROGEN
- Lifetime – > 2 YEARS IN COMMERCIAL PKG.
- High concentrations – TO 1 ATM.
- Selectivity – H₂ IN CO; CO IN H₂, H₂S IN H₂
- High temperatures – BEGUN, SOME PROGRESS
- Response times – BEGUN, ~3 SEC AT HIGH CONC
- Testing in real fuel cell environments – BEGUN
Critique from 2001 Review

“This work replicates prior art”

Response:

• Today’s porous-electrode amperometric gas sensors have serious failings, especially in fuel cell applications:
  – Interferences (cross-sensitivities)
  – Instability in high concentrations of hydrogen
  – High cost
  – Limited temperature ranges (-20°C to +60°C)
  – Slow response times (>20 s)

• Significant improvements have been made, and patents and publications pending
Critique from 2001 Review

“Approach to future development not well outlined”

Response:

• Aggressive pursuit of improved catalysts for selective CO sensors
• Exploration of poisoning phenomenon as a means of measuring low CO in high-hydrogen streams
• Aggressive investigation of solid-state sensors for all temperature ranges
• Two new test facilities to investigate sensors under harsh fuel cell conditions
Critique from 2001 Review

“Work in fuel cell environment, especially wet gases”

Response:

• User facility at IIT being modified to accommodate high partial pressures of water, at high temperature – design nearly complete

• Beginning experiments at Argonne’s fuel cell test facility, which includes all elements of PEM system (reformer, shift, PrOx, stack)
Critique from 2001 Review

“Interact with other sensor developers and users”

Response:

• Solicitation of clients for the SSTUF user facility
• Working with Argonne National Laboratory fuel cell program
• Ongoing relationship with J&N Enterprises, Valparaiso, IN, in support of new sensor development and commercial-ization of new sensor products and improvements
Critique from 2001 Review

“Environmental hydrogen-in-air sensors available”

Response:

• Stability, lifetime, and low cost are not simultaneously available
• Existing sensors have poor selectivity; interferences from alcohols, hydrocarbons, and many other common gases
• Existing sensors exhibit large drifts on continuous exposure
• Existing sensors have either limited temperature range (electrochemical) or high power requirements (metal oxide)
• Inexpensive side-product of development of sensor for hydrogen in anaerobic environments
• Faster response times through new reference electrodes
New H₂ and CO Sensors with Ag/AgCl Reference and Polymer Barriers Do Not Fatigue and Are Linear to Very High Concentrations
Faster Response Through Data Processing

![Graph showing signal response over time with a conventional response at 40 seconds and rate of rise maximum at 3 seconds.](image)
Differential Signal Yields Faster Data

CO Data Available At 3 s
H$_2$ Response
with Ag/AgCl Reference and Polymer Barrier
No Fatigue in Anoxic Matrix; Wide Linearity

H$_2$ in N$_2$
Hydrogen Sulfide on Sputtered Gold Electrode
(Anaerobic, Some H2 Interference)
Working With Argonne

- Waited until prototype sensors were fully tested in the lab
- Needs to be unobtrusive so as not to interfere with ongoing research
- Long term measurements on authentic reformates
- Portable datalogger and sensor management console
- Experiments beginning now (mid-April)
Datalogging System for ANL Installation
Sensor Management Console for ANL

- Manifold
- Potentiostats
- Flow-meter
- Data
- Gas In/out
Shared Sensor Technology
User Facility (SSTUF)

- Funded by ANL
- Facility to test sensors for fuel cell applications under conditions approximating in-service use
- For use by staff for subscribers or clients, or by subscribers
- Tests run by disinterested third-party agents under standard conditions to produce data that can be compared with other manufacturers
- Confidentiality
- Reconfigurable for different sensor types and conditions
Specifications

- Test chamber 10 cm diameter x 25 cm cylindrical
- Temperatures RT to 450 °C
- Pressures 0 to 4 atm gauge
- Gases: nitrogen, hydrogen, carbon dioxide, and carbon monoxide in any proportion at 200 to 800 scc/min
- Gas composition programmable
- Water vapor partial pressure variable over wide range
- System operates from script file that controls most variables in very flexible way
SSTUF System – Part I

16 analog in
10 analog out
16 digital I/O

Labview operating program
SSTUF System – Part II

Four channel gas mixer and pressure control

Oven and 950 W of heaters
Control of Water Vapor Partial Pressure
(Design Only)

Heated transfer line

Sensor test chamber at $T = T_2$

Partial pressure of water is vapor pressure at $T_1$ when $T_1 < T_2$
High-Temperature Sensors

• NASICON-based “high-temperature” sensors
• Proprietary method for making purest NASICON as measured by XRD
• Sensors are active in “intermediate” temp range of 50 to 300°C (too high for porous-electrode sensors and too low for other solid-state sensors) where many fuel-cell sensors are needed
• Electrodes and doping provide selectivity
• Fast response
NO$_x$ Sensors Based on NASICON

Using Ag/AgCl Reference Electrode
NASICON: Na Super Ionic CONductor ($Na_3Zr_2Si_2PO_{12}$) Made by Solid-Phase Reaction Method
Response of NASICON Sensor

90% Response time: 10s

T=50 °C

100% H₂

N₂ base

Time / min

E / mV
NASICON Sensors in Potentiometric Mode

NO$_2$ response

\[
E / \text{mV} = 89.9 \times \log \left( \frac{\text{NO}_2}{\text{ppm}} \right)
\]

\[ T = 180 \, ^\circ \text{C} \]

Nernst slope 89.9 mV/dec.
Summary

• We have addressed the concerns of last year’s review
• New knowledge has been incorporated into products without delay
• We have achieved substantial improvement in sensor properties
• We have patents and publications pending
• Sensors for CO and H₂S are in commercial use with corporate partner, with hydrogen due out soon
Future Focus

• Newly-developed sensors will be tested at Argonne on 24/7 fuel cell pilot plant
• Shared Sensor Technology User Facility (SSTUF) will work with sensor developers to test sensors under harsh conditions
• Continued improvements in response times and temperature ranges
• Continued research into causes and control of cross-sensitivities
• Continued movement of developments into commercial applications
• Completion of final deliverables by May 2003, including completed sensors