Biological Hydrogen Production Workshop

September 24, 2013

The Hydrogen Program at NREL: A Brief Overview

“Integration is the Word”
NREL Fuel Cell & Hydrogen Technologies Program

- Renewable Hydrogen Production
- Hydrogen Delivery
- Hydrogen Storage
- Fuel Cell Manufacturing R&D
- Fuel Cells
- Technology Validation
- Codes, & Standards
- Analysis
- Market Transformation
- Education
Hydrogen Production from Renewable Sources at NREL

Xcel Energy and NREL’s Integrated Renewable Hydrogen System

- 10 kW Photovoltaics
- DC-DC Converter
- 100 kW Wind Turbine Northern Power Systems
- AC-DC Converter
- Excess Grid-Compatible Electricity
- Utility Grid
- ASCO Transfer Switch
- AC Power
- H-Series (PEM) Electrolyzer Proton Energy Systems 2.2 kg/day
- HOGEN 40RE (PEM) Electrolyzer Proton Energy Systems 13 kg/day
- Hydrogen Output (100-200 psi)
- Compression to 3500 psi Pressure Products Industries
- 115 kg Hydrogen Storage Capacity at 3500 psi CP Industries
- Unit under test
- 115 kg Hydrogen Storage Capacity at 6000 psi FIBA Technologies
- H₂ Filling Station for FCEVs and H₂ ICEs
- 60 kW ICE Genset Hydrogen Engine Center
- 5 kW Fuel Cell (PEM) Altery Systems
- HMXT-100 (Alkaline) Teledyne Energy Systems 12 kg/day

March 2011
Refueling at NREL’s Hydrogen Station
ESIF: West Elevation
ESIF: Northwest Elevation
Major ESIF Laboratories/Capabilities

View All Distribution Buses

- **Electricity Laboratories**
  1. Power Systems Integration
  2. Smart Power
  3. Energy Storage
  4. Electrical Characterization
  5. Energy Systems Integration

- **Thermal Laboratories**
  6. Thermal Systems
  7. Thermal Storage Materials
  8. Optical Characterization and Thermal Systems
  9. Thermal Distribution Bus

- **Fuel Laboratories**
  9. Energy Systems Fabrication
  10. Manufacturing
  11. Materials Characterization
  12. Electrochemical
  13. Energy Systems Sensor
  14. Fuel Cell Development
  15. High-Pressure Testing
  16. Fuel Distribution Bus

- **Data, Analysis, and Visualization**
  16. ESIF Control Room
  17. Visualization Room
  18. Secure Data Center
  19. High Performance Computing

Supervisory Control and Data Acquisition (SCADA) System
Integrating Basic Science & Translational R&D to Understand and Develop Photobiological Algal Systems for Producing Hydrogen at NREL

Translational Research & Development (EERE:FCT)
Goal: Develop algal systems (enzymes or organisms) capable of sustained \( \text{H}_2 \) photoproduction under aerobic conditions

(a) Developed chemochromic sensors for detection of \( \text{H}_2 \) by isolated algal colonies
(b) Identified and cloned the algal HYDA1 and HYDA2 [FeFe]-hydrogenases genes
(c) Introduced HYDA1, HYDA2 and their maturation genes into \textit{E. coli} for mass-production of the respective enzymes
(d) Developed computational models of gas diffusion in clostridial [FeFe]-hydrogenase; generated and tested mutants for \( \text{O}_2 \) tolerance (no positive transformants with high hydrogenase activity have been identified, yet).
(e) Shifted R&D direction towards the introduction of the clostridial hydrogenase (higher \( \text{O}_2 \) tolerance) gene into \textit{Chlamydomonas}, using an algal strain with no native hydrogenase activity. Demonstrated expression of Ca1 in \textit{Chlamydomonas} and \( \text{H}_2 \) photoproduction.
(f) Performed computational modelling of the interaction between ferredoxins and hydrogenases.
(g) Expressed clostridial hydrogenase in double knock-out algal strain and demonstrated \( \text{H}_2 \) production in vivo

Basic Research (SC:BES/BER)
Goal: understand structure, function and transcriptional regulation of hydrogenases

(a) Identified the maturation proteins responsible for assembly of algal hydrogenases using chemochromic sensors.
(b) Expressed bacterial [FeFe]-hydrogenases in \textit{E. coli} and found that clostridial hydrogenases have higher tolerance to \( \text{O}_2 \) inactivation.
(c) Generated an algal strain with no native hydrogenase background activity.
(d) Generated a collection of cyanobacterial Hox operon mutants.
(e) Demonstrate higher reductant flux in vitro towards \( \text{H}_2 \) production with fused Fd/H2ase.
(f) Developed high throughput high-sensitivity biological sensor for single colony \( \text{H}_2 \) production.
**PHOTOBIOLOGY: Improving Algal Photosynthetic Hydrogen Production – O₂ tolerance**

**Scientific Achievement**

A more oxygen-tolerant Clostridial hydrogenase expressed in *Chlamydomonas* catalyzed photo-hydrogen production

**Significance and Impact**

Oxygen sensitivity is a major limitation to the use of photosynthetic microbes for solar hydrogen

**Research Details**

- Photosynthetic water-splitting utilizes sunlight energy to split water.
- Green algae can link water-splitting to hydrogen production using hydrogenases, but only for short periods due to high sensitivity to oxygen.
- Bacterial hydrogenases (Cal) showing higher oxygen tolerance were expressed in a hydrogenase deficient algal mutant (Posewitz, CSM)
- Under photosynthetic conditions, the Cal cells showed 40-fold higher tolerance to oxygen.
- This is an essential step towards engineering green algae for efficient photo-production of hydrogen from water splitting.

**GFP Screening and Oxygen Inactivation Kinetics of Photo-Hydrogen Production:** Under illumination, photosynthesis produces hydrogen detected as a GFP halo that identified Cal expressing cells. Exposure of anaerobic cells to oxygen inactivates native algal hydrogenase (HydA1, red trace) at a faster rate than bacterial hydrogenase (Cal, green trace).

Seth Noone, Kath Ratcliff, Reanna Davis, Matt Wecker, Jon Meuser, Matthew C. Posewitz, Paul W. King and Maria L. Ghirardi
FERMENTATION: Developed Genetic Tools in *Clostridium thermocellum* for Improved Hydrogen Production from Cellulose

**Scientific Achievement**

NREL has developed proprietary genetic tools to stably manipulate the genome of *Clostridium thermocellum* for improved hydrogen production.

**Significance and Impact**

*C. thermocellum* exhibits one of the highest rates of cellulose hydrolysis. This in-house capability enables us to engineer its metabolic pathways to tailor the production of desirable biofuels and biochemicals including hydrogen.

**Research Details**

- *Clostridium thermocellum* combines cellulose hydrolysis with H₂ production, hence is a model microbe for consolidated bioprocessing (CBP).
- Yet the competing metabolic pathways (top figure) lower the yield of H₂ from cellulose, a technical barrier as to its techno-economic feasibility.
- We have developed genetic tools and obtained mutants lacking the competing pyruvate-to-formate reaction, as evidenced by a lack of formate production in the mutant (red arrow, lower figure).
- The mutant exhibited a 50% increase in the specific activity of H₂ production and up to 60% increase in ethanol production.
- Improving H₂ yield and total H₂ output via additional genetic engineering forms the thrust of this research I building an H₂ economy.

Pin-Ching Maness, Katherine Chou, & Lauren Magnusson
Strong NREL Capacity in Artificial Photosynthesis (Analogous to Natural Systems)

- Artificial: Work in Progress
- Natural: Poor Efficiency
- Biohybrid: Nexus

**Photocatalysis**

- PC/ET: Photon capture and energy transfer
- CS/et: Charge separation and electron transport
- Cat: Catalysis and fuel formation

**Diurnal Issue Common to All**

- H₂, CH₃OH from H₂O & CO₂

**Key**

- PC/ET: Photovoltaic
- CS/et: Charge separation and electron transport
- Cat: Catalysis and fuel formation
Control is often more important than power (or efficiency).

*Photosynthesis did not evolve to make us biofuels nor necessarily to be the most efficient. It evolved because it lets organisms survive.*
Thank You!

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