Research Challenges for Non-Photosynthetic Solar Fuels Production

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NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Acknowledgements

NREL:

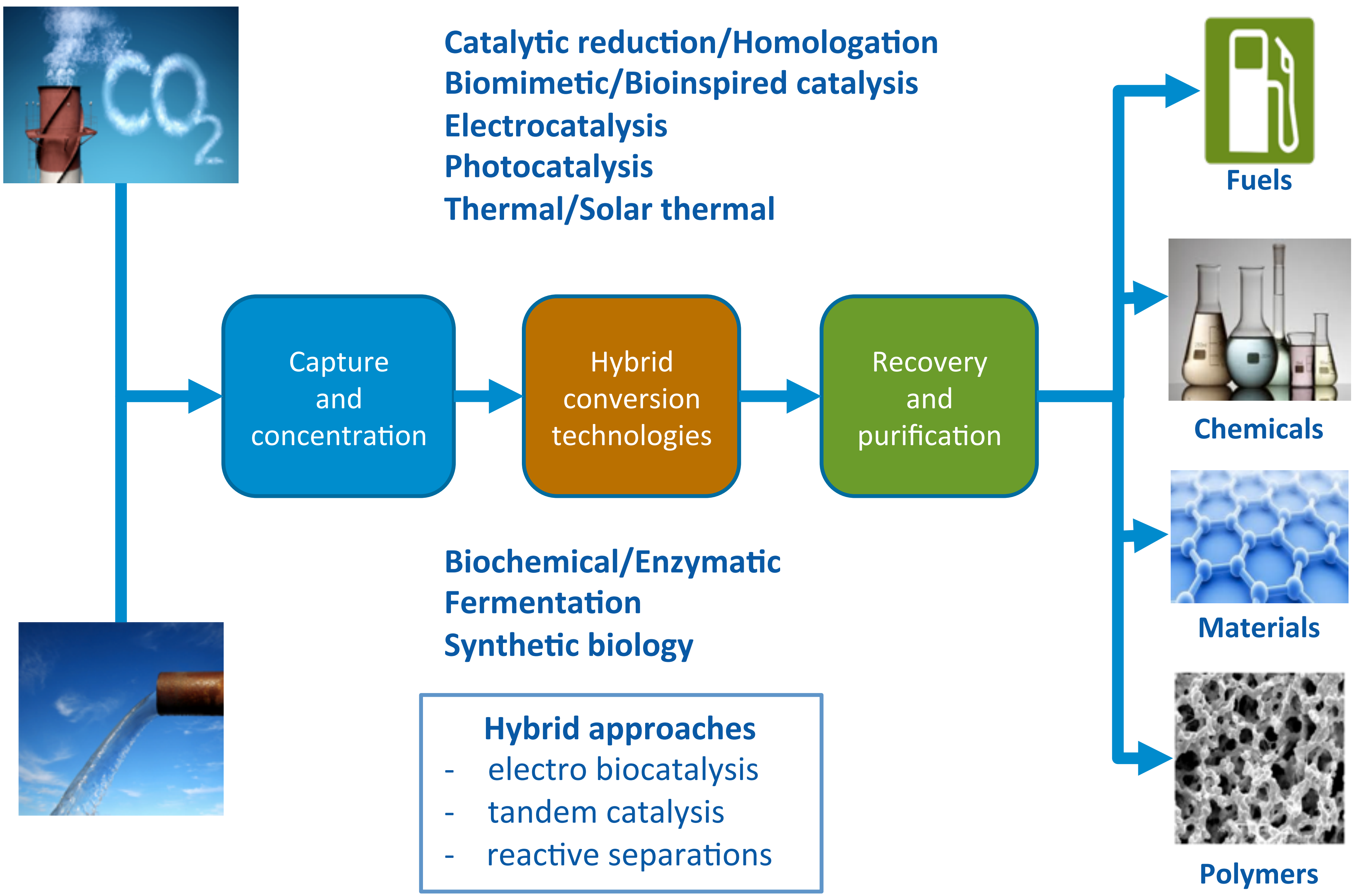
PinChing Maness, Ling Tao, Paul King, Todd Deutsch, John Turner, Nate Neale, Bryan Pivovar, Mark Ruth, Kevin Harrison

CARBON TEAM:

Karl Mueller, PNNL; Blake Simmons, LBNL; Roger Aines, LLNL, Christine Negri, Argonne; Amy Halloran, Sandia; Babs Marrone, LANL; Cindy Jenks, Ames Lab

CARBON National Lab Workshop Participants (March 2017)

Integrated Approach for Adding Value to CO_2



Integrated Approach for Adding Value to CO_2

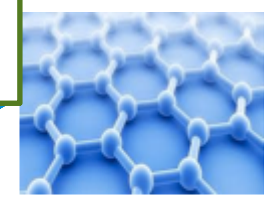
Catalytic reduction/Homologation
Biomimetic/Bioinspired catalysis
Electrocatalysis
Photocatalysis
Thermal/Solar thermal

Fuels

• Cost • Efficiency • Performance • Reliability • Scalability •

Materials ↔ Interfaces ↔ Components/Organisms ↔ Systems

Chemicals

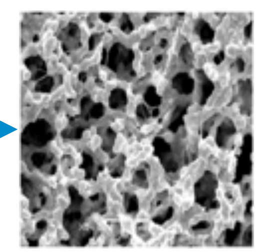


Materials

Biochemical/Enzymatic
Fermentation
Synthetic biology

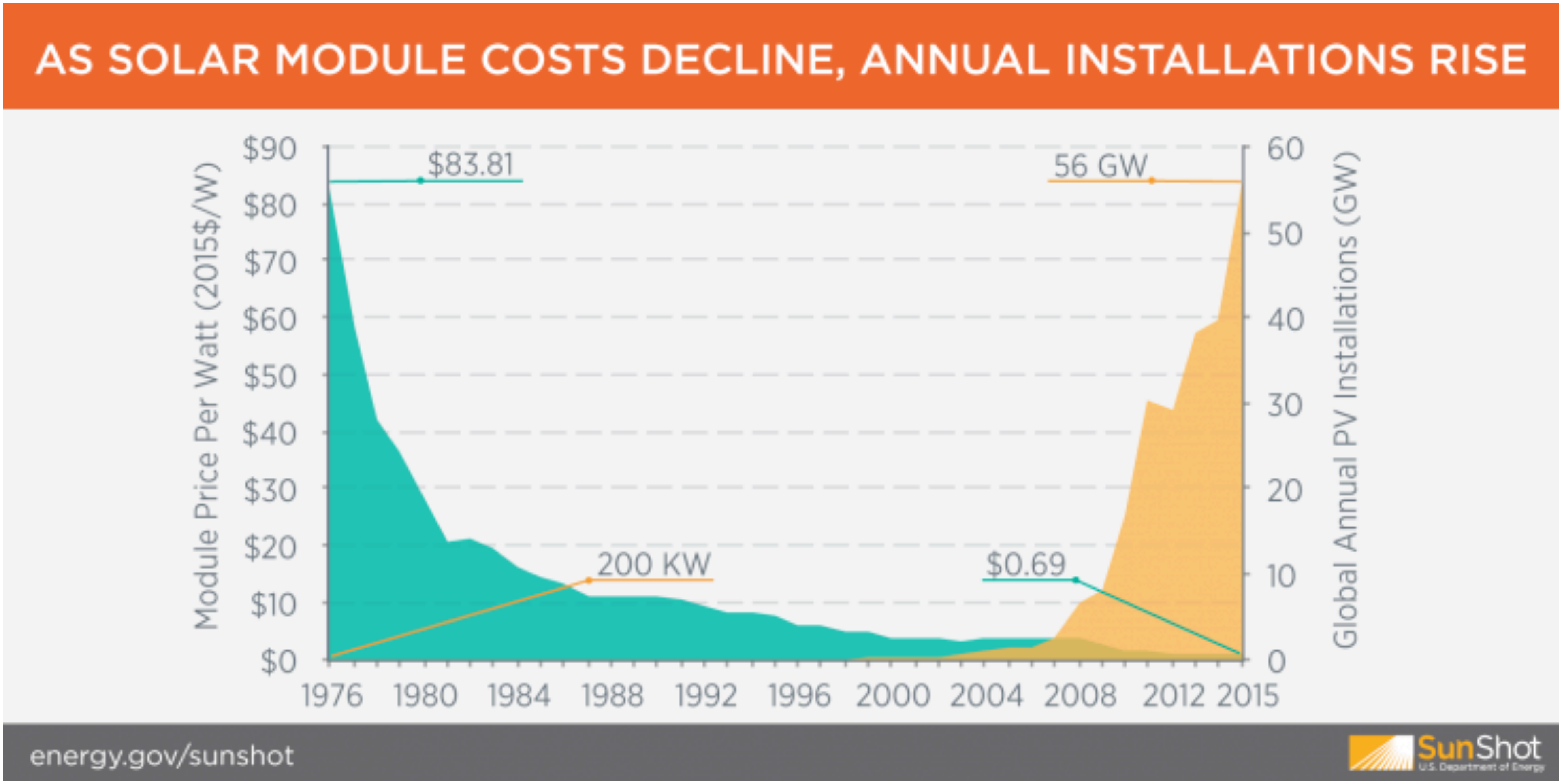
Hybrid approaches

- electro biocatalysis
- tandem catalysis
- reactive separations



Polymers

Why Now?



- Changing energy landscape and market opportunities
  - Curtailment, storage, products
- Advances in electrochemistry, materials discovery, synthesis characterization, catalysis science, synthetic biology

R&D Opportunities and Challenges

Efficient Generation of reductants from Renewable Energy

- Electrolysis, PEC water splitting, …

Rewiring biology by coupling anthropogenic reductants with biological processes (C-C)

- Couple the efficiency and cost advantages of abiotically generated reducants (e-, $_{H2}$, other) with the selectivity of bioprocesses
- Electro-biocatalysis; Synthetic biology

Reactive capture for CO_2 and waste gases

- Couple CO_2 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

- $CH_4 + CO_2$
- Innovative supports for tandem catalysis
- Reaction and reactor engineering

Innovative materials and product synthesis and processing from CO_2-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, Reliabilty, 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?
H_2 and CO_2 uptake
New chasses for synbio?
Design and control of interfaces?

Reactive capture for CO_2 and waste gases

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

Innovative hybrid approaches and tandem reactions, catalysis and biocatalysis

How do we create tandem approaches?
New chemistries (H_2 + CO_2 → C-C)
Couple chem/bio approaches?
Novel reaction and reactor engineering?

Innovative materials and product synthesis and processing from CO_2-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

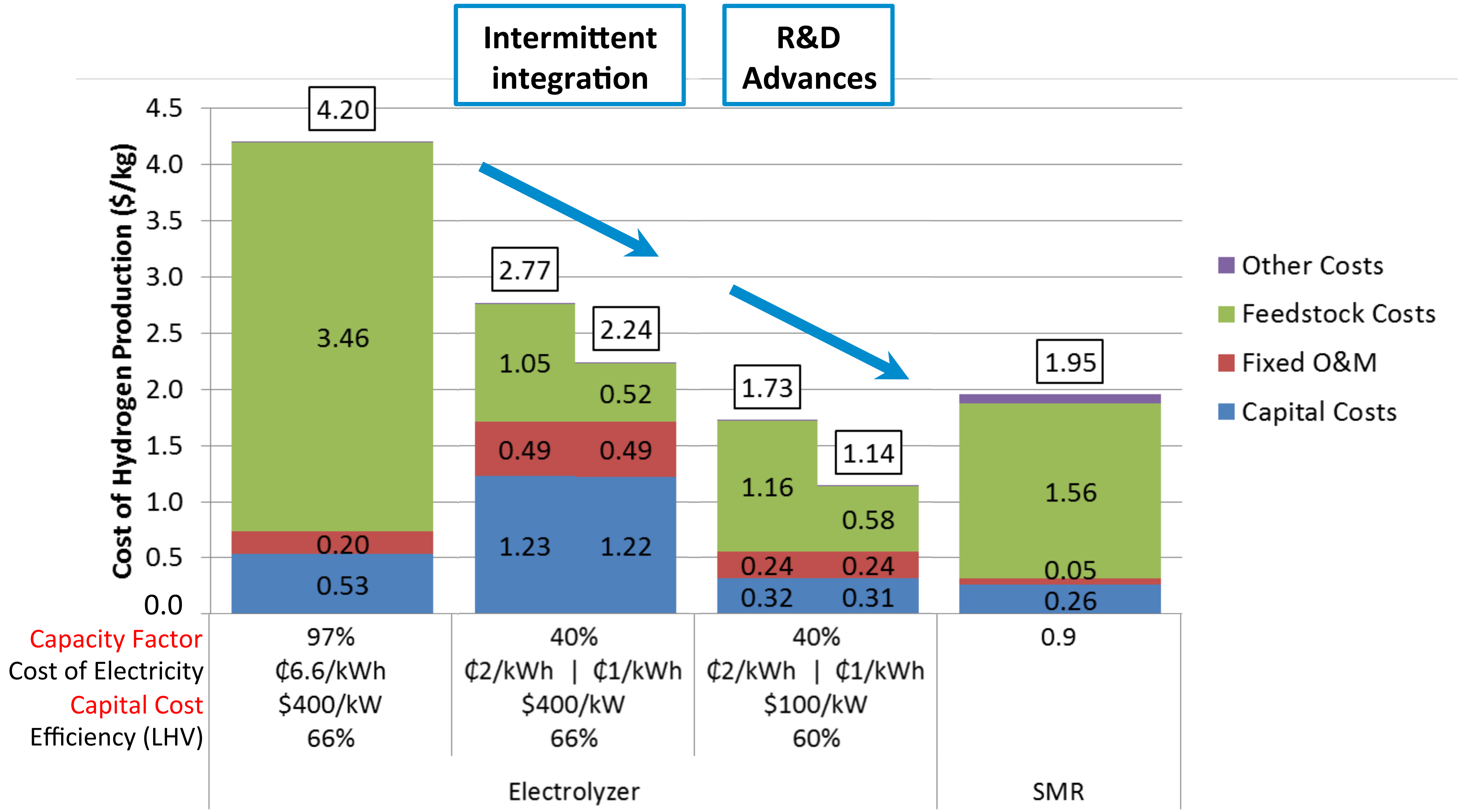
- new reactions
- mechanisms
- selectivity

Synthetic biology

- H_2 and CO_2 uptake
- productivity/selectivity/robustness
- bioenergetics (pathways and control)

New Concepts …

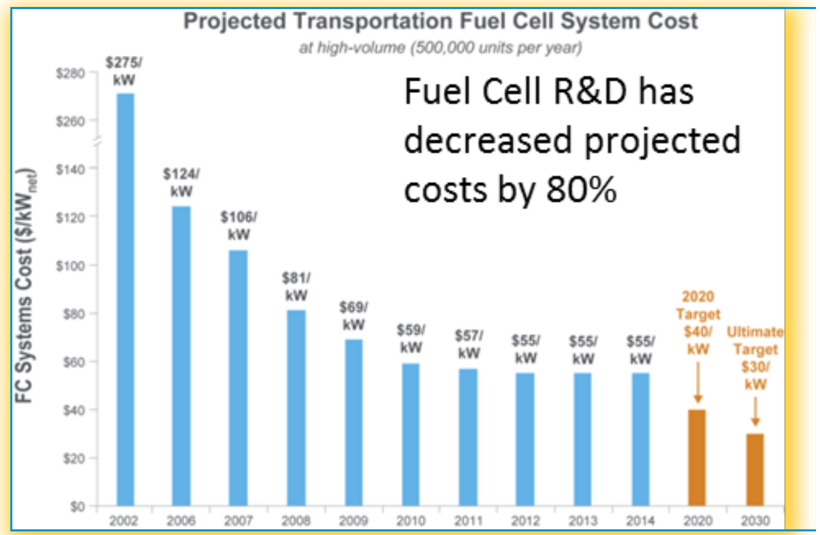
R&D for H_2 by Electrolysis



1 kg H_2 ≈ 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



PEC Water Splitting: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

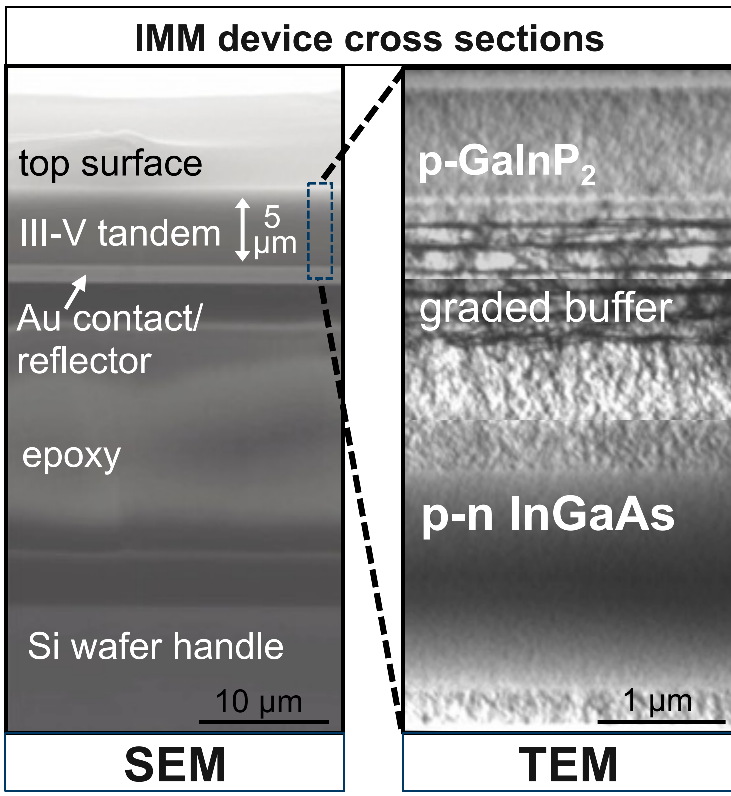
Approach

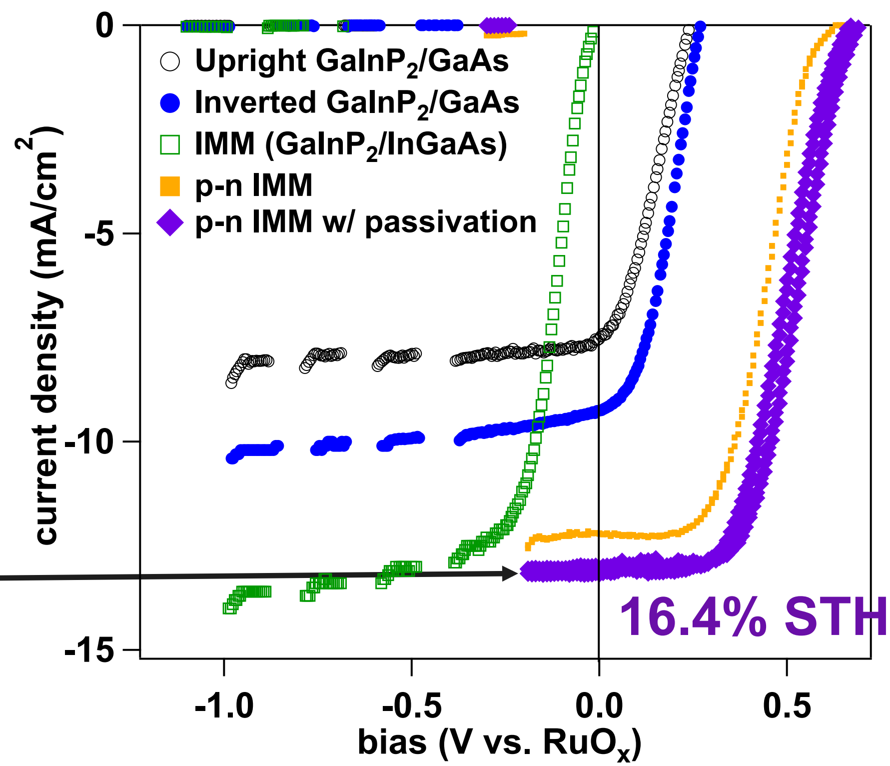
- **Inverted metamorphic multijunction (IMM) PEC** device enables more ideal bandgaps
- Grown by **organometallic vapor phase epitaxy**
- Incorporates **buried p/n GaInP$_2$ junction** and **AlInP passivation layer**

Solar-to-hydrogen Efficiency

16.4%

Benchmarked under outdoor sunlight at NREL





Nature Energy, **2**, *17028 (2017)*

Understanding and Designing more stable and efficient solar fuel generators

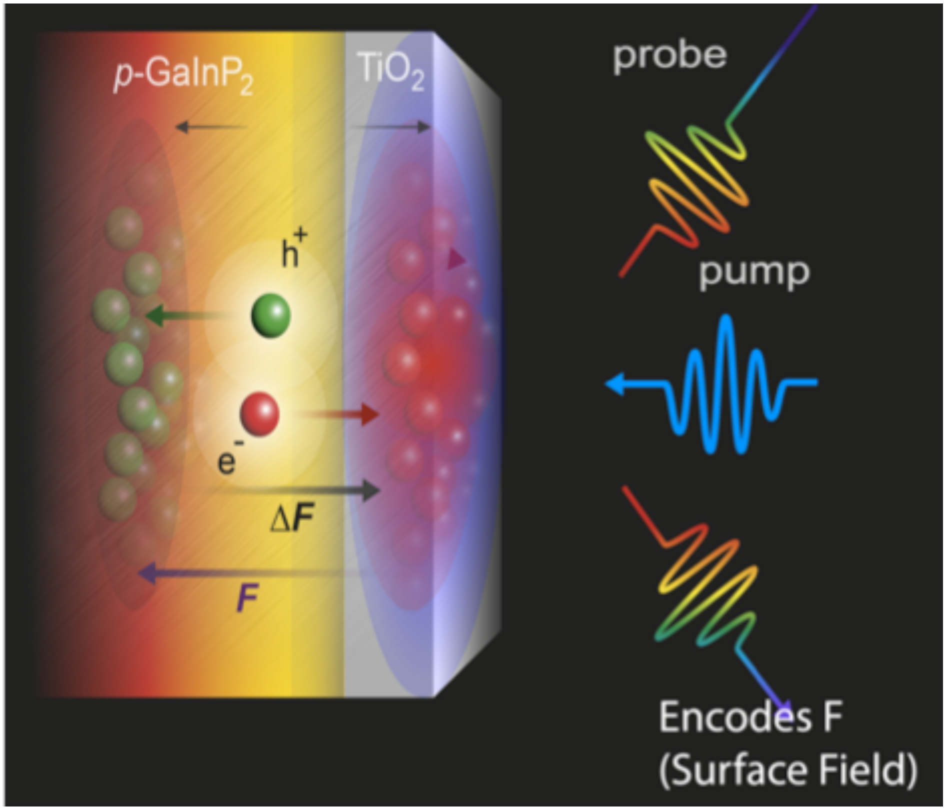
New ultrafast laser spectroscopy technique uncovers how photoelectrodes produce solar hydrogen from water

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

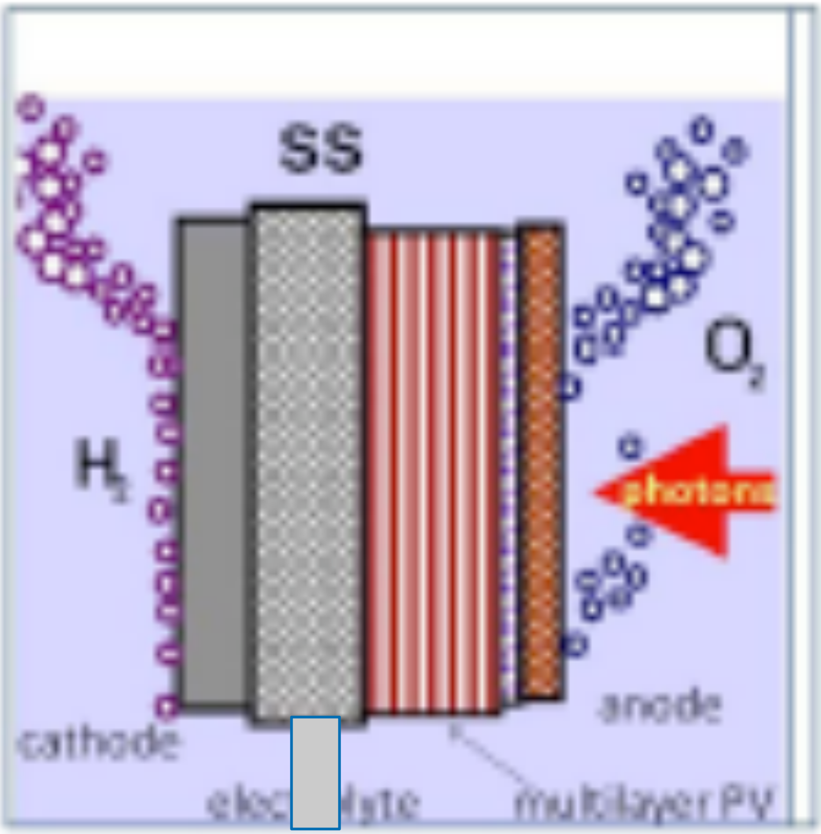


The transient photoreflectance (TPR) technique technique measures short-lived electrical fields that arise due to charges generated by light that are driven in opposite directions by the properties of the interface.

Science ***350****, 1061-1065, (2015)*

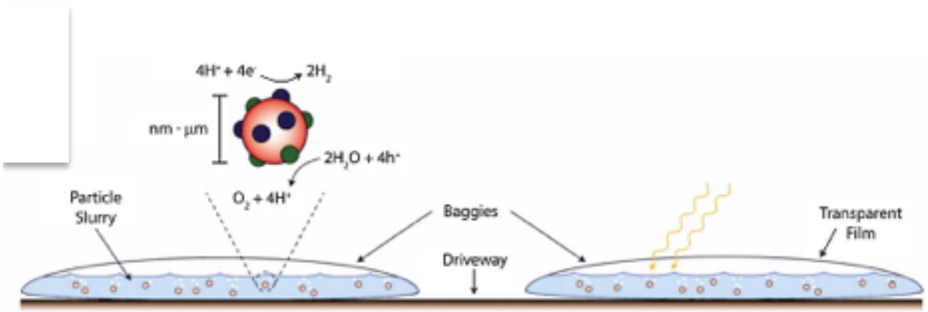
Cell and Module Testing

Material Challenges *(the big four)*
Photoelectrochemical Hydrogen Production Material

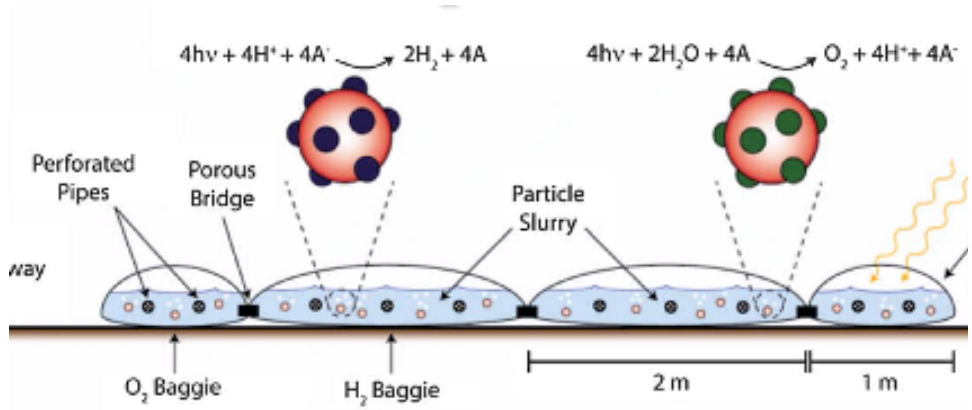


- Photomaterials
  - Efficiency
  - Energetics
  - Coupling to catalytic rxns
- Catalysis – Efficient selective catalysis at low overpotential
- Interfacial Materials, Membranes – keep O_2 from fuel; charge/ion balance
- Material Durability – semiconductor/catalyst must be stable in electrolyte solution
- Protective coatings

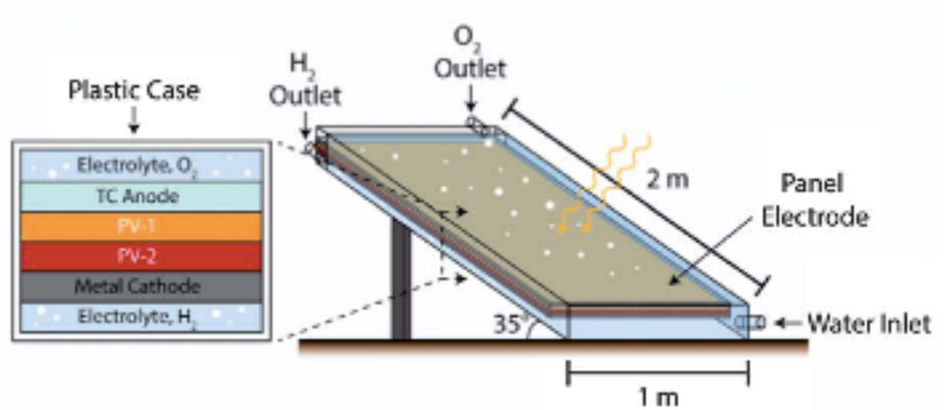
Approaches to PEC Hydrogen



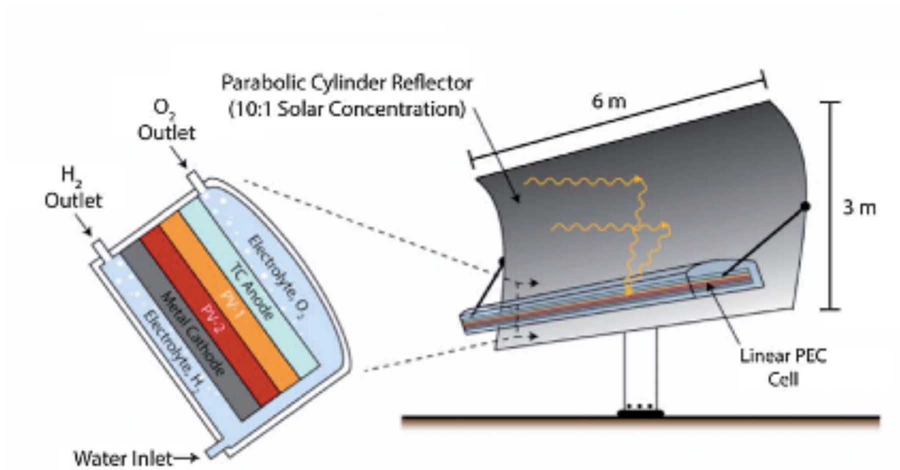
1) Single Bed, 10%



2) Double Bed, 5%



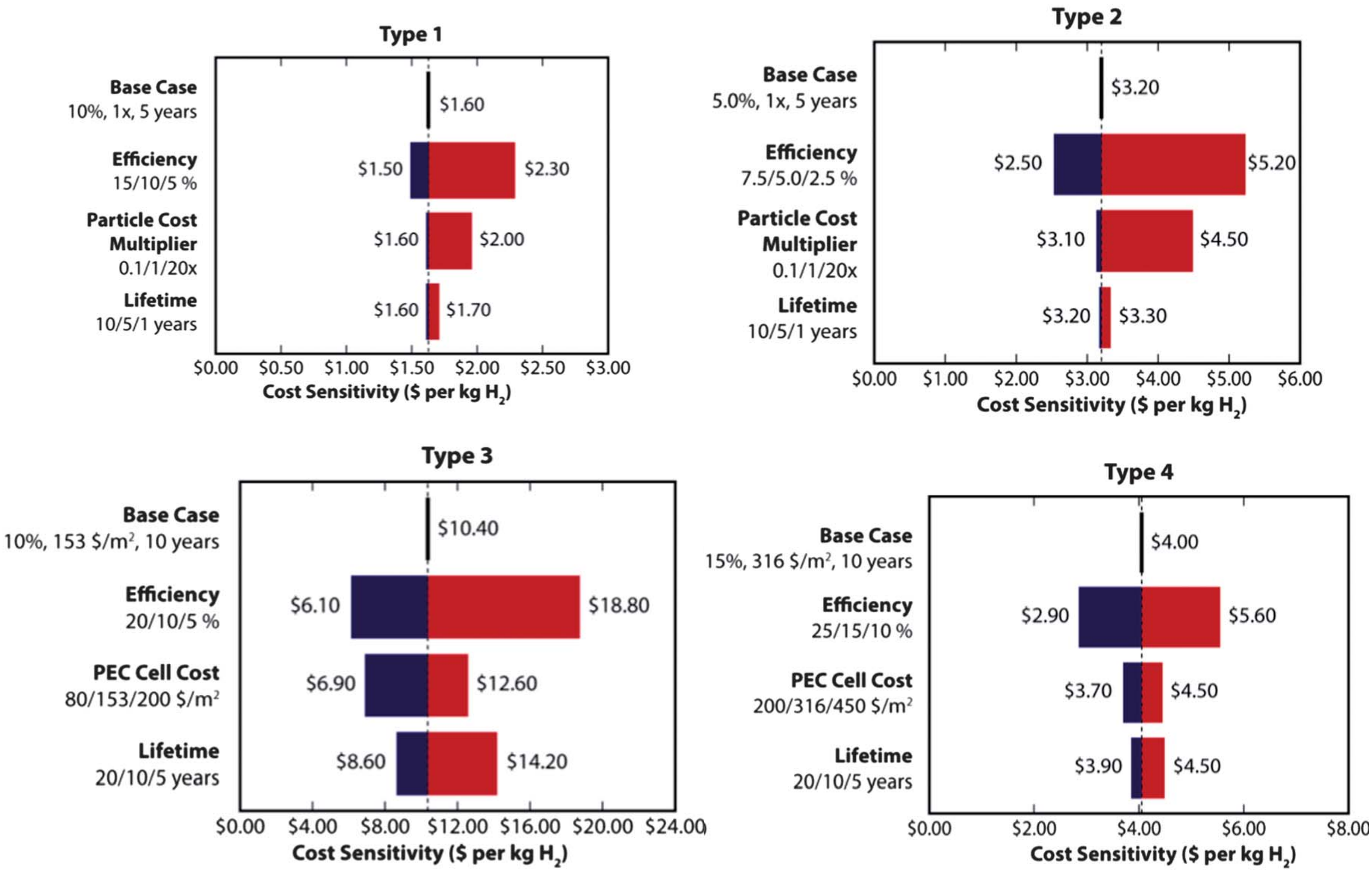
3) Fixed Panel, 10%



4) Concentrator, 15%

Energy Environ. Sci., ***6,*** *1983 (2013)*

Technoeconomic Analyses: Approaches to PEC Hydrogen



Energy Environ. Sci., ***6***, *1983 (2013)*

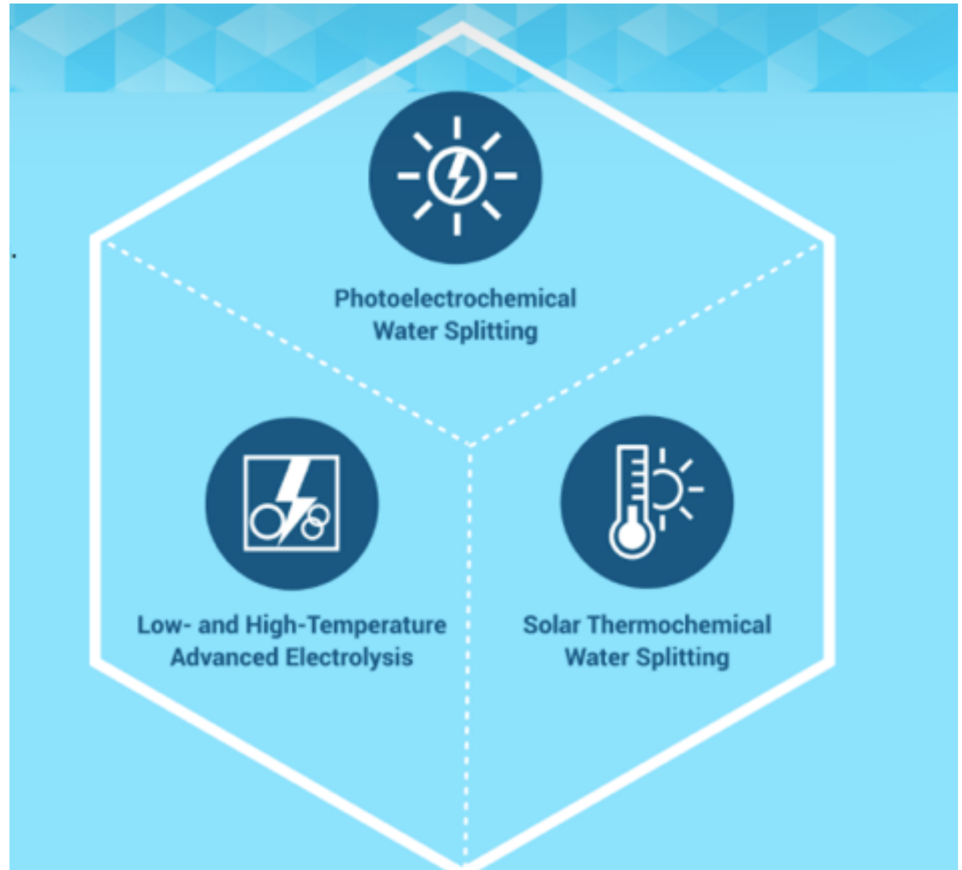
HydroGEN Consortium

HydroGEN
Advanced Water Splitting Materials

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
- Durabiliity
- Systems Integration
- Analysis



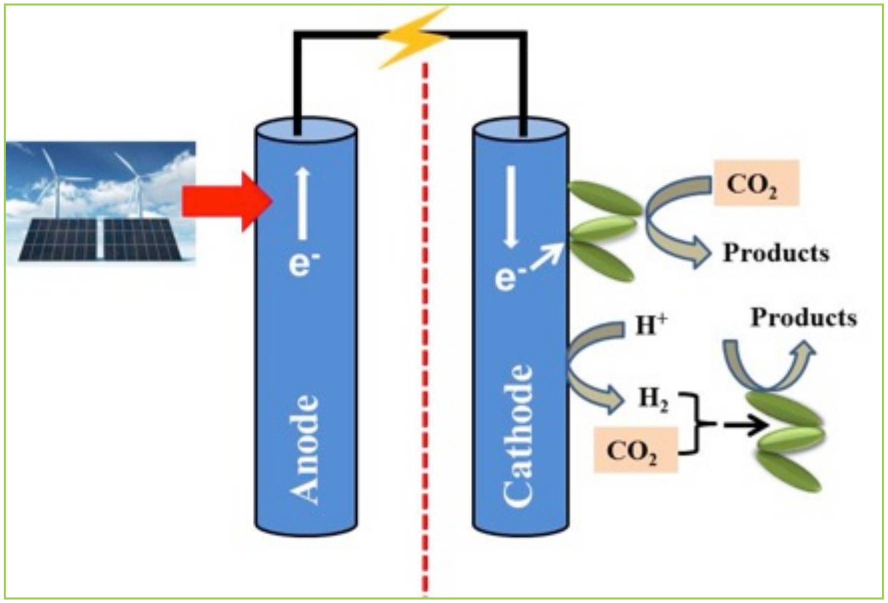
https://www.h2awsm.org

Energy Materials Network
U.S. Department of Energy

NREL National Renewable Energy Laboratory
Berkeley Lab
Sandia National Laboratories
INL Idaho National Laboratory
Lawrence Livermore National Laboratory
SRNL

BioHybrid Approaches (Electrochem, H_2, Mediators)

Electrosynthesis



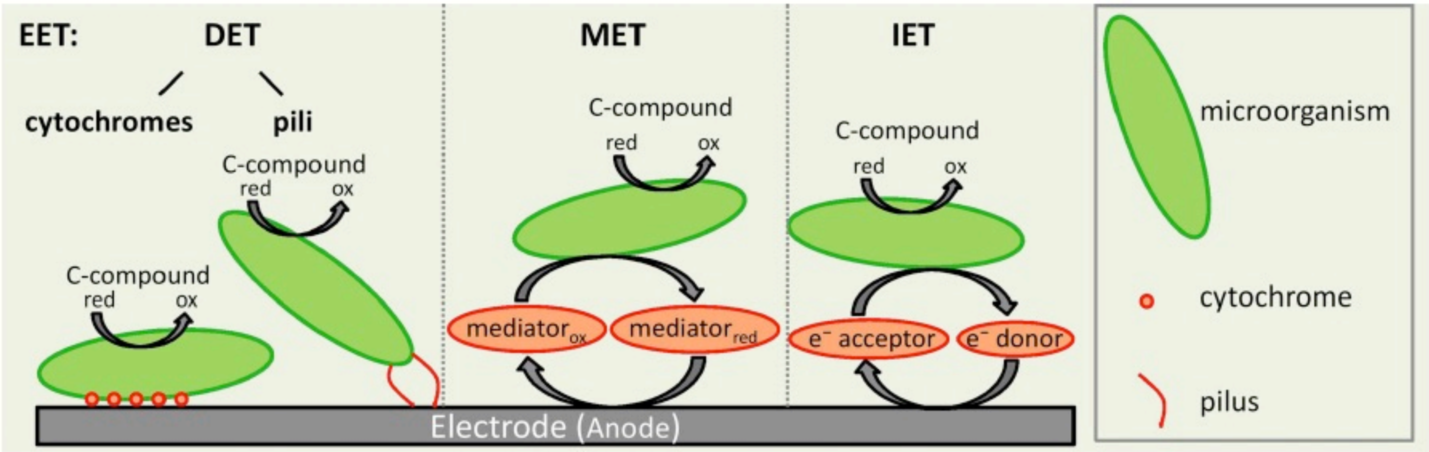
The Electric Economy Meets Synthetic Biology

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.

Electroactive Bacteria – Molecular Mechanism

(1) Direct Electron Transfer (2) Mediated ET (3) Indirect ET



Three possible electron transfer mechanisms

(1) Direct via conducting pili or c-type cytochrome (multi-heme)

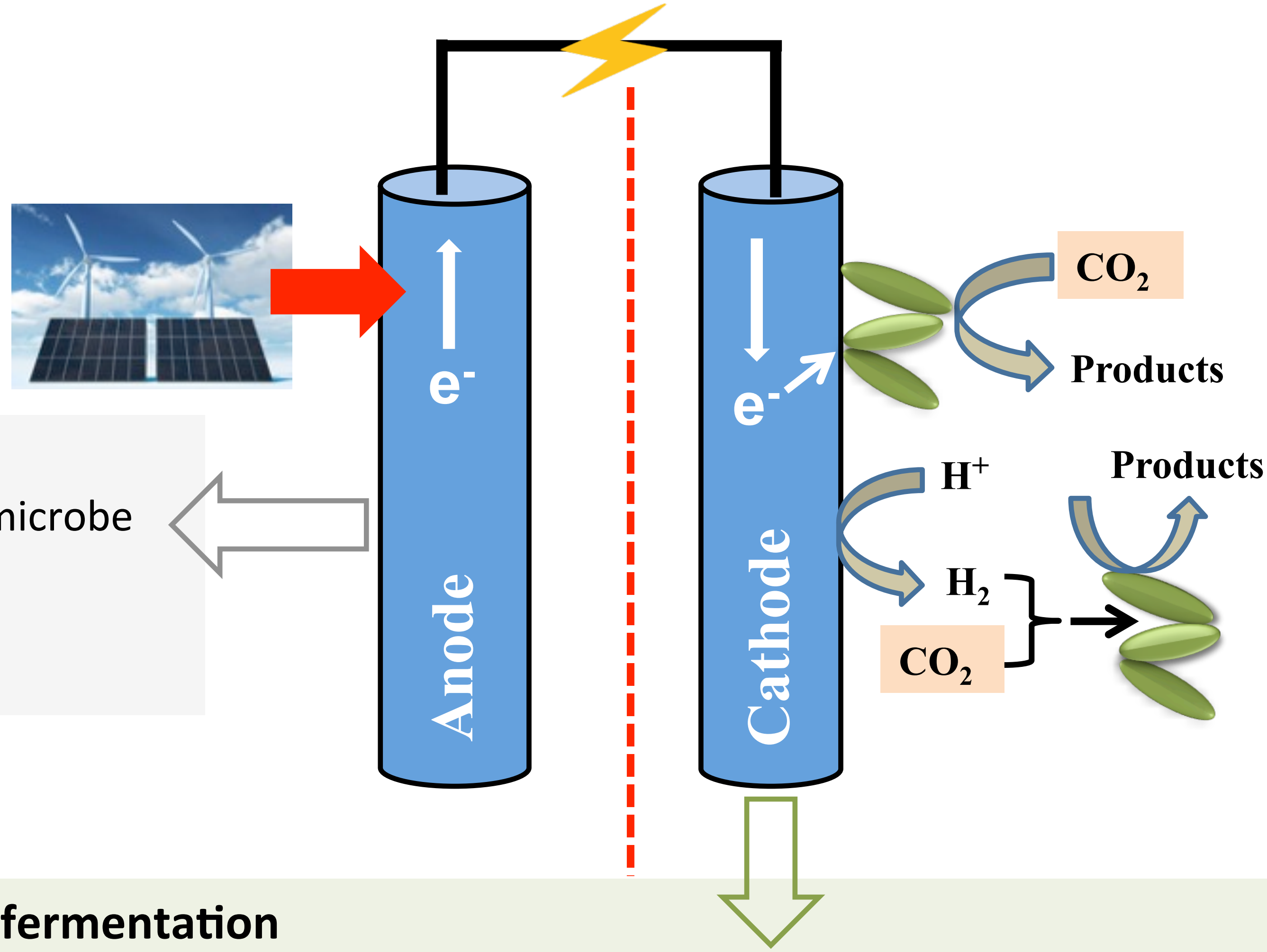
(2) Mediators released by the cells (flavin, quinones)

(3) Exogenously added electron shuttles (i.e. H_2, formate,Fe^{++})

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

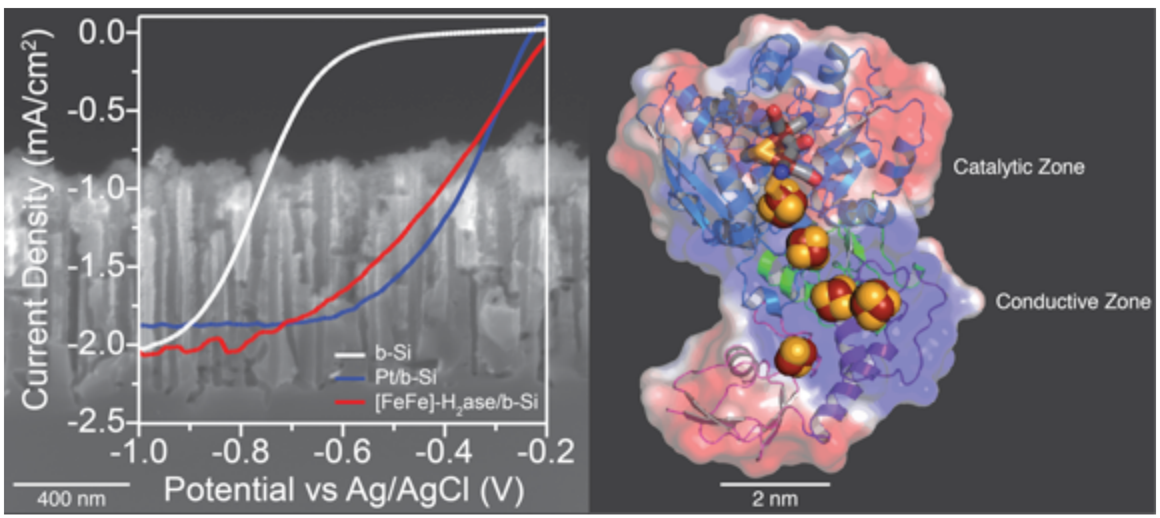
Electrofermentation

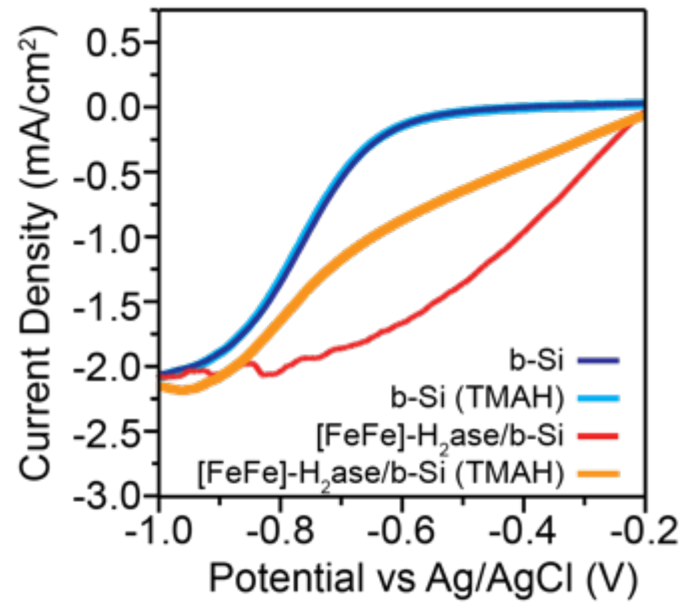
- Matching energetics and kinetics between microbes and electrode
- Mechanisms of electron transfer between microbe and electrode
- Understanding bioenergetics to increase carbon, electron, and energy flux
- Synbio, metabolic engineering to control and design pathways
- Enhanced H_2 and CO_2 uptake by designer chassis microbes
- Biofilm formation; mechanism of microbial attachment
- Biofouling

Water Splitting by a Bioassisted Black Si Photocathode

- **[FeFe]-H_2ase 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}**

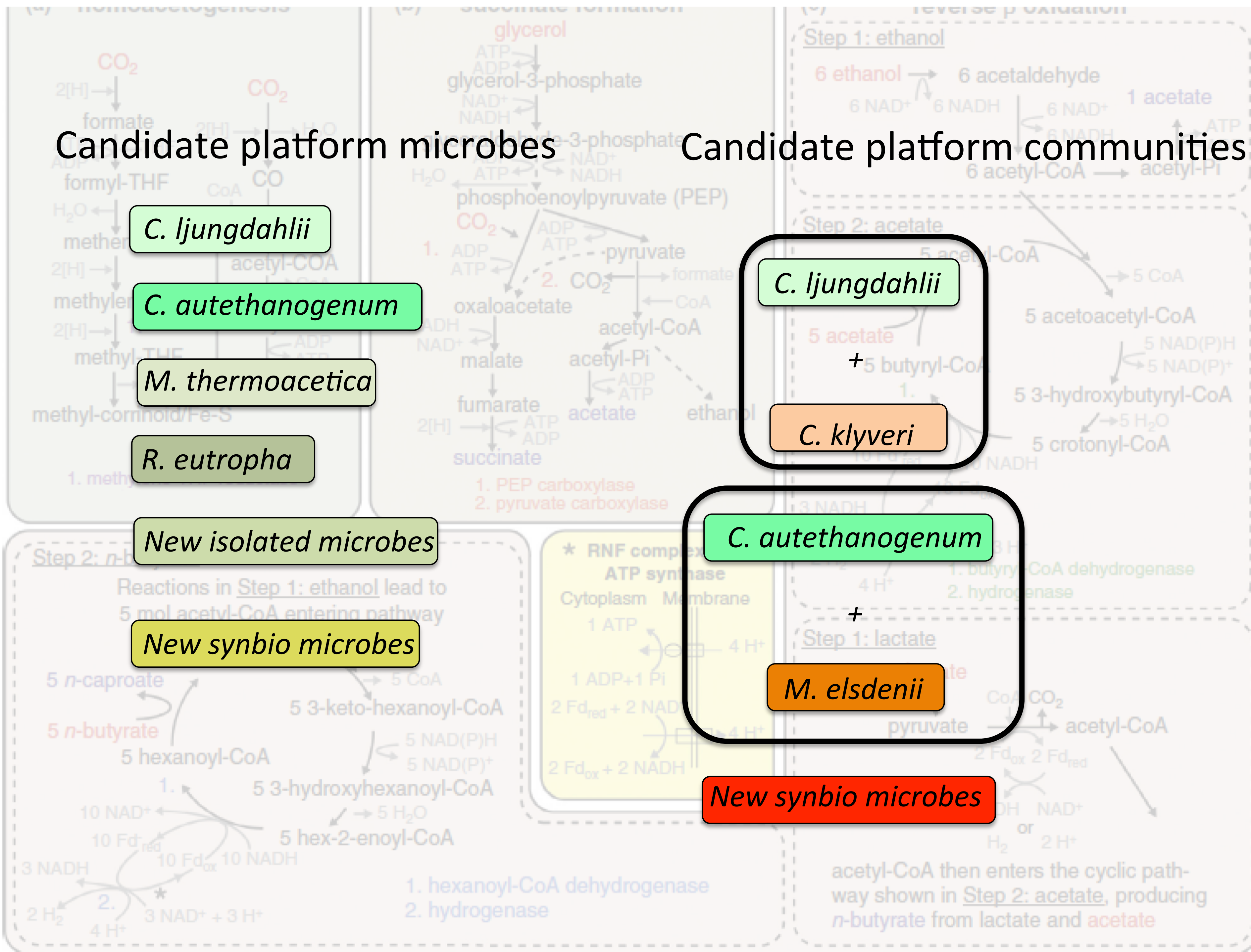
TMAH (Me_4NOH) etch to remove sharp surface features shows nanostructured b-Si surface critical to effective binding interaction with [FeFe]-H_2ase





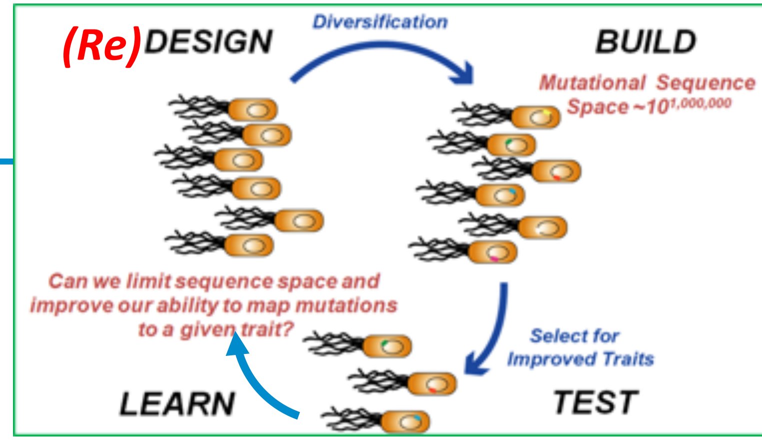
≤12 pmol/cm^2 TOF = 1300 s^{-1} TON ≈ 10^7

ACS Appl. Mater. Interfaces **2016**, *8*, 14481

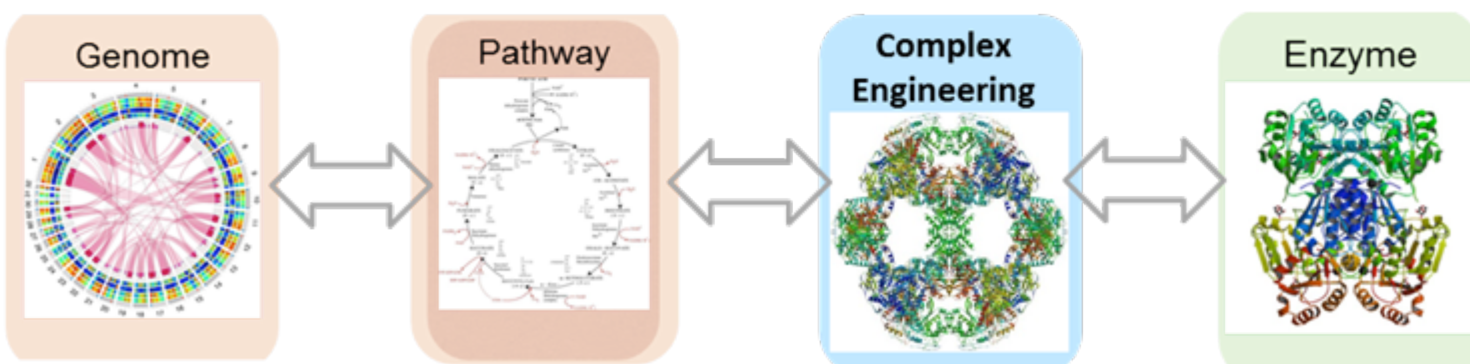


Candidate platform microbes
C. ljungdahlii
C. autethanogenum
M. thermoacetica
R. eutropha
New isolated microbes
New synbio microbes
Candidate platform communities
C. ljungdahlii
+
C. klyveri
C. autethanogenum
+
M. elsdenii
New synbio microbes

Synbio Toolbox

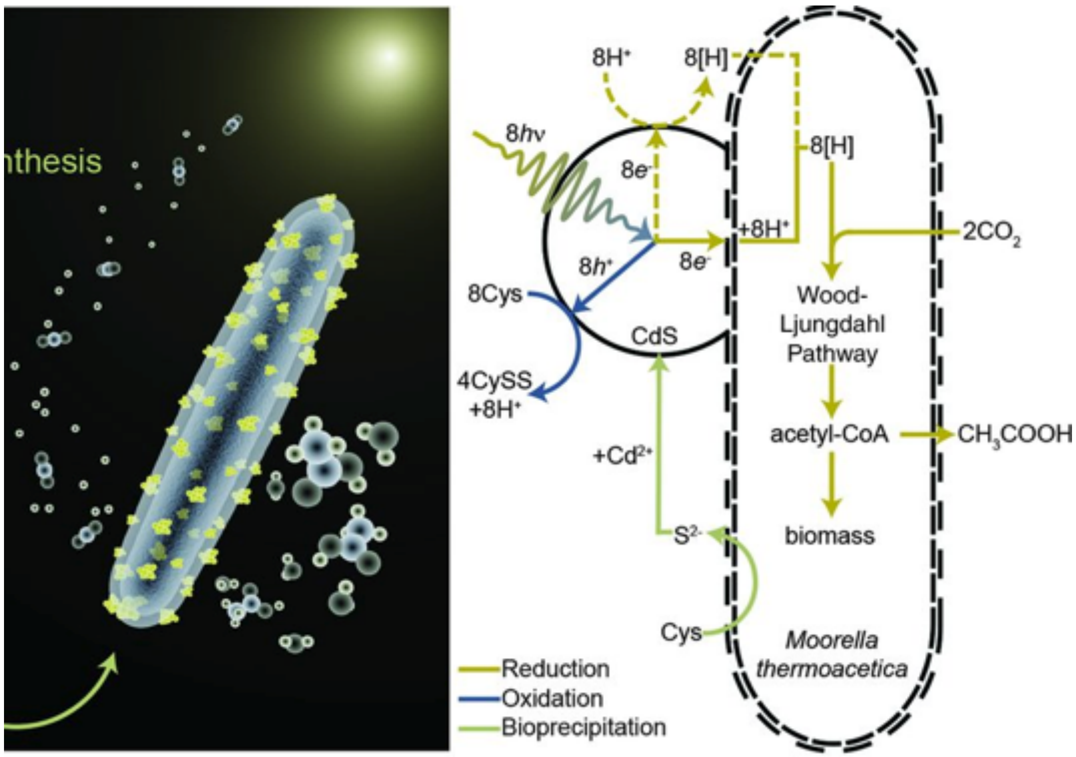


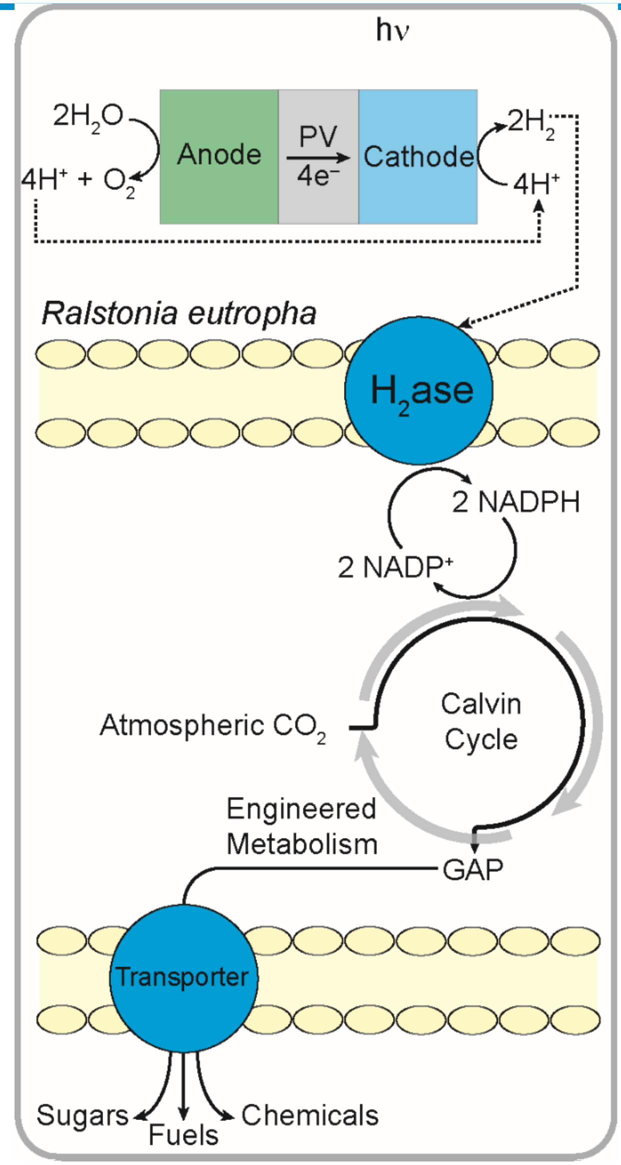
- Advanced genetic toolbox:
  - Develop robust DNA transfer methods/CRISPR
  - Knock-out/Knock-in genes
  - Alter expressed patterns/levels
  - Conduct systems biology based approaches (-omics)
  - Conduct ^{13}C-metabolic flux analysis (^{13}C-MFA; carbon/electron flow)
  - Develop predicted genome-scale 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



Maness, Simmons

Coupling Anthropogenic Reductants with Microbes





Yang,… Science 351, 74 (2016)

Nocera, Silver, … Science 352, 1210 (2016)

Challenges/Opportunities: CO_2 to Products

Carbons

***e.g.* carbon fiber, CNTs**
Graphene, …
(Structural Carbon)

- Remove oxygen
- Make products

Approaches

- Electrocatalysis
- Pyrolysis

Challenges

- Coupling electricity to catalysis
- Product purity
- Efficient catalysis

Carbonates

***e.g.* cement, aggregate, polycarbonates**

- Alkalinity: HCO_3^-
- Cations for product

Approaches

- Electrolysis
- Direct reaction from solvents capturing CO_2 as CO_3

Challenges

- Efficient electrolysis
- Cation sourcing, *e.g.* seawater

Hydrocarbons

***e.g.* polymers, fuels, chemicals**

- Provide hydrogen
- Make polymers

Approaches

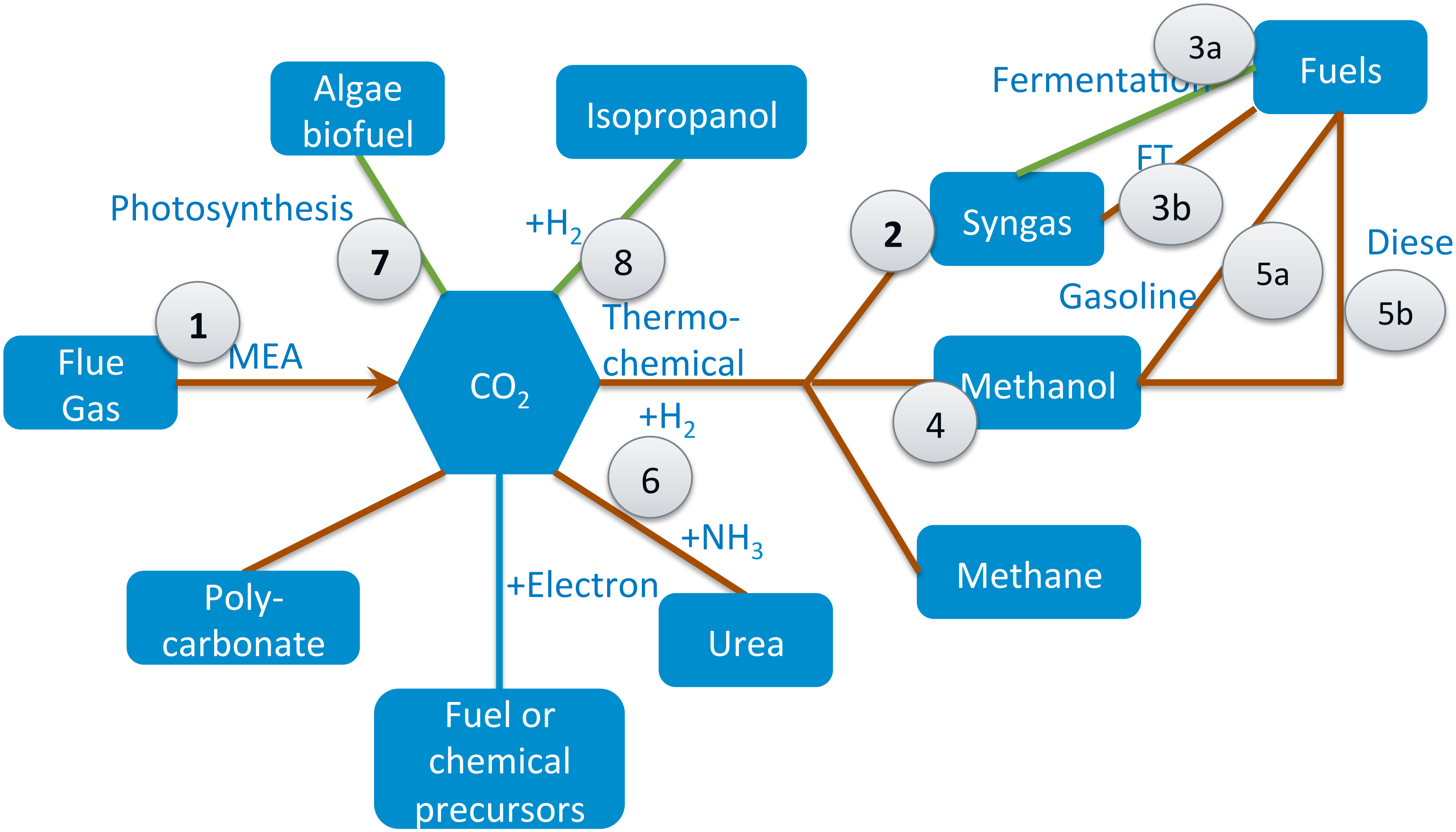
- Catalysis to make C-C and polymer precursors

Challenges

- Low-C Hydrogen
- De-oxygenation
- Selectivity
- Integrated capture/ reaction

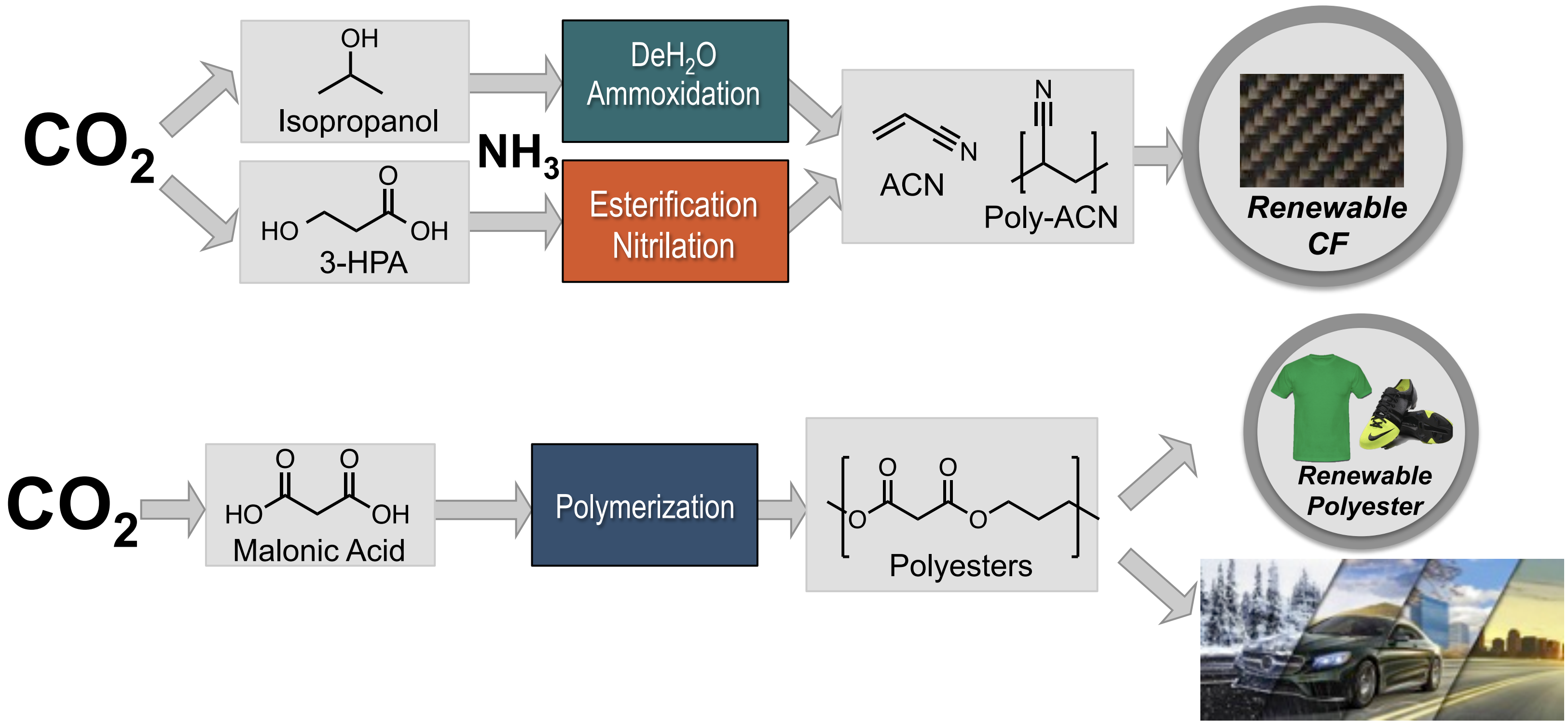
Adapted from R. Aines, CARBON workshop, March 2017

CO_2 Utilization Pathways



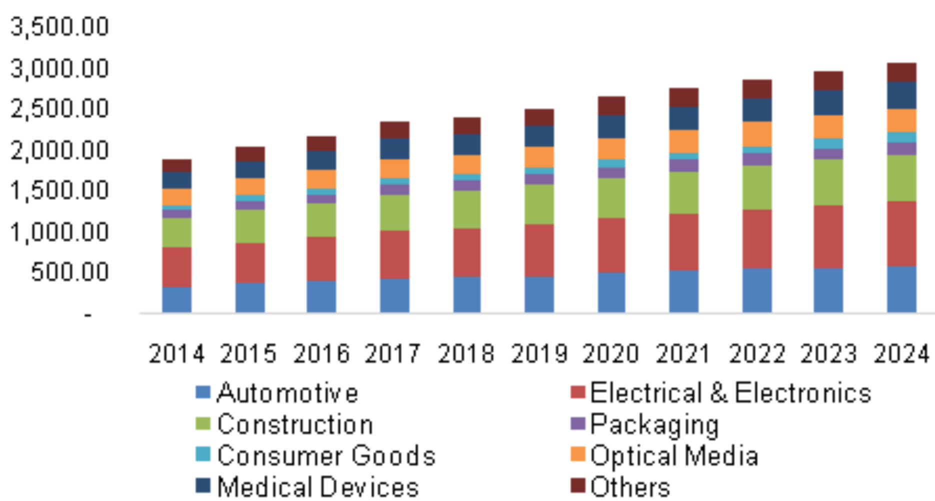
Ling Tao, Mary Biddy, ….

CO_2-Based Materials and Polymers



Polycarbonate Market

3% of current polymer GDP



Carbon Fiber: Large and Growing Market

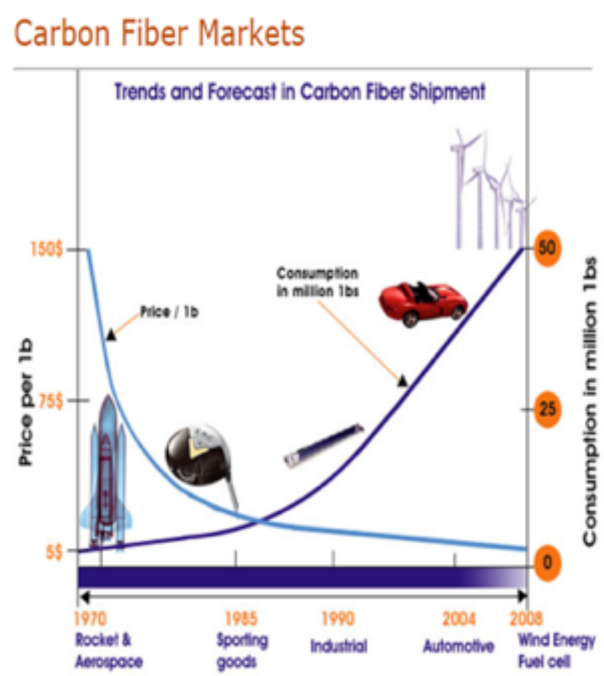
2005—$90 million market size,
2015—$2 billion
2020—projected to reach $3.5

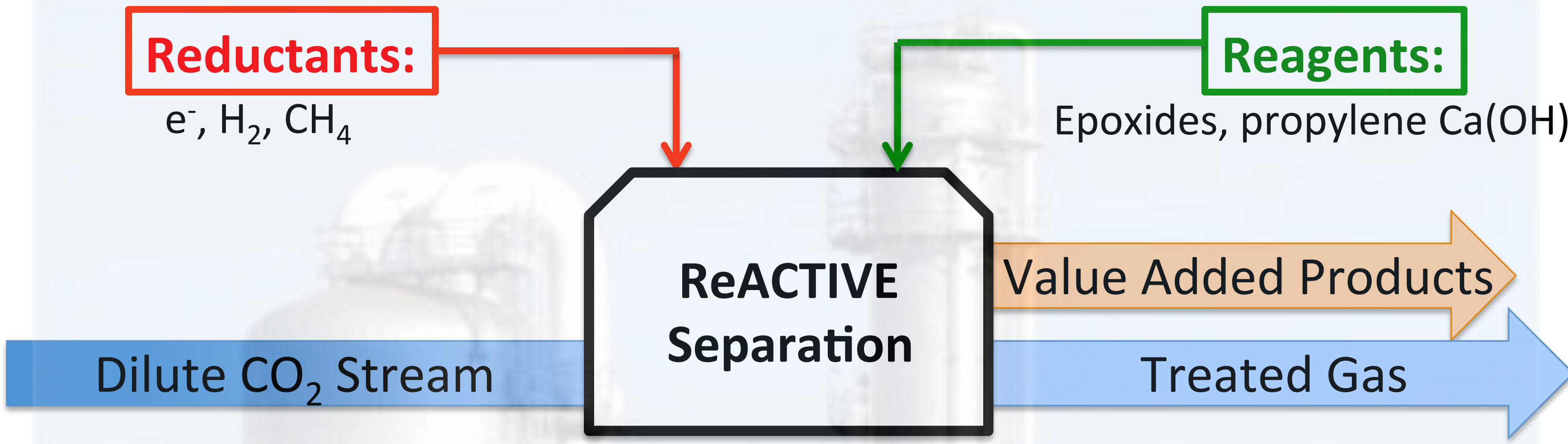
The North America region is expected to be the largest market globally due to the increased demand from **aerospace & defense, wind energy, infrastructure, and automotive industry.**

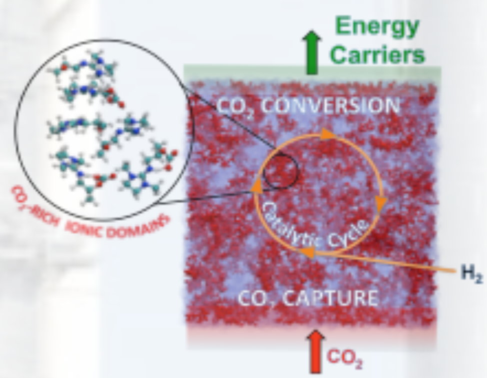
U.S. Composite Materials Demand Forecast ($Billion)

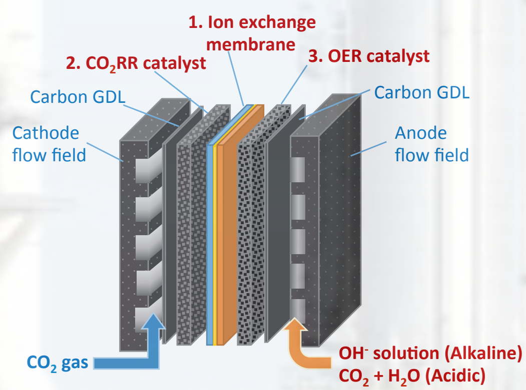
Applications	2015	2021	CAGR (2015-2021)
Transportation	2.4	3.3	5.2%
Marine	0.4	0.5	3.2%
Wind Energy	0.2	0.4	8.0%
Aerospace	0.8	1.4	9.5%
Pipe & Tank	0.7	0.9	3.0%
Construction	1.4	1.8	4.1%
Electrical & Electronics	0.7	0.9	3.8%
Consumer Goods	0.4	0.5	3.6%
Others	0.4	0.5	5.7%
Total ($B)	7.5	10.2	5.1%

Source: Lucintel









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

Acknowledgements

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