Research Challenges for Non-Photosynthetic Solar Fuels Production

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July 8, 2017
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Acknowledgements

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CARBON TEAM:
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CARBON National Lab Workshop Participants (March 2017)
Integrated Approach for Adding Value to CO₂

- Capture and concentration
- Hybrid conversion technologies
- Recovery and purification

Catalytic reduction/Homologation
Biomimetic/Bioinspired catalysis
Electrocatalysis
Photocatalysis
Thermal/Solar thermal

Biochemical/Enzymatic
Fermentation
Synthetic biology

Hybrid approaches
- electro biocatalysis
- tandem catalysis
- reactive separations

Fuels
Chemicals
Materials
Polymers
Integrated Approach for Adding Value to CO$_2$

- Catalytic reduction/Homologation
- Biomimetic/Bioinspired catalysis
- Electrocatalysis
- Photocatalysis
- Thermal/Solar thermal

Hybrid approaches
- Electro biocatalysis
- Tandem catalysis
- Reactive separations

Materials ↔ Interfaces ↔ Components/Organisms ↔ Systems

Cost • Efficiency • Performance • Reliability • Scalability •
• Changing energy landscape and market opportunities
  • Curtailment, storage, products
• Advances in electrochemistry, materials discovery, synthesis characterization, catalysis science, synthetic biology
Rewiring biology by coupling anthropogenic reductants with biological processes (C-C)
- Couple the efficiency and cost advantages of abiotically generated reductants (e-, H₂, other) with the selectivity of bioprocesses
- Electro-biocatalysis; Synthetic biology

Reactive capture for CO₂ and waste gases
- Couple CO₂ capture with reduction/reaction
- New catalytic reactions
- Catalytic membranes
- Alternative capture/reactive media,
- Innovative electrochemical processes

Innovative hybrid approaches and tandem reactions, catalysis and biocatalysis
- CH₄ + CO₂
- Innovative supports for tandem catalysis
- Reaction and reactor engineering

Innovative materials and product synthesis and processing from CO₂-based precursors
- Existing and new materials
- In-kind replacements
- New functionality

Fit-for-purpose water treatment
R&D Opportunities and Challenges

Efficient Generation of reductants from Renewable Energy

- Cost, Efficiency, Performance, Reliability, Scalability

REWIRING BIOLOGY BY COUPLING ANTHROPOGENIC REDUCTANTS WITH BIOLOGICAL PROCESSES (C-C)

Understand bioenergetics to increase carbon, e-, energy flux? Kinetic matching of abiotic/biotic? H₂ and CO₂ uptake New chasses for synbio? Design and control of interfaces?

INNOVATIVE HYBRID APPROACHES AND TANDEM REACTIONS, CATALYSIS AND BIOCATALYSIS

- How do we create tandem approaches?
- New chemistries (H₂ + CO₂ → C-C)
- Couple chem/bio approaches?
- Novel reaction and reactor engineering?

REACTIVE CAPTURE FOR CO₂ AND WASTE GASES

- How do we lower the energy requirements/costs and create efficient processes?

INNOVATIVE MATERIALS AND PRODUCT SYNTHESIS AND PROCESSING FROM CO₂-BASED PRECURSORS

- New processing concepts?
- Beyond in-kind replacements?
- TEA, LCA

FIT-FOR-PURPOSE WATER TREATMENT
Foundational R&D Needs (to name a few)

Design and control of energy and charge generation and transport

New materials
- photoelectrodes
- electrodes
- membranes
- catalysts
- power electronics

Interfacial Science
- energy, charge, mass transfer
- control and design

Catalysis, Electrocatalysis
- new reactions
- mechanisms
- selectivity

Synthetic biology
- H₂ and CO₂ uptake
- productivity/selectivity/robustness
- bioenergetics (pathways and control)

New Concepts …
R&D for H₂ by Electrolysis

1 kg H₂ ≈ 1 gallon of gasoline equivalent (gge)
Electrolyzer Component R&D Needs

- **Electrocatalysts**
  - Improved OER performance and durability
  - PGM replacement; Supports for Ir catalysts

- **Membranes**
  - Resistance to differential pressures/cycling
  - Alkaline systems

- **Durability/Testing**
  - Degradation mechanisms; accelerated testing

- **Cell/Electrode Layer**
  - Impact of operating conditions
  - Electrode structure/performance
  - Manufacturing/Scale-up
  - Model development

- **Bipolar Plates/Porous transport layers**
  - Structure/performance; Corrosion
  - Manufacturing/Scale-up

- **Balance of Plant**
  - Lower cost power supplies, inverters; DC systems
  - High temperature compatible materials
  - Impact of operating conditions

![Projected Transportation Fuel Cell System Cost](chart.png)

Fuel Cell R&D has decreased projected costs by 80%
PEC Water Splitting: $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$

**Approach**

- Inverted metamorphic multijunction (IMM) PEC device enables more ideal bandgaps
- Grown by *organometallic vapor phase epitaxy*
- Incorporates *buried p/n GaInP$_2$ junction* and *AlInP passivation layer*

**Solar-to-hydrogen Efficiency**

16.4%

Benchmarked under outdoor sunlight at NREL

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*SEM* and *TEM* IMM device cross sections

- Top surface
- III-V tandem
- Au contact/reflecter
- Epoxy
- Si wafer handle

- p-GaInP$_2$
- Graded buffer
- p-n InGaAs

- Current density (mA/cm$^2$)
- Bias (V vs. RuO$_x$)

Understanding and Designing more stable and efficient solar fuel generators

New ultrafast laser spectroscopy technique uncovers how photoelectrodes produce solar hydrogen from water

NREL’s new probe measures transient electrical fields and shows how semiconductor junctions convert sunlight to fuels

The field formed by the TiO$_2$ layer drives electrons to the surface where they reduce water to form hydrogen.

The oxide prevents photocorrosion by keeping holes away from the surface

This new understanding will lead to more stable and efficient solar fuel generators

Cell and Module Testing

• Inverted metamorphic junction (IMM) PEC device enables more ideal bandgaps
• Grown by organometallic vapor phase epitaxy
• Incorporates buried p/n GaInP2 junction and AlInP passivation layer

Approach: Solar-to-hydrogen Efficiency

16.4% Benchmarked under outdoor sunlight at NREL

-1.0 -0.5 0.0 0.5

current density (mA/cm²)

-1.0 -0.5 0.0 0.5

bias (V vs. RuO2)

Upright GaInP2/GaAs
Inverted GaInP2/GaAs
IMM (GaInP2/InGaAs)
p-n IMM
p-n IMM w/ passivation

16.4% STH

Si wafer handle

epoxy

Au contact/reflectors

III-V tandem

µm

SEM

TEM

IMM device cross sections
Material Challenges *(the big four)*

Photoelectrochemical Hydrogen Production Material

- Photomaterials
  - Efficiency
  - Energetics
  - Coupling to catalytic rxns

- Catalysis – Efficient selective catalysis at low overpotential

- Interfacial Materials, Membranes – keep $O_2$ from fuel; charge/ion balance

- Material Durability – semiconductor/catalyst must be stable in electrolyte solution

- Protective coatings
Approaches to PEC Hydrogen

1) Single Bed, 10%
2) Double Bed, 5%
3) Fixed Panel, 10%
4) Concentrator, 15%

Technoeconomic Analyses: Approaches to PEC Hydrogen

HydroGEN Consortium

Accelerating research, development and deployment of advanced water splitting technologies for clean sustainable hydrogen production

HydroGEN offers a suite of capabilities that partners can leverage capabilities (81) and expertise in a number of areas:

- Computational tools and modeling
- Materials synthesis
- Process and manufacturing scale-up
- Materials and device characterization
- Durability
- Systems Integration
- Analysis

https://www.h2awsm.org
BioHybrid Approaches (Electrochem, H₂, Mediators)

**Electrosynthesis**

- **Innovation**
  - Beating photosynthesis by coupling anthropogenic reductants with biological process
  - Microbial catalysis offers high selectivity toward tailored products
  - The advances in synthetic biology underpin this innovation to cost effectively convert waste carbon to fuels, chemicals, and materials.

*The Electric Economy Meets Synthetic Biology*
Three possible electron transfer mechanisms

1. Direct via conducting pili or c-type cytochrome (multi-heme)
2. Mediators released by the cells (flavin, quinones)
3. Exogenously added electron shuttles (i.e. H₂, formate, Fe²⁺)

More understanding could guide the design of better mechanism to accelerate electron transfer and provide the breakthrough solution to match current density between electrode and microbes.

Figure from Sydow 2014. Appl Microbiol Biotechnol 98: 8481.
Biohybrid: Science Challenges

**Electrochemistry**
- Surface area limits microbe attachment
- Internal lost
- Scale up

**Electrofermentation**
- Matching energetics and kinetics between microbes and electrode
- Mechanisms of electron transfer between microbe and electrode
- Understanding bioenergetics to increase carbon, electron, and energy flux
- Synbio, metabolic engineering to control and design pathways
- Enhanced H₂ and CO₂ uptake by designer chassis microbes
- Biofilm formation; mechanism of microbial attachment
- Biofouling
**Water Splitting by a Bioassisted Black Si Photocathode**

- [FeFe]-H₂ase enzyme immobilized directly onto a nanoporous silicon (black Si) photoelectrode surface catalyzes HER on a black Si photoelectrode comparable to Pt
- Current densities >1mA cm⁻²

\[
\text{≤12 pmol/cm}^2 \quad \text{TOF} = 1300 \text{ s}^{-1} \quad \text{TON} \approx 10^7
\]
Candidate platform microbes

- C. ljungdahlii
- C. autethanogenum
- M. thermoacetica
- R. eutropha

Candidate platform communities

- New isolated microbes
  - C. ljungdahlii + C. klyveri
  - C. autethanogenum + M. elsdenii

New synbio microbes

- C. autethanogenum
- M. elsdenii

New synbio microbes

- R. eutropha
Synbio Toolbox

• Advanced genetic toolbox:
  – Develop robust DNA transfer methods/CRISPR
  – Knock-out/Knock-in genes
  – Alter expressed patterns/levels
  – Conduct systems biology based approaches (-omics)
  – Conduct $^{13}$C-metabolic flux analysis ($^{13}$C-MFA; carbon/electron flow)
  – Develop predicted genome-scale models (energy/electron/carbon)
  – Algorithms and automated assembly
  – “Synthetic parts” library for modular plug-and-play (promoters, synthetic pathways)
  – Predictive (re)design and optimization of synthetic pathways
  – High throughput screen/sensor to screen DNA libraries

• Accelerate the design-build-test-redesign cycle for microbial redesign
Coupling Anthropogenic Reductants with Microbes
**Challenges/Opportunities: CO₂ to Products**

<table>
<thead>
<tr>
<th>Carbons</th>
<th>Carbonates</th>
<th>Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>e.g.</em> carbon fiber, CNTs, Graphene, … (Structural Carbon)</td>
<td><em>e.g.</em> cement, aggregate, polycarbonates</td>
<td><em>e.g.</em> polymers, fuels, chemicals</td>
</tr>
<tr>
<td><em>Remove oxygen</em></td>
<td>• Alkalinity: $\text{HCO}_3^-$</td>
<td>• Provide hydrogen</td>
</tr>
<tr>
<td><em>Make products</em></td>
<td>• Cations for product</td>
<td>• Make polymers</td>
</tr>
<tr>
<td><strong>Approaches</strong></td>
<td><strong>Challenges</strong></td>
<td><strong>Challenges</strong></td>
</tr>
<tr>
<td>• Electrocatalysis</td>
<td>• Efficient electrolysis</td>
<td>• Low-C Hydrogen</td>
</tr>
<tr>
<td>• Pyrolysis</td>
<td>• Direct reaction from solvents capturing CO₂ as CO₃</td>
<td>• De-oxygenation</td>
</tr>
<tr>
<td><strong>Challenges</strong></td>
<td><strong>Approaches</strong></td>
<td>• Selectivity</td>
</tr>
<tr>
<td>• Coupling electricity to catalysis</td>
<td>• Catalysis to make C-C and polymer precursors</td>
<td>• Integrated capture/reaction</td>
</tr>
<tr>
<td>• Product purity</td>
<td><strong>Challenges</strong></td>
<td><strong>Challenges</strong></td>
</tr>
<tr>
<td>• Efficient catalysis</td>
<td><strong>Challenges</strong></td>
<td>• Efficient electrolysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Cation sourcing, <em>e.g.</em> seawater</td>
</tr>
</tbody>
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*Adapted from R. Aines, CARBON workshop, March 2017*
CO₂ Utilization Pathways

Photosynthesis → Flue Gas → CO₂

1. MEA
2. Syngas → 3b. Fuel (Gasoline)
3a. Fermentation
3b. FT
4. Methanol → 5a. Fuel (Gasoline)
5b. Diesel
6. +H₂ → Urea
7. Algae biofuel
8. Isopropanol → 2. Syngas

Poly-carbonate
Fuel or chemical precursors

Flue Gas → MEA → CO₂ → Photosynthesis

Ling Tao, Mary Biddy, …
**CO₂-Based Materials and Polymers**

- **CO₂** → Isopropanol → DeH₂O Ammoniation → Poly-ACN
- **CO₂** → Malonic Acid → Polymerization → Polyesters

- **Polycarbonate Market**
  - 3% of current polymer GDP

- Graph showing market growth from 2014 to 2024:
  - Automotive
  - Construction
  - Consumer Goods
  - Medical Devices
  - Electrical & Electronics
  - Packaging
  - Optical Media
  - Others
Carbon Fiber: Large and Growing Market

2005—$90 million market size,
2015—$2 billion
2020—projected to reach $3.5

The North America region is expected to be the largest market globally due to the increased demand from aerospace & defense, wind energy, infrastructure, and automotive industry.
**Reductants:**
e\(^-\), H\(_2\), CH\(_4\)

**Reagents:**
Epoxides, propylene Ca(OH)\(_2\)

**Value Added Products**

**Challenges:**
- Energy intensity
- Process integration
- Cost
- Advanced materials development

**Challenges:**
- Reducing equivalents
- Catalyst reactivity/selectivity in media
- Catalytic membranes
- Alternative media
- Electrochem

*From C. Matranga, NETL*
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