Real-time Ionic Liquid Electrochemical Sensor for Highly Sensitive and Selective hydrogen Detection and Quantification

PI: Xiangqun Zeng

Departments of Chemistry, Chemical and Biomedical Engineering,

University of Missouri, Columbia, MO 65211

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DOE Hydrogen Program

2024 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID # SCS038

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Project Goal and Objectives

Goal:

(i) achieving H_2 detection at the ppb level, (ii) design, optimization, and miniaturization of an innovative ionic liquid-based hydrogen sensor, (iii) developing a full-scale prototype and the characterization, calibration, and validation of its analytical performance for continuous hydrogen monitoring with high sensitivity and specificity in its expected commercialization translation.

Objectives:

1. **Advance and optimize a miniaturized electrochemical H_2 sensor to detect and quantify ppb level H_2 leak**
   - *Use experimental, computational, and engineering approaches to optimize a miniaturized H_2 sensor with enhanced ppb level sensitivity and high specificity regarding ambient interferent gases and various environmental conditions for continuous and real-time H_2 sensing*
2. **Develop and validate a full-scale H_2 sensor prototype**.
   - Develop a compact, energy-efficient electronic system capable of accurate result visualization and data management for the miniaturized H_2 sensor developed for a full-scale H_2 sensor prototype
3. **Characterize and validate the full-scale H_2 sensor prototype and benchmark its analytical performance in the field**.
   - *Characterize the full-scale H_2 sensor prototype and validate and benchmark its analytical performance by collaboration with the National Renewal Energy Lab for independent metrological performance validation toward commercialization*.

Any proposed future work is subject to change based on funding levels

Project Overview

H_2 Sensing Barriers

Current Technology:

- Pd-based H_2 sensors: sensing materials degradation, humidity & CO poison effects, signal drift with time.
- Metal oxides-based H_2 sensors: poor selectivity, sensor materials can be poisoned
- Indirect colorimetric H_2 sensor: not real-time response, sensing materials degrade, and sensitivity dependent on temperature.
- Traditional Electrochemical H_2 sensor: Evaporation or decomposition of electrolyte/solvent, Electrolyte is corrosive, Limited lifetime or response characteristics if the products of the reactions are electrode poisons.
- **The needs:** high sensitivity to detect ppb level of emission of H_2; high stability in ambient conditions; high permissibility in harsh conditions; miniaturization, low cost, low power, and real-time sensing

Timeline

Project Start Date: tentative 05/01/2024
Project End Date: tentative 04/30/2027

Budget

In negotiation

Any proposed future work is subject to change based on funding levels

Team and Partners

Project Lead: **PI, Xiangqun Zeng, Departments of chemistry, chemical and biomedical engineering, Univ. of Missouri**

H_2 sensor and sensor system development, testing, and validation

Co-PI(s) and Partner organization(s) and role(s)

- **Wei Lai, Department of Chemical and material engineering, Michigan State Univ.,**
H_2 sensing mechanism investigation
- **Yong Xu, Department of Electrical and computer Engineering, Wayne State Univ.,**
H_2 sensor chip design and fabrication
- **Hongwei Qu, Department of Electrical and computer engineering, Oakland Univ.,**
H_2 sensor system prototype development
- **William Buttner and David Peaslee, National Renewable Energy lab (NREL)**
***H_2* sensor prototype test, validation, and benchmarking**

Potential Impact

Real-time and Continuous-use H_2 Sensor Meet Cost/Utility/Capability requirements:

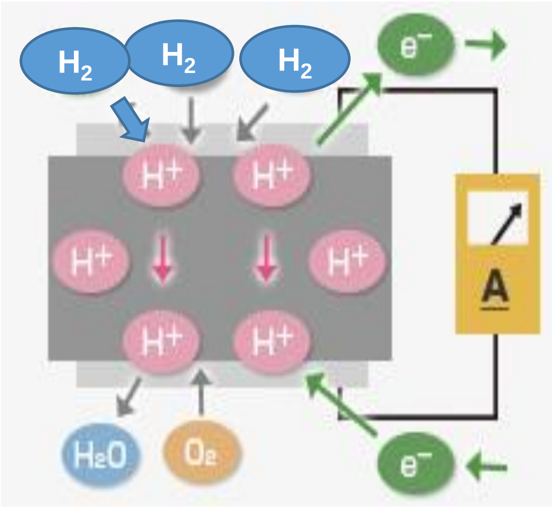
Our novel real-time, highly sensitive and selective electrochemical H_2 sensor with robust sensing materials aim to fill the current technical gap in H_2 sensing technologies and deliver a combination of accuracy, reliability, small size, low cost, real-time measurement and autonomous operation that could provide revolutionary capability for monitoring the H_2 emission and the H_2 leakage rate in various applications involving the use of H_2

Project Technical Approach

Traditional Electrochemical Hydrogen Sensor

WE

CE



Working electrode (WE):

H_2 + Pt → $2Pt\text{-}H_{ad}$ (Tafel step)
$Pt\text{-}H_{ad}$ → H^+ + e + Pt (Volmer step)
or Heyrovsky step
H_2 + Pt → H^+ + e + $Pt\text{-}H_{ad}$

Counter Electrode (CE):

$1/2O_2 + 2H^+ + 2e \rightarrow H_2O$

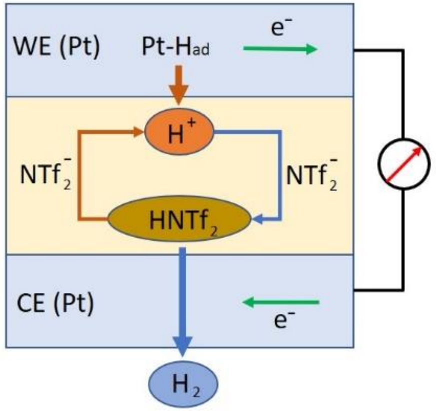
Key problems:

- Evaporation/decomposition of electrolyte/solvent
- Electrolyte is corrosive
- Thermal instability at both high and low temperatures
- Limited lifetime or response characteristics if the product of the reactions are electrode poisons

Project Technical Approach

Ionic liquid electrochemical H_2 sensor for continuous H_2 monitoring

Sensing mechanisms and reactions



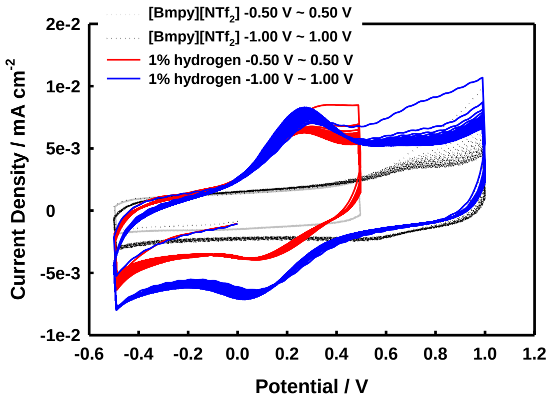
WE:

$$2Pt + H_2(g) \rightleftarrows 2Pt\text{-}H_{(ad)}$$
$$Pt\text{-}H_{(ad)} \rightleftarrows Pt + H^+ + e^-$$
$$H^+ + NTf_2^- \rightarrow HNTf_2$$

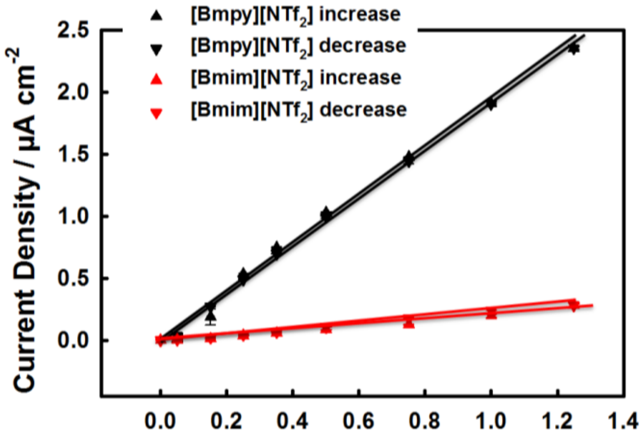
CE:

$$HNTf_2 + e \rightarrow H_2 + NTf_2^-$$

Reversibility

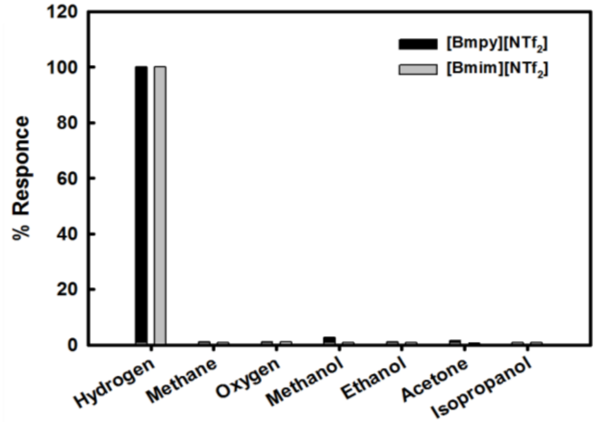


Linearity

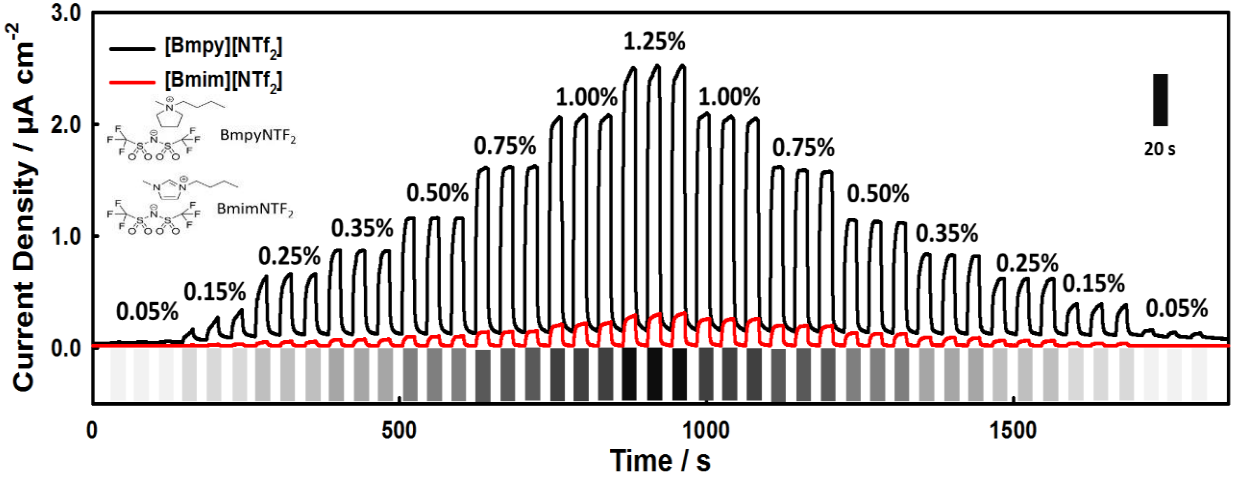


- Sensitive
- Reproducible
- Fast and real-time
- Quantitative

Selectivity



Real-time sensing and repeatability

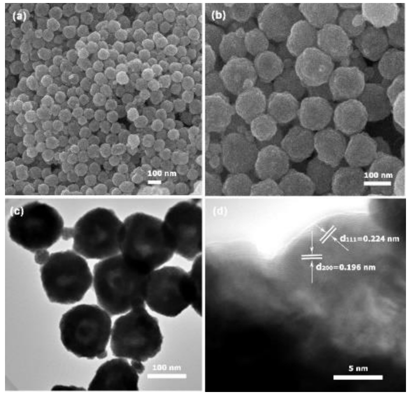


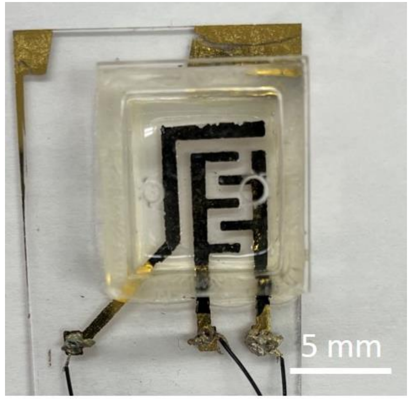
Accomplishments and Progress

Bimetallic nanocrystal synthesis and characterization for miniaturized H_2 sensor

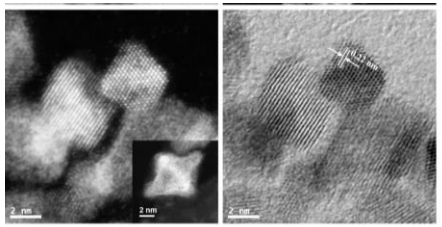
- **Metal nanocrystals with high surface areas and controlled surface structures provide high sensitivity and selectivity for electrochemical sensing.**
- **Metal nanocrystals with unique shape and size allow for the understanding of the structure-activity relationships for electrocatalysis**
- **Developed new methods for successfully synthesizing Bimetallic nanocrystals with over 10 times reduction in size compared to the nanoparticles made before.**
- **Characterized Bimetallic nanocrystals by multiple techniques to determine their physical and chemical properties by XRD, XPS, and TEM**

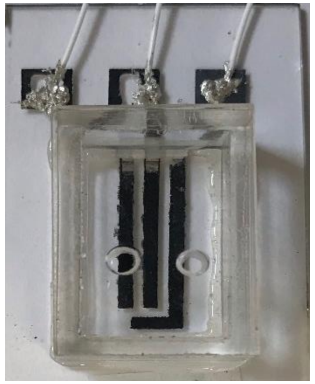
Prior work: Bimetallic nanoparticle and miniaturized H_2 sensor device





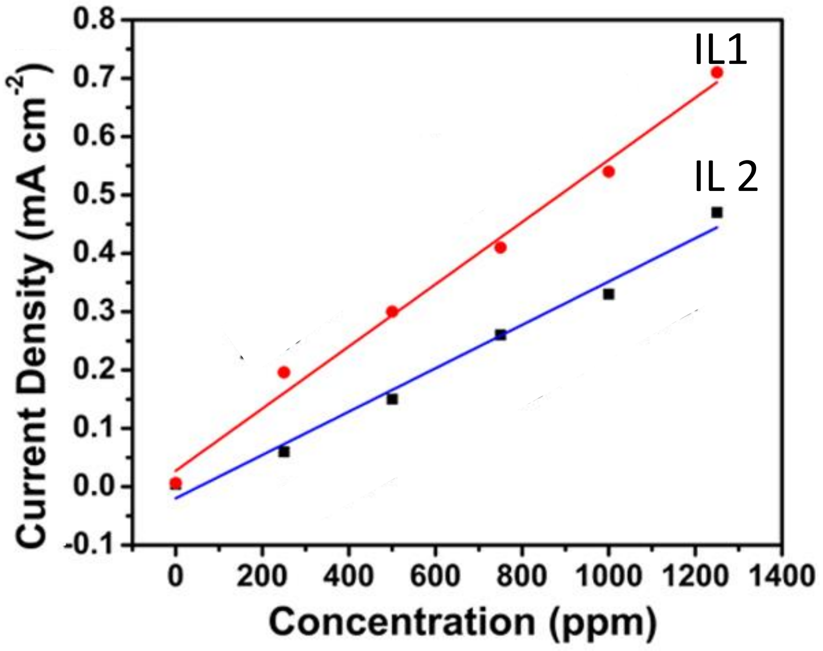
Current work: Bimetallic nanocrystal and miniaturized H_2 sensor device



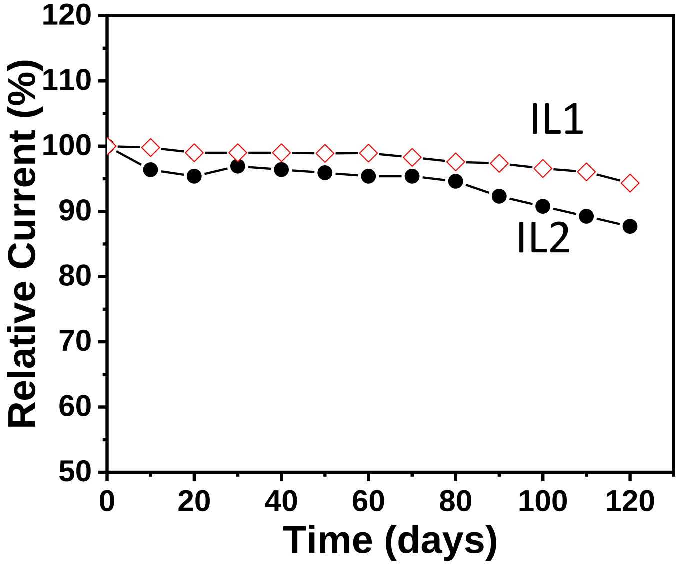


Accomplishments and Progress

H_2 sensing sensitivity



H_2 sensor stability



Highly selective with none or negligible interference from common ambient gaseous species: O_2, N_2, CO_2, CO, common hydrocarbon and volatile organic Compounds

4.8 ppm detection limits achieved

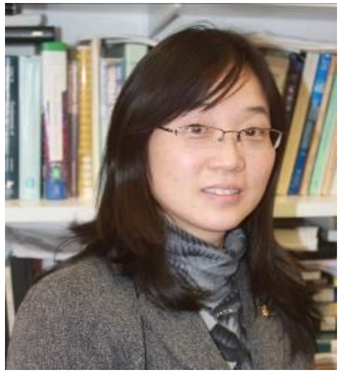
H_2 sensor with bimetallic nanocrystals and Ionic Liquids provide high sensitivity, high selectivity, and high stability for real-time and continuous sensing H_2

Safety Planning and Culture

- This project is not REQUIRED to submit a safety plan to the Hydrogen Safety Panel (HSP)

- Safety Plan and Culture
  - Key personnel attended the Hydrogen Laboratories: Safety Considerations Webinar on September 14, 2023.
  - Specific Team members assigned for management, assessment, and inspection roles for safety and safety hazards
  - Design Monthly Safety meetings to achieve the best safety practices and lessons learned.
  - Laboratory personnel completed the Univ. Chemical Safety training and reporting safety concerns.

Collaboration and Coordination

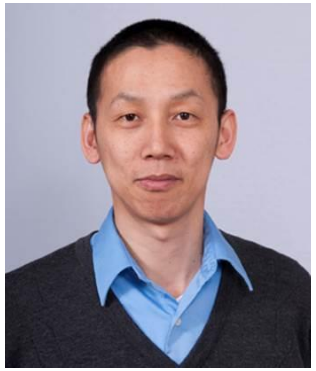


Dr. Xiangqun Zeng
Professor of Chemistry, Chemical and Biomedical Engineering, Univ. of Missouri Columbia
Role: Principal Investigator
Expertise: Analytical chemistry, electrochemistry, and chemical and biosensor science.

Co-PIs

Wei Lai
Material scientist, Associate Professor
Materials Design, Characterization Atomistic Simulation

MSU



Yong Xu
Sensor Engineer Professor
Micro/nano Sensor design & Fabrication

WSU

Hongwei Qu
Electrical Engineer Professor
MEMS Electronic Circuits & devices

OU

William Buttner
Director
HSR&D program

NREL

David Peaslee
Hydrogen Systems Researcher III

NREL

Consultants

Mike Sevilla
Physical chemist Emeritus distinguished professor
Free radical chemistry

OU

Jiwu Zhang
Biomedical Engineer and Entrepreneur

EZ Lab & GDA

DEI/Community Benefits Plans and Activities

Year	DEI activities
1	DEI training for all team members
2	Recruit female and minority students and/or postdocs for this project.
2	Develop community outreach program such as workshops of H_2 economy and hydrogen sensor technology for local K-12 schools and/or community colleges
3	Broadly disseminate results of research and development in minority serving and underserved communities
3	Identify minority business enterprises, minority owned business, woman owned businesses and veteran owned businesses for commercialization activities.

Remaining Challenges and Barriers

- Developing miniaturized H_2 sensor with extremely high sensitivity for real-time and continuous detection of H_2 in real-world conditions

♦ Sensor stability or signal drift in real-world conditions

→ Temperature

→ Humidity

→ Sensing elements' stability

♦ Technical and economic challenges

→ Complexity

→ Cost

→ Size

→ Power consumption

Proposed Future Work

Systematic H_2 sensor optimization with novel electrolyte and electrode materials to achieve real-time H_2 sensing with ppb level sensitivity and H_2 sensor prototype development and validation in real world conditions

- **Sensing materials optimization**

  enhance H_2 / H^+ transport, suppress transport of interferents and provide a mechanism for ppb level of sensitivity for H_2 detection.

- **Sensing method development**

  ♦ **provide high selectivity for H_2 sensing with multi-gas detection capability**

  ♦ **multi-mode sensing to provide cross validation and calibration**

- **Sensing system integration**

  ♦ **H_2 sensor prototype meets cost/utility/capability requirements**

H_2 sampling/Preconcentration

Detection & Quantification

Enhancement & Calibration

Validation of H_2 sensing in real-world conditions

H_2 Sensor system prototype

Real time sensor signal processing

Electronic system: Computation; decision making; data storage & communication; Power & power management

Miniaturized H_2 sensor prototype

- **Accurate**
- **Reliable**
- **Robust**
- **Small size**
- **Low power**
- **Low cost**
- **Mobile**

Research Tasks and Schedule

Objective 1. Advance/optimize a miniaturized H_2 sensor with ppb sensitivity	Y1	Y2	Y3
(i). Develop metallic catalytic electrode materials (Zeng/Lai)	x	x	
(ii). Optimize ionic liquid (IL) properties (Lai/Zeng/Sevilla)	x	x	
(iii). Miniaturized H_2 sensor chip development and optimization (Xu)	x	x	
(iv). Miniaturized H_2 sensor chip characterization for H_2 sensing performance (Zeng/Xu)	x	x	
Milestones/decision points: < 10 ppb sensitivity achieved at ambient conditions			
Objective 2. Develop a full-scale H_2 sensor prototype			
(i). Develop miniaturized instrumentation electronics (Qu)	x	x	
(ii). Develop software for sensor control, data processing, and calibration (Qu)	x	x	
(iii). Sensor system integration, characterization, and validation (Qu/Xu)		x	x
Milestones/decision points: a full-scale miniaturized and integrated H_2 sensor prototype that has similar or better performance compared to benchtop instruments			
Objective 3. Validate and benchmarking the full-scale H_2 sensor prototype			
(i) H_2 sensor system performance lab testing (Zeng/Qu/Xu)	x	x	x
(ii) H_2 sensor system performance field testing and benchmarking (Zeng/Qu/Buttner/Post)			x
End project goals: a miniaturized full-scale H_2 sensor prototype with a limit of detection (LOD) < 10 ppb, high reliability (>99.99% accuracy, <0.1% drift in 90 days) at varying ambient conditions, real-time sensing, H_2 sensor system miniaturization and low cost .			x

Project Summary

Our DOE project is to advance our innovative ionic liquid-based electrochemical hydrogen sensor with extremely high sensitivity and specificity and develop a full-scale H_2 sensor prototype, and the characterization and validation of its analytical performance for expected commercialization translation for monitoring the environmental impacts of hydrogen economy.

Table 1. Features of IL electrochemical H_2 sensor prototype

Detection limit	<10 ppb	Wireless	Bluetooth
Linear range	10 ppb to 100ppm	Lifetime	> 2 years
Response time	< 30 s	Temperature	-30 to 80 °C
Drift	< 0.1% in 90 days	Humidity	0-98%
Size, weight	< 5 in^3, < 4 oz.	Calibration	1 year interval
~ Cost	< $ 50 /unit	Power	5V battery
Average power	< 300 mW* (use mode dependent. Equivalent power consumption will be much smaller for practically reasonable periodical sensing)		

Figure. 1

Successful development of our real-time, highly sensitive, and selective ionic liquid-based electrochemical H_2 sensor will fill the current technology gap and deliver a combination of accuracy, reliability, small size, low cost, real-time measurement, and autonomous operation that could provide a revolutionary capability for monitoring the H_2 emission and the H_2 leakage rate in various applications involving the use of H_2 .