Overview of CO_2 Capture/Utilization Integration for Workshop

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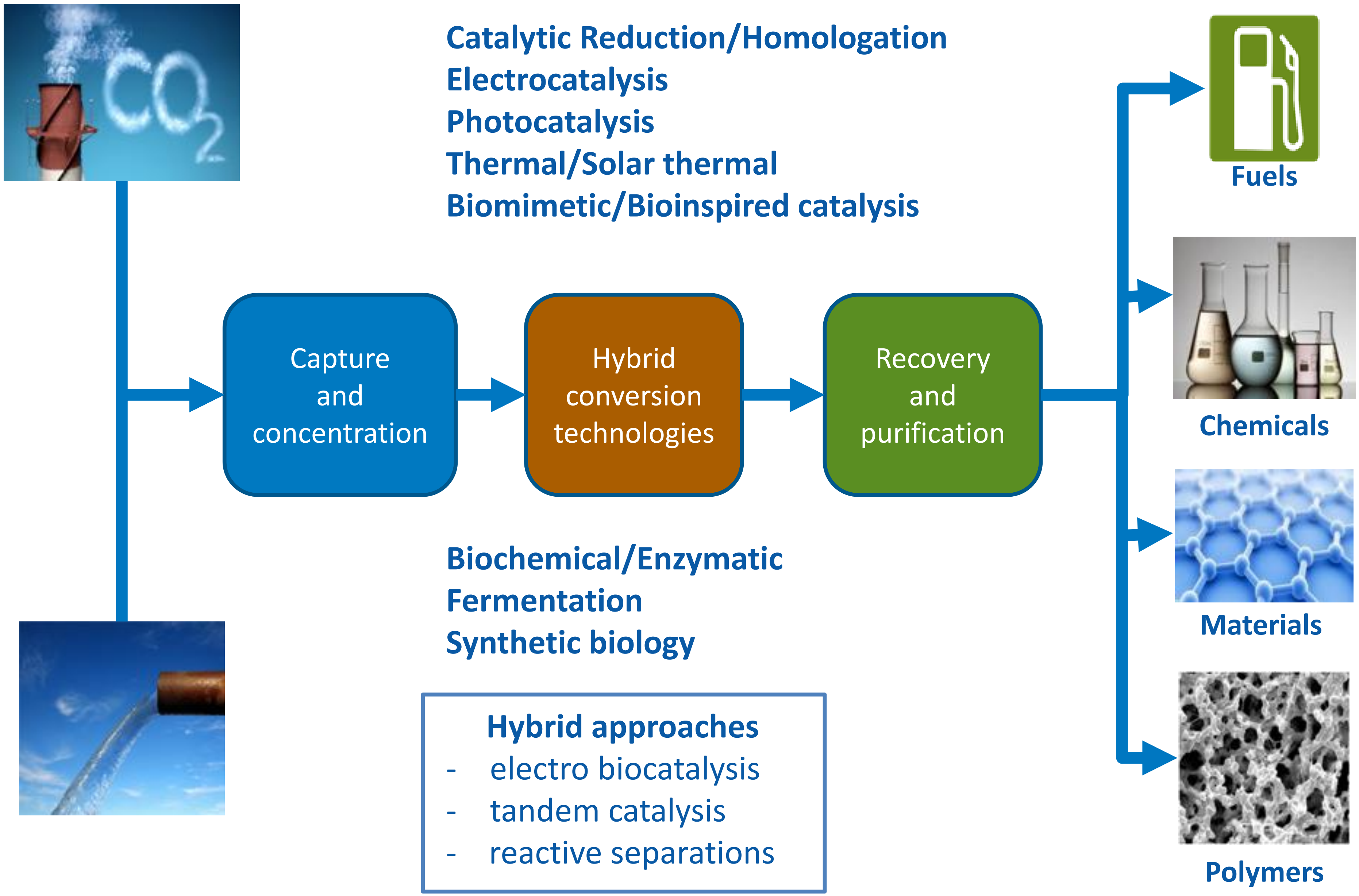
Integrated Approach for Adding Value to CO_2



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

Capture and concentration → Hybrid conversion technologies → Recovery and purification

Biochemical/Enzymatic
Fermentation
Synthetic biology

Hybrid approaches
- electro biocatalysis
- tandem catalysis
- reactive separations

Integrated Approach for Adding Value to CO_2

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

- Cost
- Efficiency
- Performance
- Reliability
- Scalability

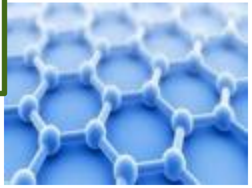
Materials ↔ Interfaces ↔ Components/Organisms ↔ Systems

Biochemical/Enzymatic
Fermentation
Synthetic biology

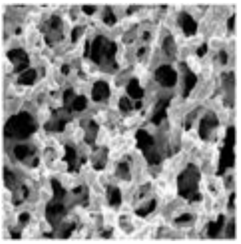
Hybrid approaches
- electro biocatalysis
- tandem catalysis
- reactive separations

Fuels

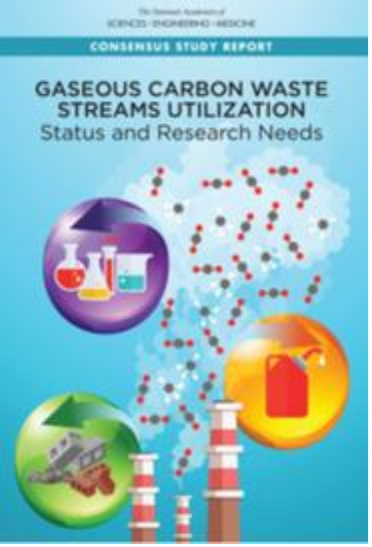
Chemicals



Materials



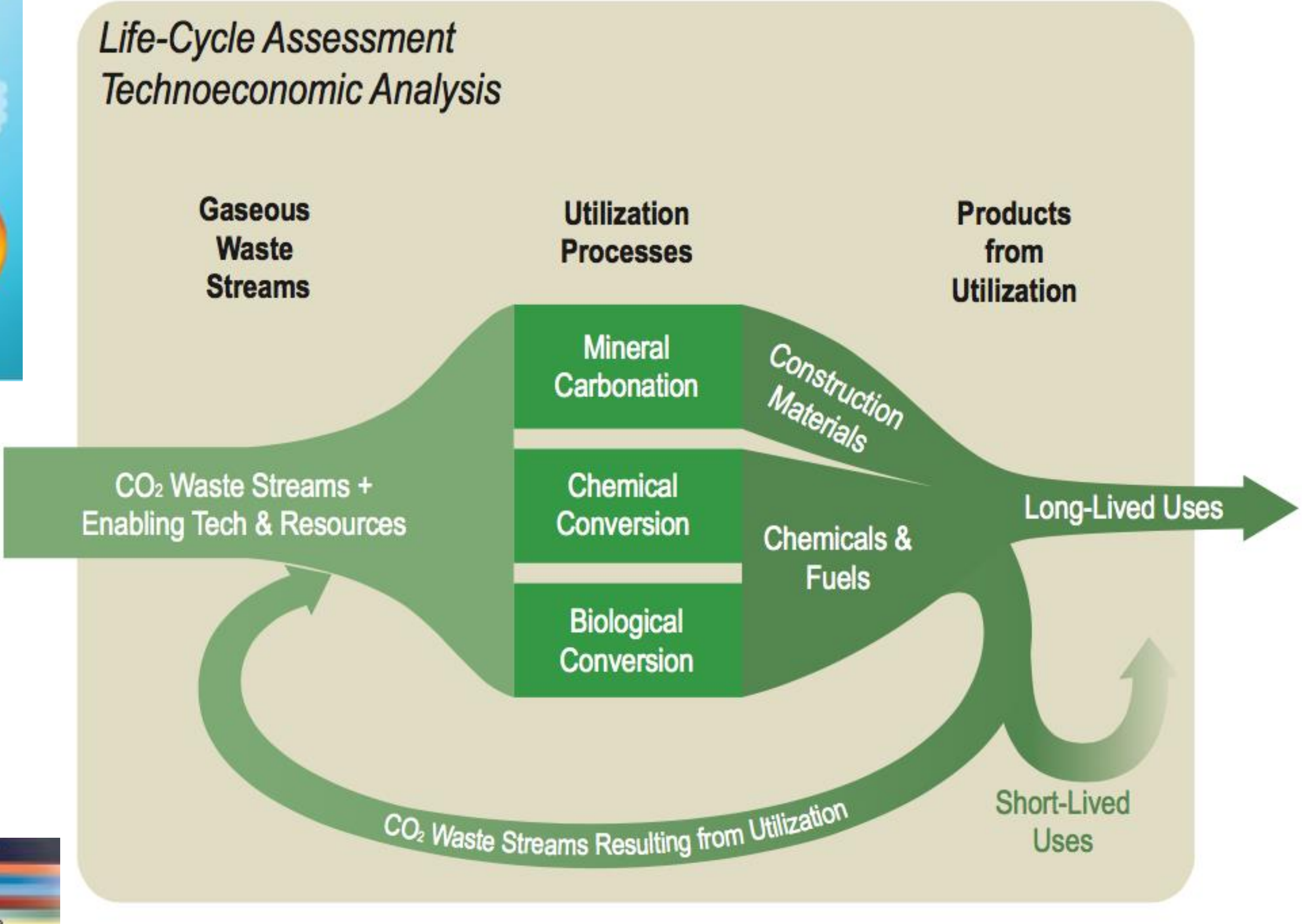
Polymers



CONSENSUS STUDY REPORT

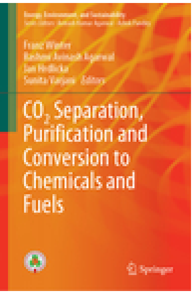
GASEOUS CARBON WASTE STREAMS UTILIZATION

Status and Research Needs



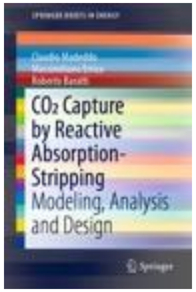
Life-Cycle Assessment

Technoeconomic Analysis



CO_2 Separation, Purification and Conversion to Chemicals and Fuels

Springer



CO_2 Capture by Reactive Absorption-Stripping

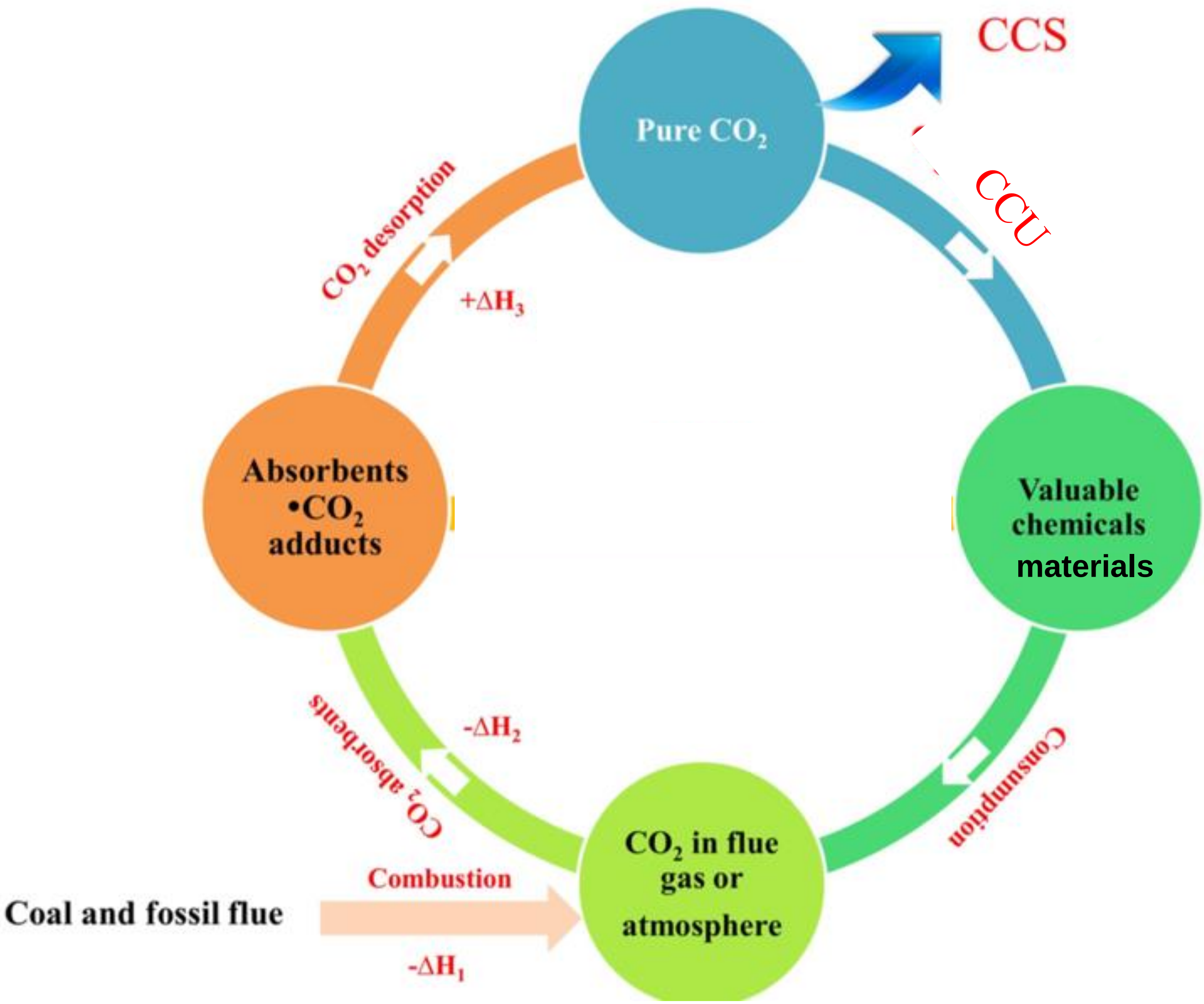
Modeling, Analysis and Design

Springer

https://www.nap.edu/catalog/25232/gaseous-carbon-waste-streams-utilization-status-and-research-needs

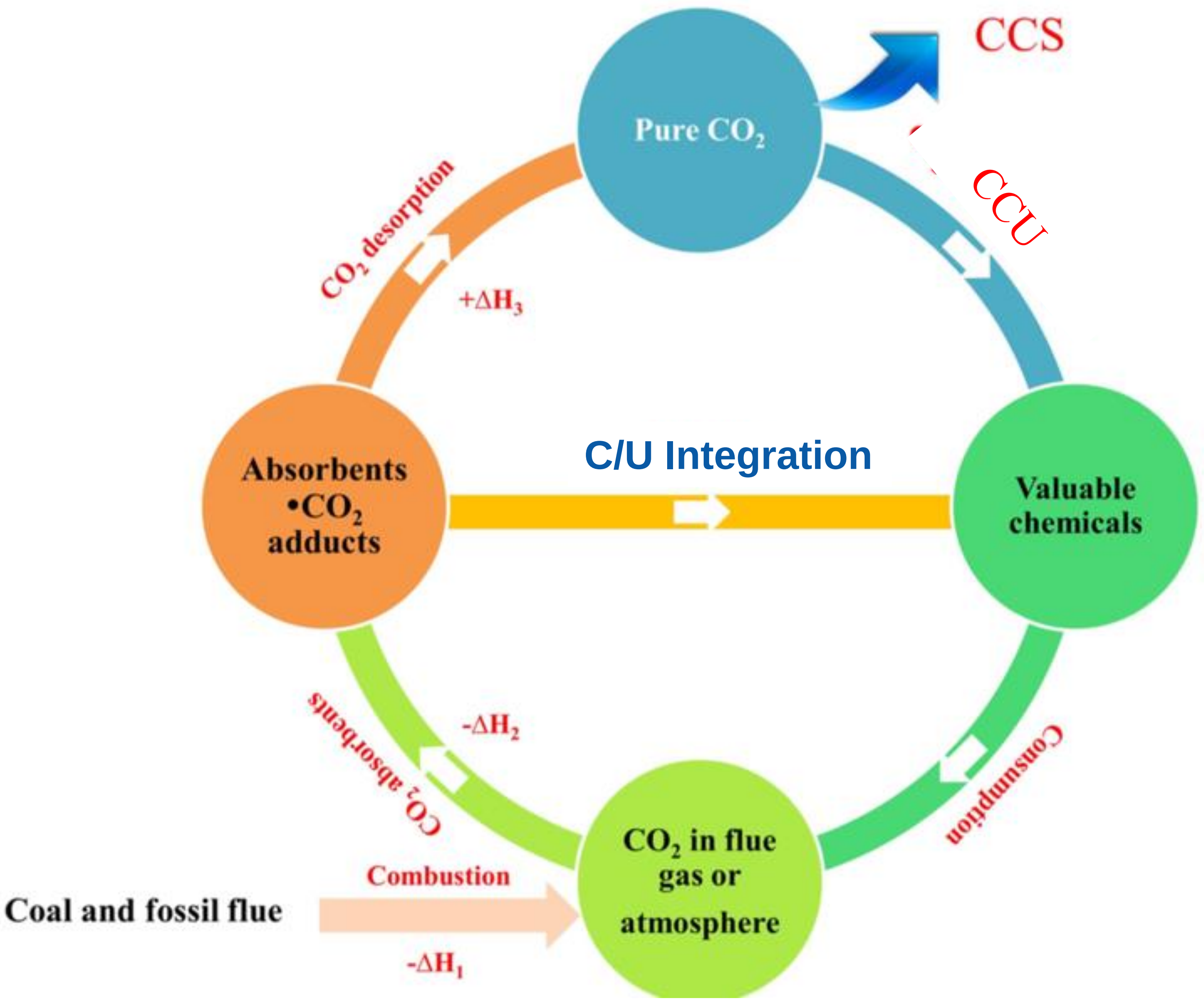
The Carbon Cycle

Capture →. Compression → Transport



Adapted from: CO2 Capture and *in situ* Catalytic Transformation
Fu et al. Frontiers in Chemistry, 2019
https://www.frontiersin.org/articles/10.3389/fchem.2019.00525/full

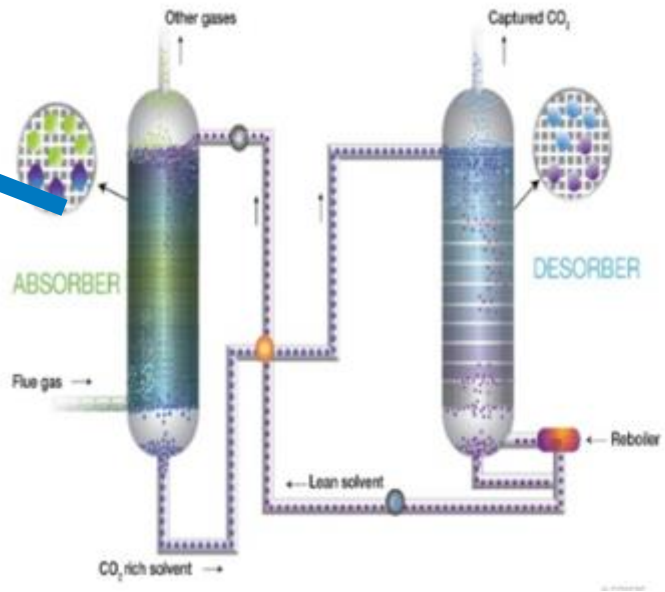
C/U Integration

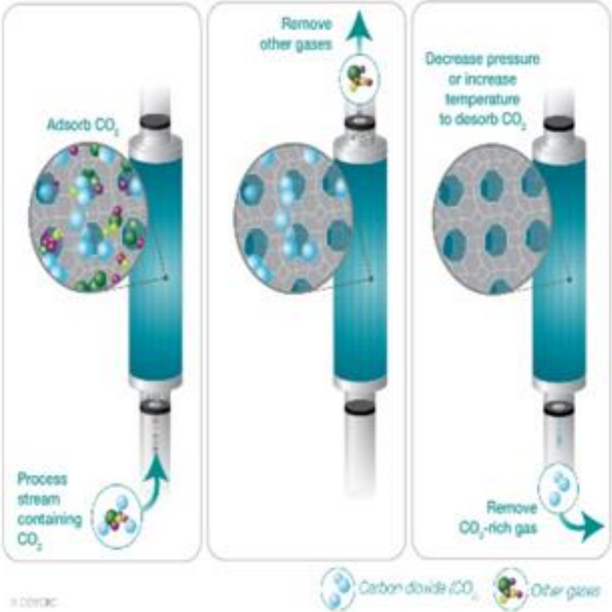


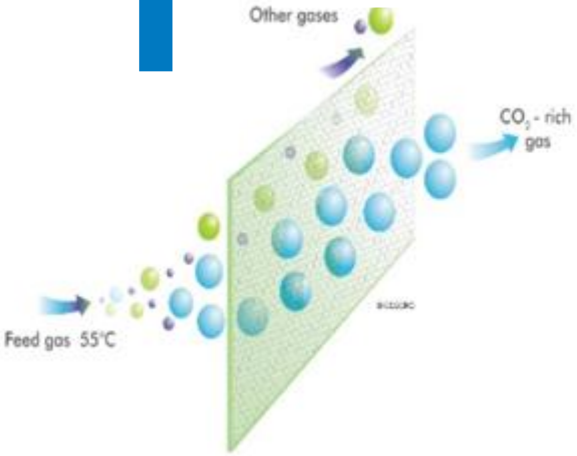
Adapted from: CO2 Capture and *in situ* Catalytic Transformation
Fu et al. Frontiers in Chemistry, 2019
https://www.frontiersin.org/articles/10.3389/fchem.2019.00525/full

Carbon Capture Technologies

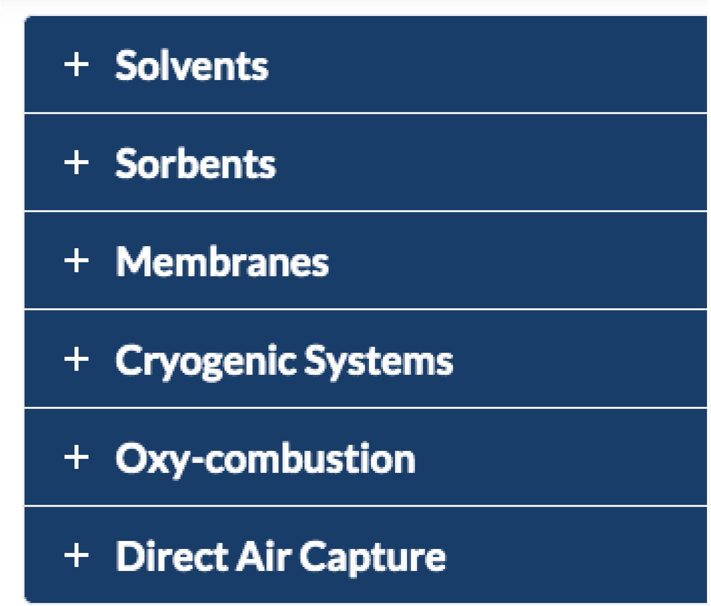
- + **Solvents**
- + **Sorbents**
- + **Membranes**
- + **Cryogenic Systems**
- + **Oxy-combustion**
- + **Direct Air Capture**



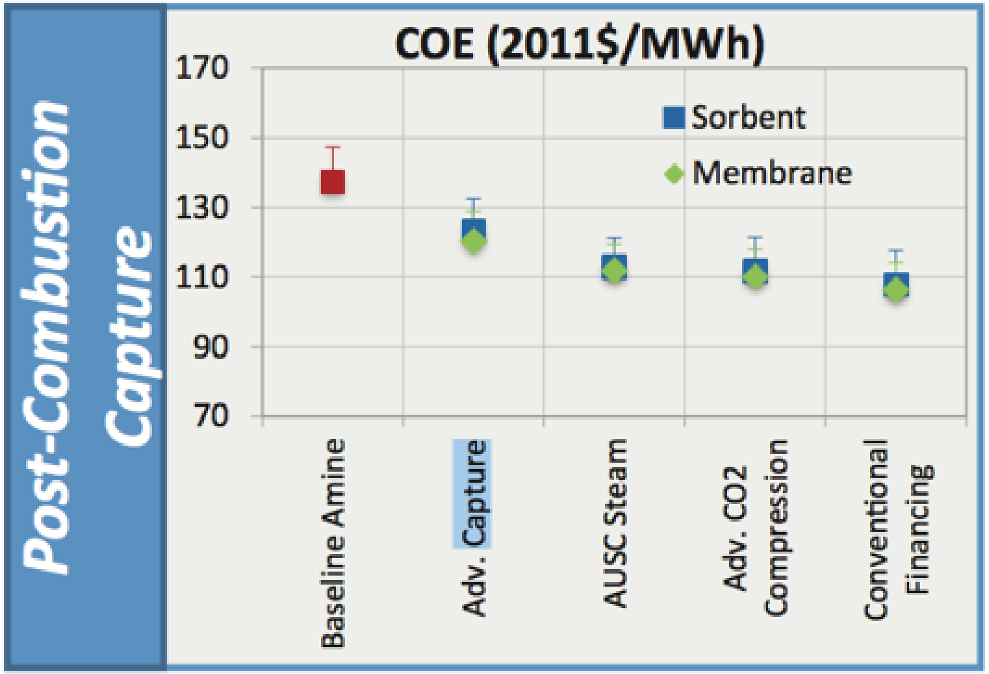




Carbon Capture Costs



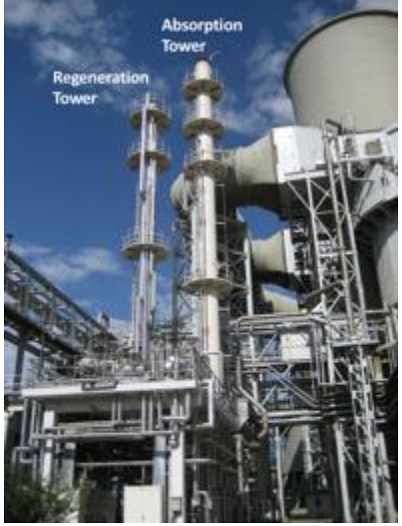
- + Solvents
- + Sorbents
- + Membranes
- + Cryogenic Systems
- + Oxy-combustion
- + Direct Air Capture

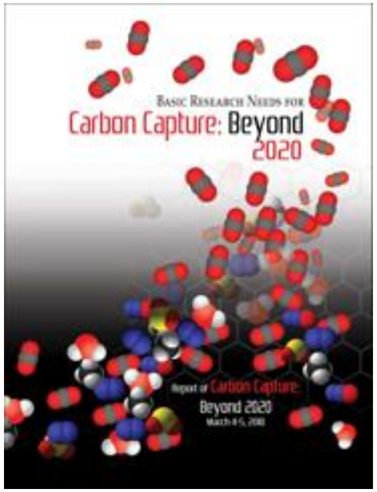


DOE Quadrennial Technology Review

MEA scrubber: Up to $150 per ton of CO2—> 90% associated with the regeneration and compression steps

Carbon Capture Status and Needs

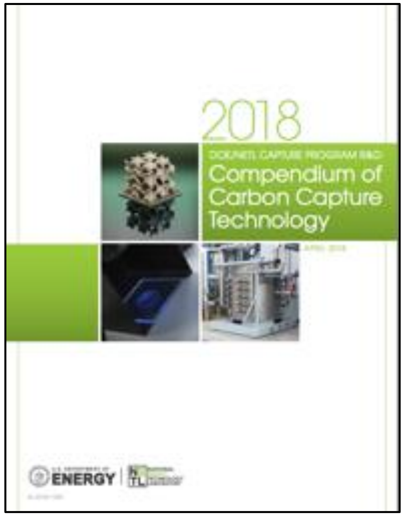




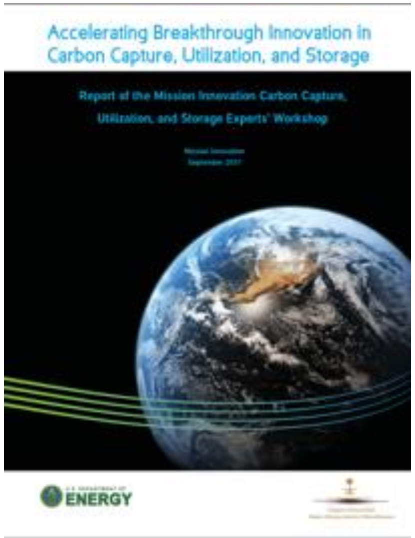
Priority Research Directions

- Interfacial Processes and Kinetics
- Novel Solvents and Chemistries
- Process Concepts Discovery
- Design, Synthesis, and Assembly of Novel Material Architectures
- Cooperative Phenomena for Low Net Enthalpy of Cycling
- Novel Hierarchical Structures in Membranes for Carbon Capture
- Membranes Molecularly Tailored to Enhance Separation Performance
- Alternative Driving Forces and Stimuli-Responsive Materials

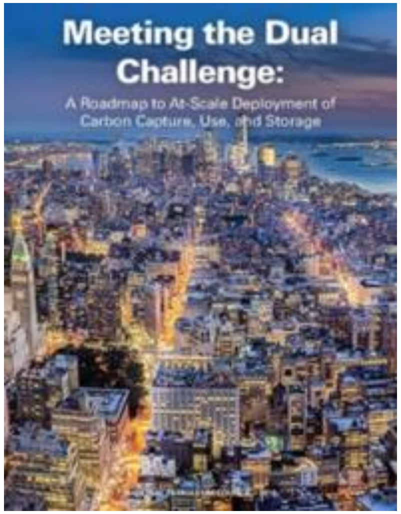
https://www.osti.gov/servlets/purl/1291240



https://www.netl.doe.gov/sites/default/files/netl-file/Carbon-Capture-Technology-Compendium-2018.pdf

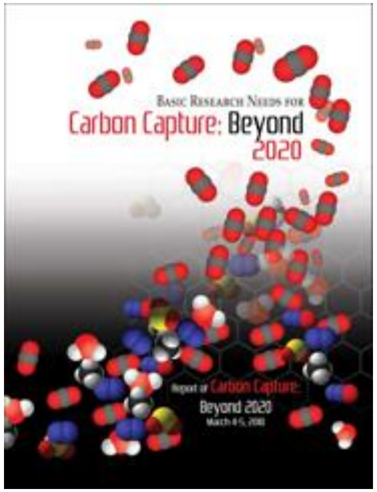


https://www.energy.gov/sites/prod/files/2018/05/f51/Accelerating%20Breakthrough%20Innovation%20in%20Carbon%20Capture%2C%20Utilization%2C%20and%20Storage%20_0.pdf



https://dualchallenge.npc.org

Carbon Capture R&D



Basic Research Needs for
Carbon Capture: Beyond 2020

Report of Carbon Capture:
Beyond 2020

Alternative Driving Force/Stimuli Responsive

- Electrical or electrochemical switching
- Electromechanical switching
- Electromagnetic irradiation and stimulation
- Magnetic switching
- Triggered phase transitions
- Electrochemical H+ generation

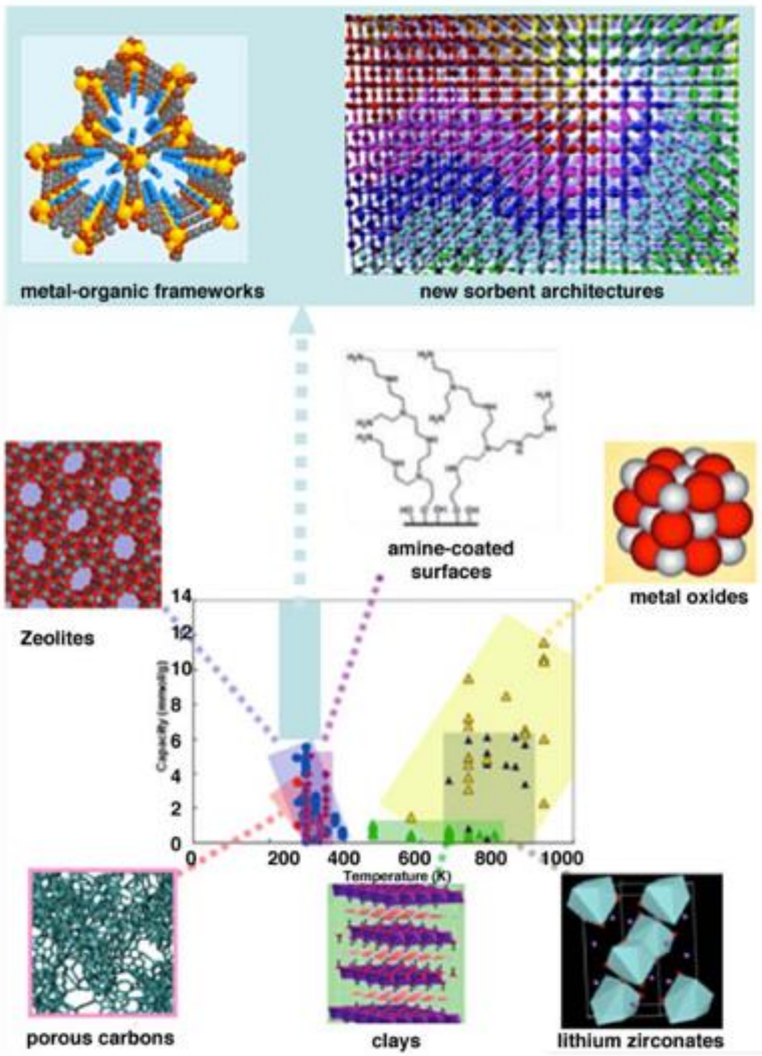
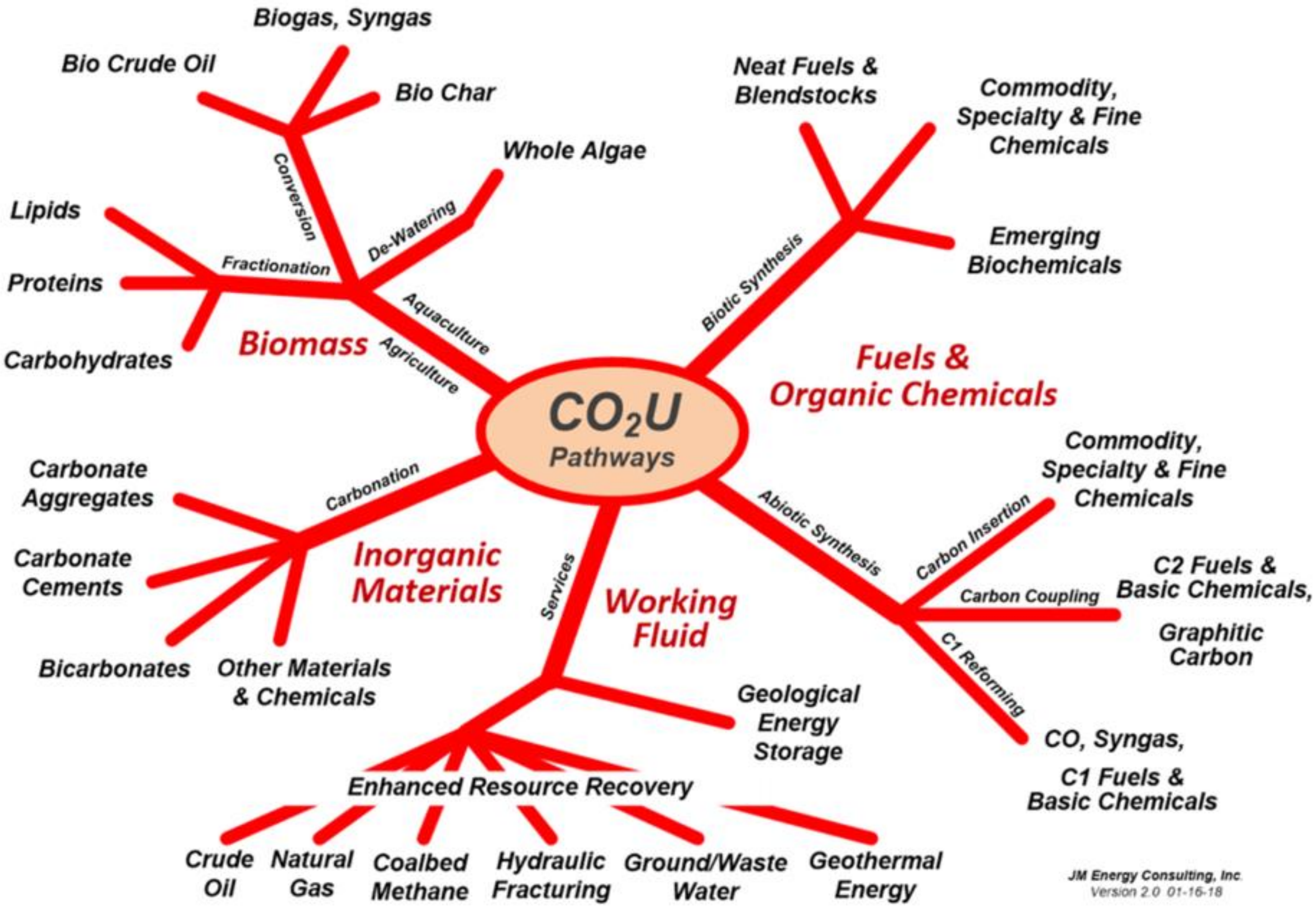


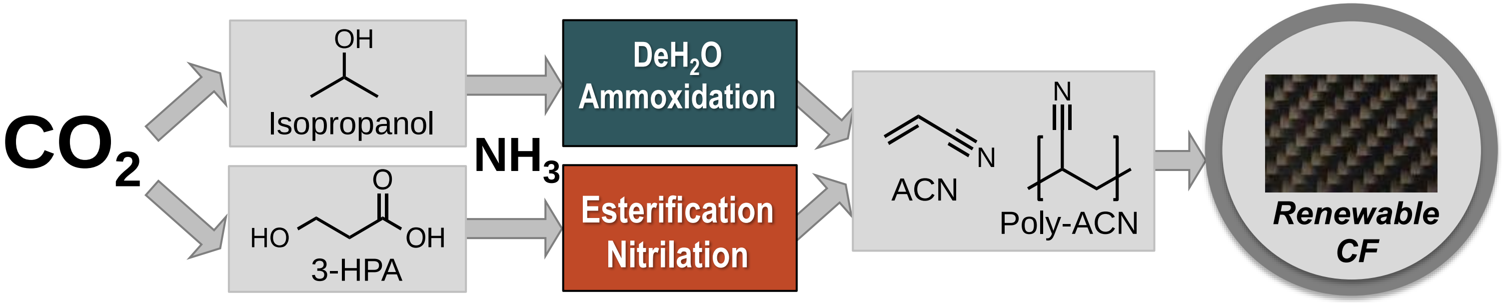
Figure 15. Currently used and researched sorbents and their capacity as a function of temperature. *Source:* Refs 2, 3, and 4.

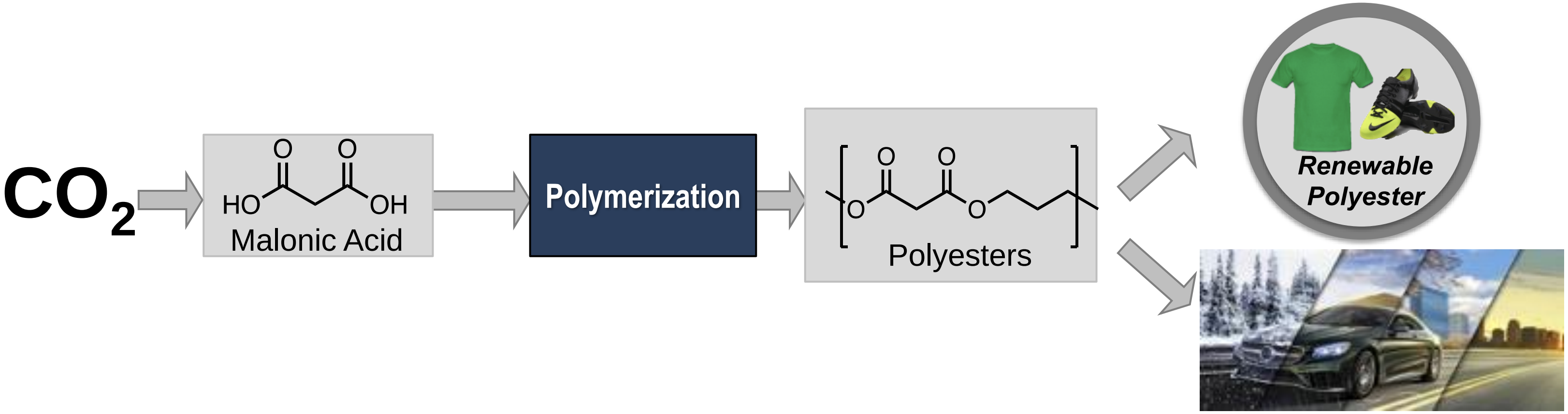
https://www.osti.gov/servlets/purl/1291240

CO2 Utilization



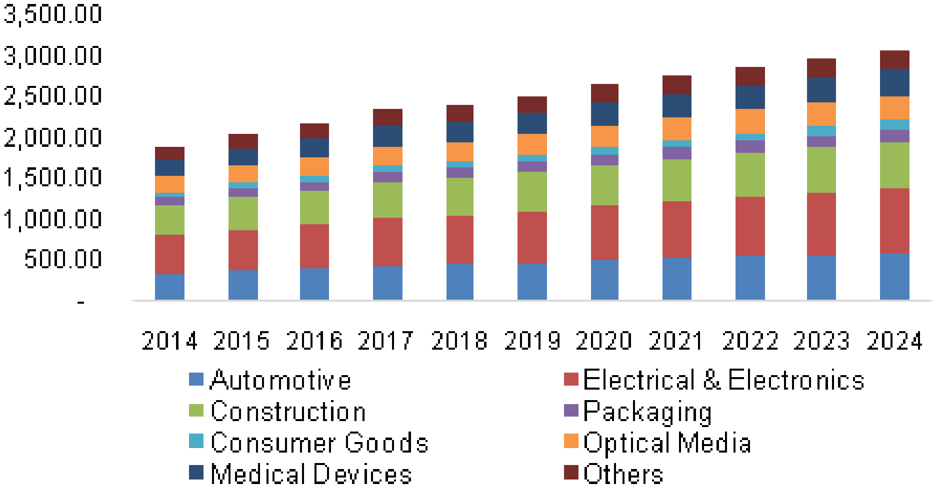
CO_2 Based Materials and Polymers





Polycarbonate Market

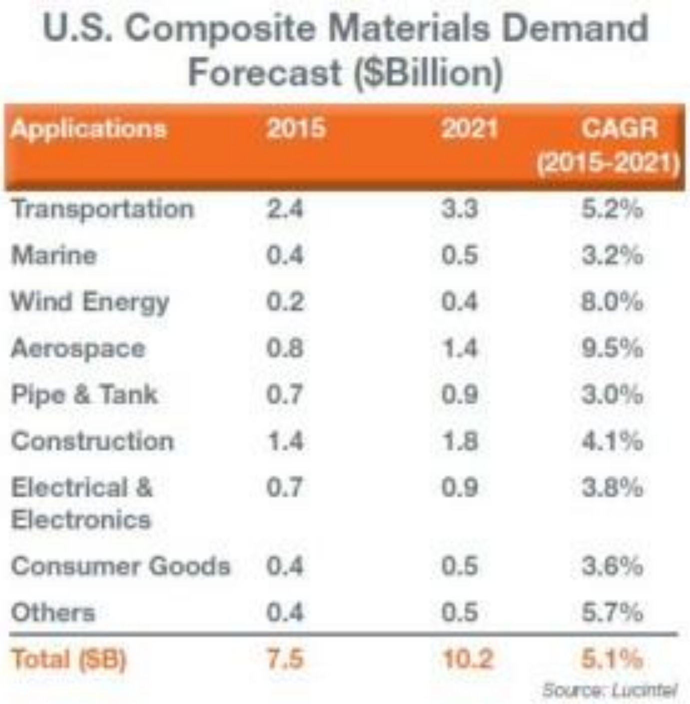
3% of current polymer GDP



Carbon Fiber: Large and Growing Market

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

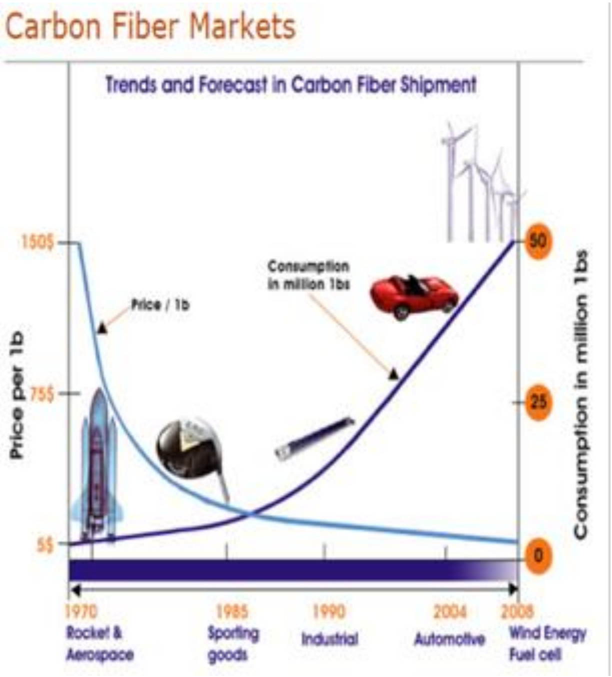
The North America region is expected to be the largest market globally due to the increased demand from **aerospace & defense, wind energy, infrastructure, and automotive industry.**



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

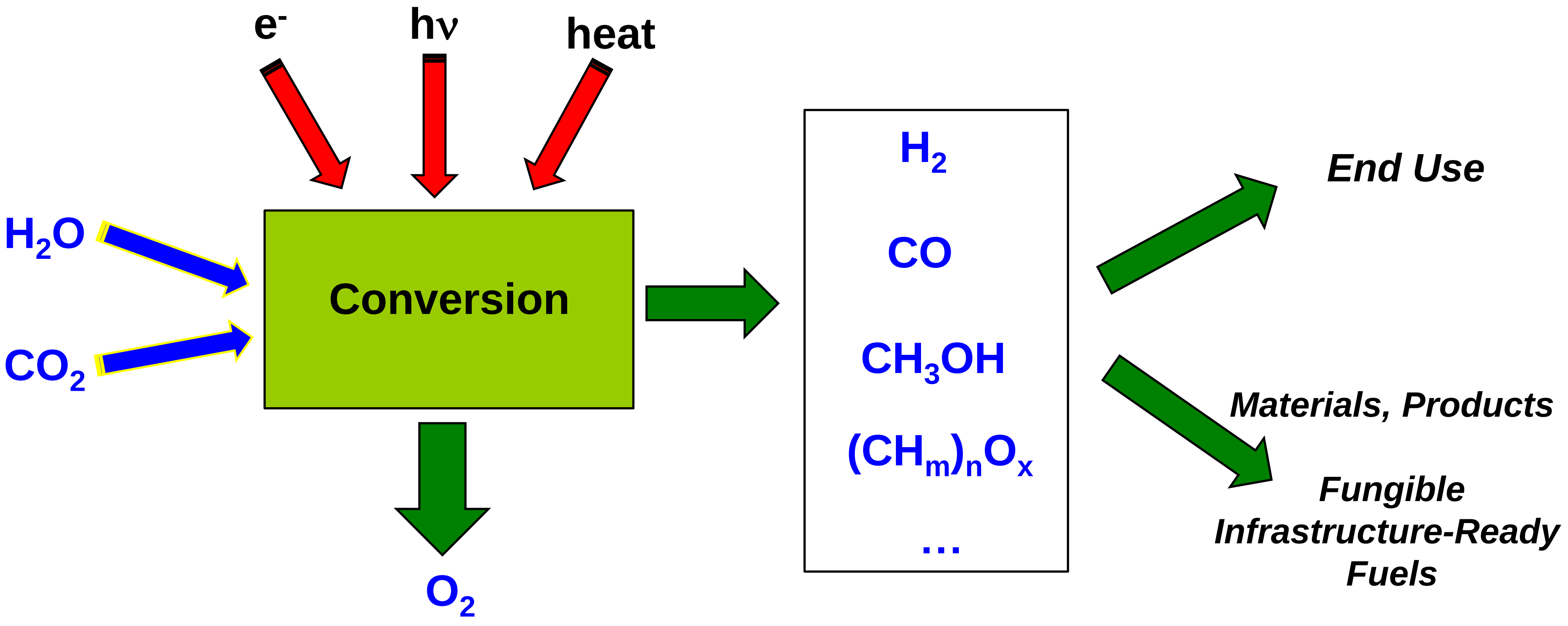
Applications	2015	2021	CAGR (2015-2021)
Transportation	2.4	3.3	5.2%
Marine	0.4	0.5	3.2%
Wind Energy	0.2	0.4	8.0%
Aerospace	0.8	1.4	9.5%
Pipe & Tank	0.7	0.9	3.0%
Construction	1.4	1.8	4.1%
Electrical & Electronics	0.7	0.9	3.8%
Consumer Goods	0.4	0.5	3.6%
Others	0.4	0.5	5.7%
Total ($B)	7.5	10.2	5.1%

Source: Lucintel



Electrons to Molecules for CCU

$H_2O + CO_2$ + energy $\longleftrightarrow$ “fuel” + O_2



e^-

$h\nu$

heat

H_2O

CO_2

Conversion

O_2

H_2

CO

CH_3OH

$(CH_m)_nO_x$

…

End Use

Materials, Products

Fungible
Infrastructure-Ready
Fuels

Chemical Energy (and electrons) comes from water oxidation: $H_2O \rightarrow 2\ e^- + 2\ H^+ + ½\ O_2$

Reducing Equivalents Generation Efficiency

	ΔE° (V)	ΔG° (kcal/mol)
$H_2O \rightarrow H_2 + ½\ O_2$	1.23	56.7

Chemical Energy comes from water oxidation: $H_2O \rightarrow 2 e^- + 2 H^+ + ½ O_2$

Reducing Equivalents Generation Efficiency

	ΔE° (V)	ΔG° (kcal/mol)
$H_2O \rightarrow H_2 + ½ O_2$	1.23	56.7
$CO_2 + H_2 \rightarrow HCOOH$		5.1
$CO_2 + H_2 \rightarrow CO + H_2O$		4.6
$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$		-4.1
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$		-31.3

Chemical Energy comes from water oxidation: $H_2O \rightarrow 2\ e^- + 2\ H^+ + \frac{1}{2}\ O_2$

Reducing Equivalents Generation

Efficiency

Selective C-C Bond Formation

Carbon Capture

	ΔE° (V)	ΔG° (kcal/mol)
$H_2O \rightarrow H_2 + \frac{1}{2}\ O_2$	1.23	56.7
$CO_2 + H_2 \rightarrow HCOOH$		5.1
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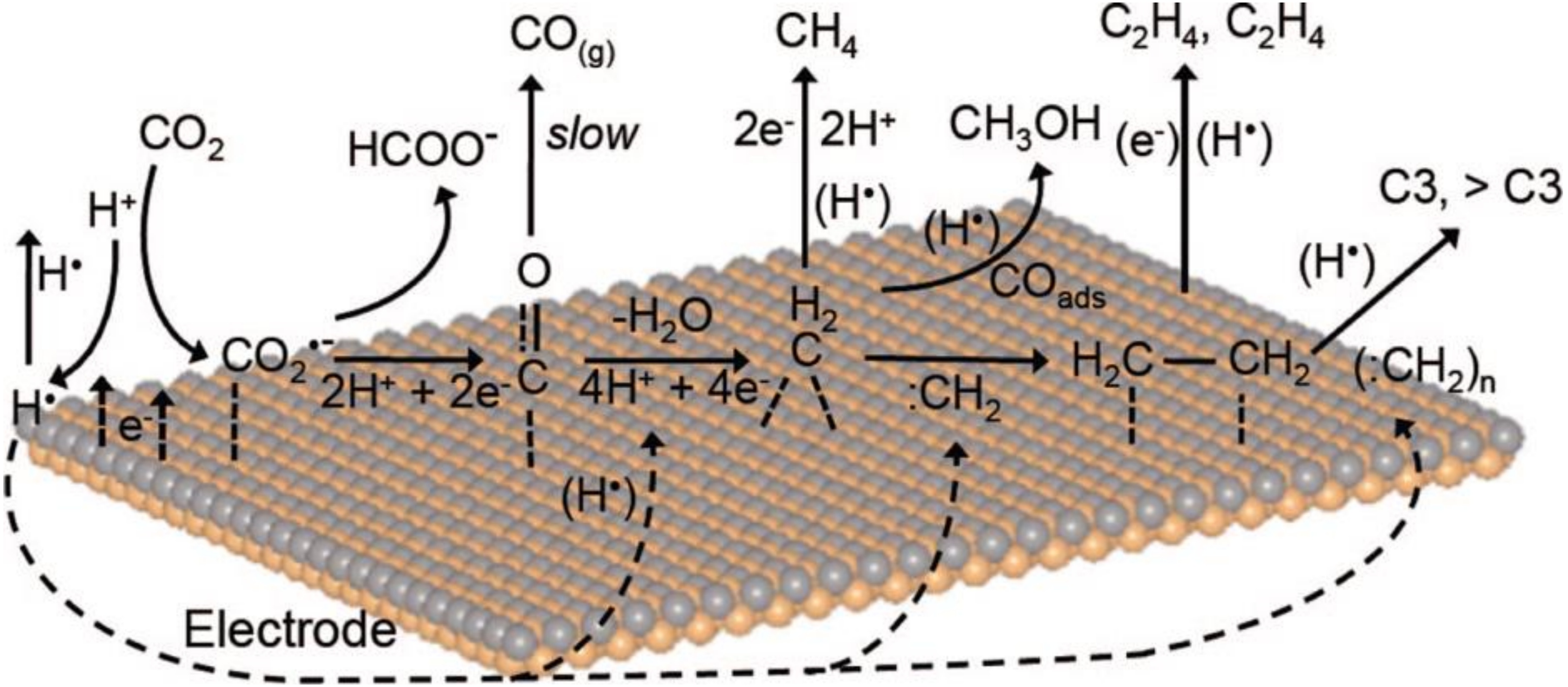
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$		-31.3

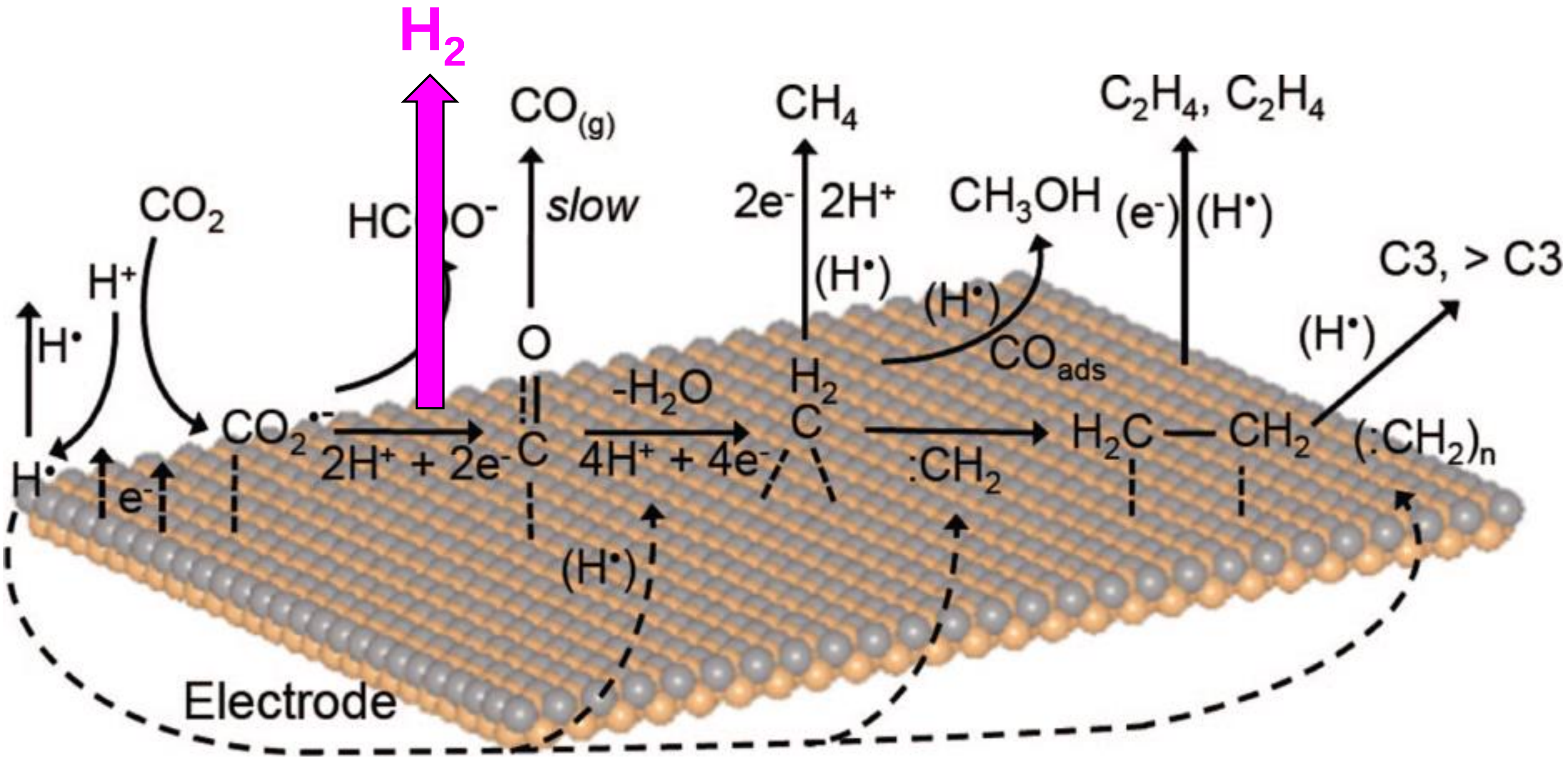
CO_2 Reduction Catalysis



Centi et al. Green Chem 2007

Multiple proton-coupled electron transfer (PCET) processes
Selectivity: Hypotheses and Concepts still needed, e.g. nanostructuring
Alloys, Tandem Catalysts

CO_2 Reduction Catalysis



Centi et al. Green Chem 2007

Multiple proton-coupled electron transfer (PCET) processes

Selectivity: Hypotheses and Concepts still needed, e.g. nanostructuring

Alloys, Tandem Catalysts

HER Overpotiential

Biological CO2U

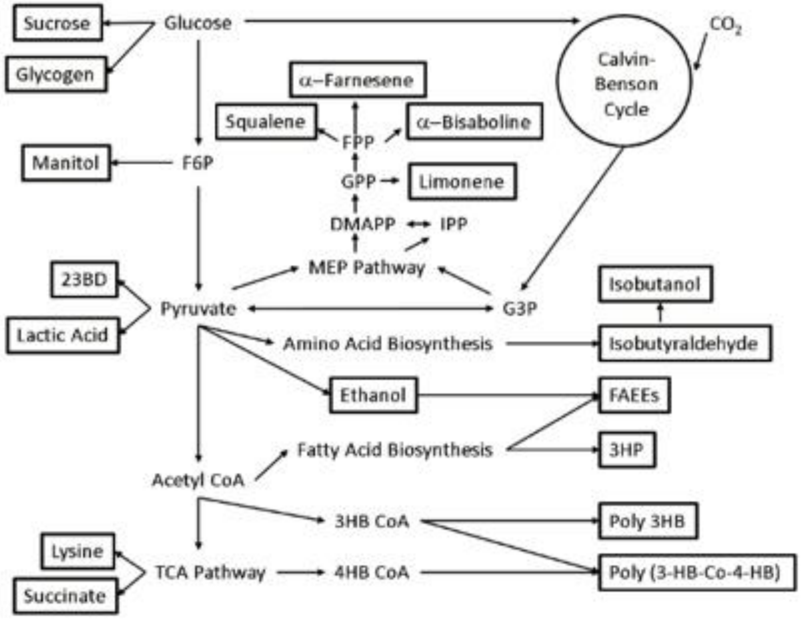


FIGURE 5-1 Example pathways for products from cyanobacteria. In the figure 23BD = 2,3-butanediol; FPP = farnesyl pyrophosphate; GPP = gross primary production; DMAPP = dimethylallyl diphosphate; IPP = isopentenyl diphosphate; 3HB CoA = 3-hydroxybutyryl-CoA; 4HB CoA = 4-hydroxybutyryl-CoA; FAEEs = fatty acid ethyl esters; 3HP = 3-hydroxypropionic acid; Poly 3HB = poly(3-hydroxybutyrate); and Poly (3-HB-Co-4-HB) = poly(3-hydroxybutyrate-co-4-hydroxybutyrate).[1]

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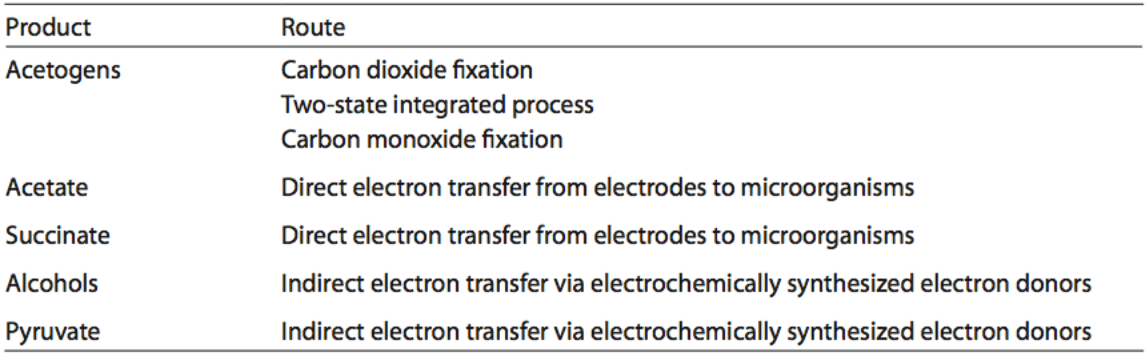
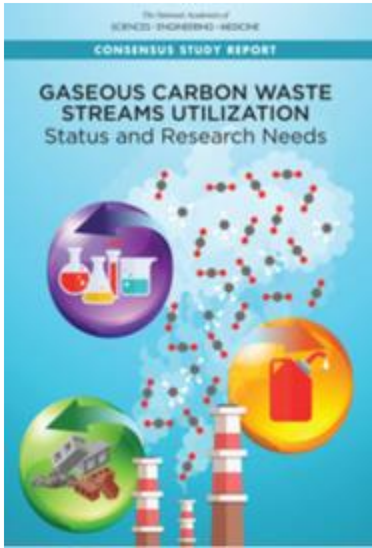
[1] Reprinted from Carroll, Austin L., Anna E. Case, Angela Zhang, and Shota Atsumi. 2018. “Metabolic engineering

TABLE 5-2 Summary of nonphotosynthetic approaches to carbon utilization products.



Product	Route
Acetogens	Carbon dioxide fixation Two-state integrated process Carbon monoxide fixation
Acetate	Direct electron transfer from electrodes to microorganisms
Succinate	Direct electron transfer from electrodes to microorganisms
Alcohols	Indirect electron transfer via electrochemically synthesized electron donors
Pyruvate	Indirect electron transfer via electrochemically synthesized electron donors



The National Academies of SCIENCES · ENGINEERING · MEDICINE

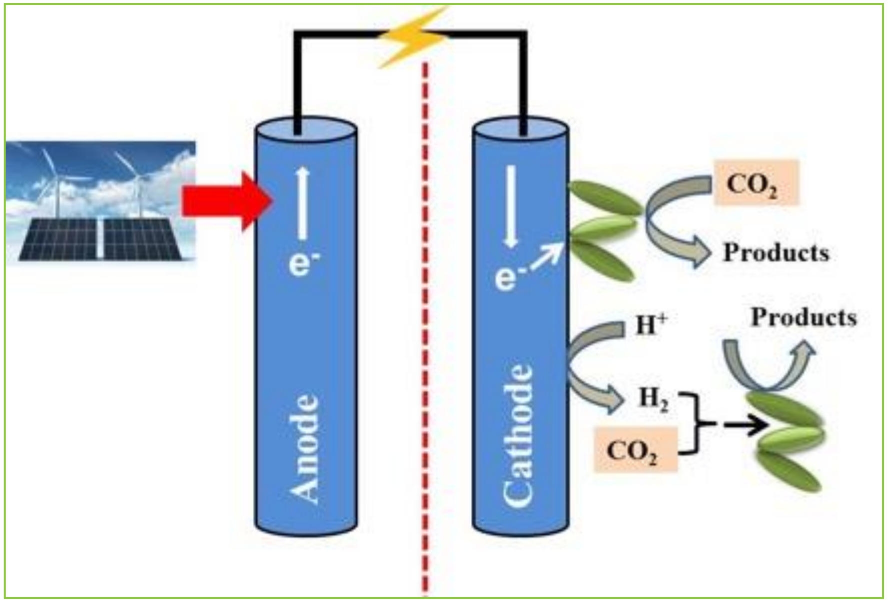
CONSENSUS STUDY REPORT

GASEOUS CARBON WASTE STREAMS UTILIZATION

Status and Research Needs

BioHybrid Approaches

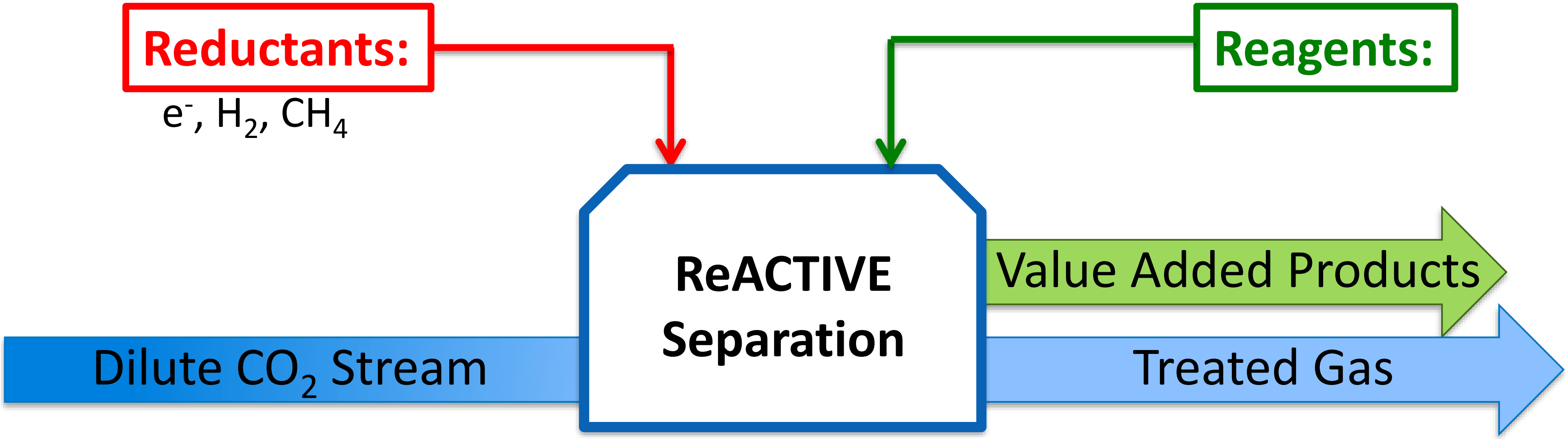
The Electric Economy
Meets
Synthetic Biology



- Beat photosynthesis by coupling **EFFICIENCY** of **anthropogenic reductants** with **SELECTIVITY** of **biological processes**
- Microbial catalysis offers high **selectivity** toward tailored products
- Advances in synthetic biology
- **Selective C-C bond** formation

(Electrochem, Solar-Driven, Mediators, $H_{2,}$ Intermediates)

Capture/Utilization Integration



Challenges:

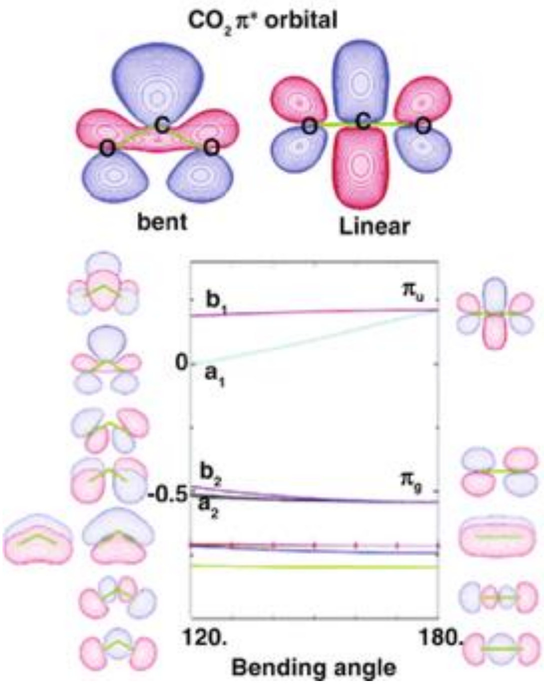
- Energy intensity
- Process integration
- Selectivity
- Activity
- Advanced materials development

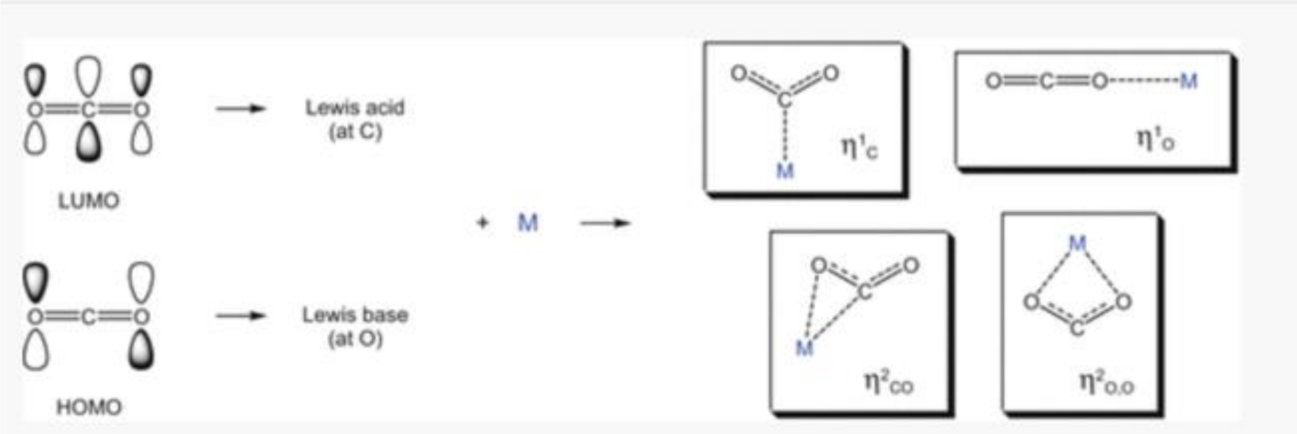
C/U Integration

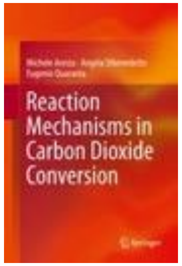
- Kinds of Reaction Media
    - solvents, sorbents (surfaces), membranes (matrices)
- Reduction/chemistry in CO2 capture solvents
    - e.g. MEA reduction- carbamates
    - make or deliver H2/e- to reaction media
    - phase-separable catalysis
- Electrochemical separation and reduction
    - bipolar membranes
    - echem control of pH (re-generation of H+)
    - seawater
- Sorbents
    - incorporation of catalysis
    - MOFs and hierarchical structures
- Membranes
    - membrane-bound reaction centers; hybrid systems (e.g. IL membranes)
- Molten Carbonates
    - feed flue gas directly; capture and chemical transformations
    - solid oxide fuel cells/electrolyzers
- Biology and hybrid approaches
    - feed flue gas directly
    - algae, cyanobacteria, engineered organisms

Effects of contaminants, control of reaction conditions selectivity, throughput (STY matching), durability, ….

CO$_2$







Aresta *et al.*

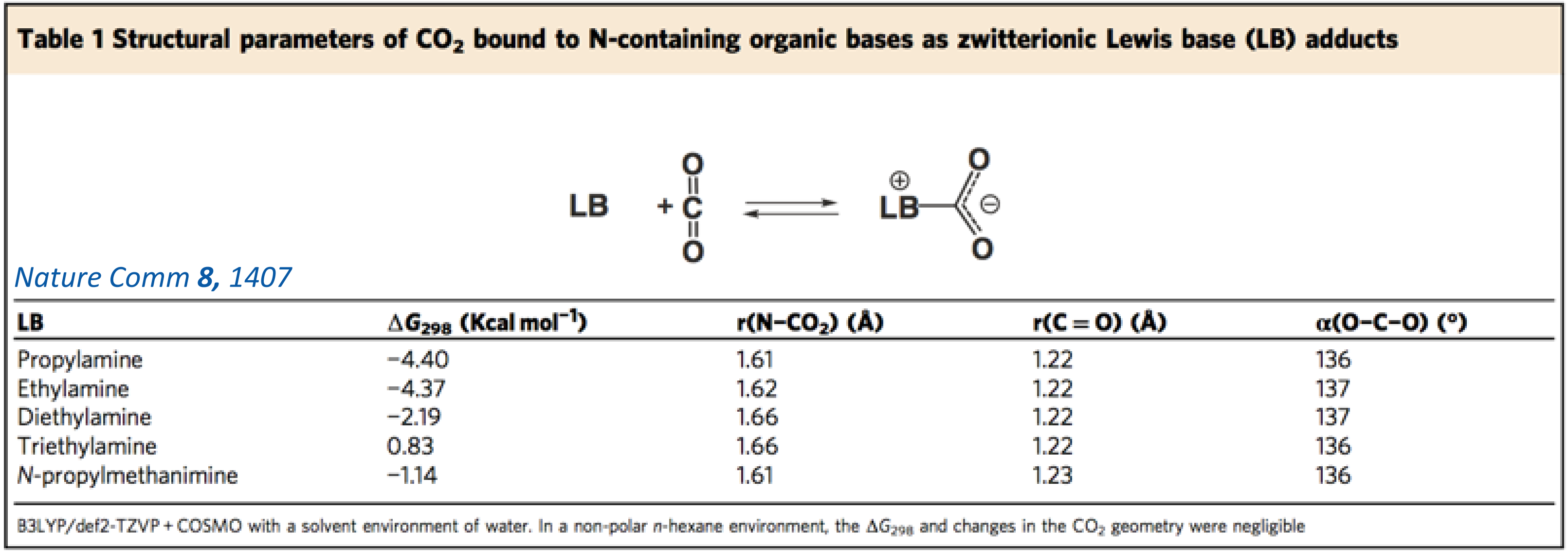


Table 1 Structural parameters of CO$_2$ bound to N-containing organic bases as zwitterionic Lewis base (LB) adducts

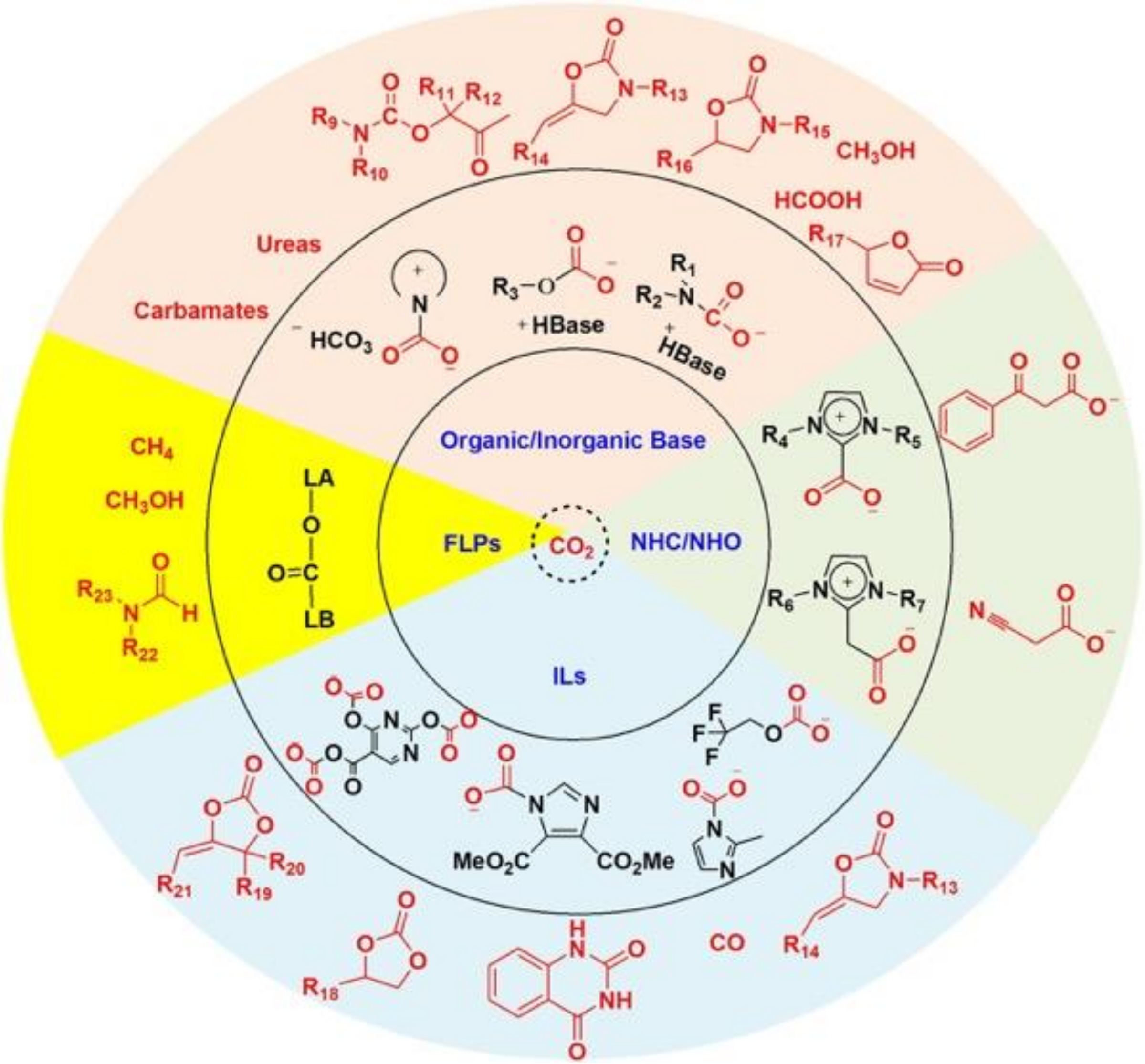
$$\mathrm{LB} + \mathrm{O{=}C{=}O} \rightleftharpoons \overset{\oplus}{\mathrm{LB}}\text{–}\mathrm{CO_2}^{\ominus}$$

*Nature Comm **8,** 1407*

LB	ΔG$_{298}$ (Kcal mol^{-1})	r(N–CO$_2$) (Å)	r(C = O) (Å)	α(O–C–O) (°)
Propylamine	−4.40	1.61	1.22	136
Ethylamine	−4.37	1.62	1.22	137
Diethylamine	−2.19	1.66	1.22	137
Triethylamine	0.83	1.66	1.22	136
N-propylmethanimine	−1.14	1.61	1.23	136

B3LYP/def2-TZVP + COSMO with a solvent environment of water. In a non-polar *n*-hexane environment, the ΔG$_{298}$ and changes in the CO$_2$ geometry were negligible

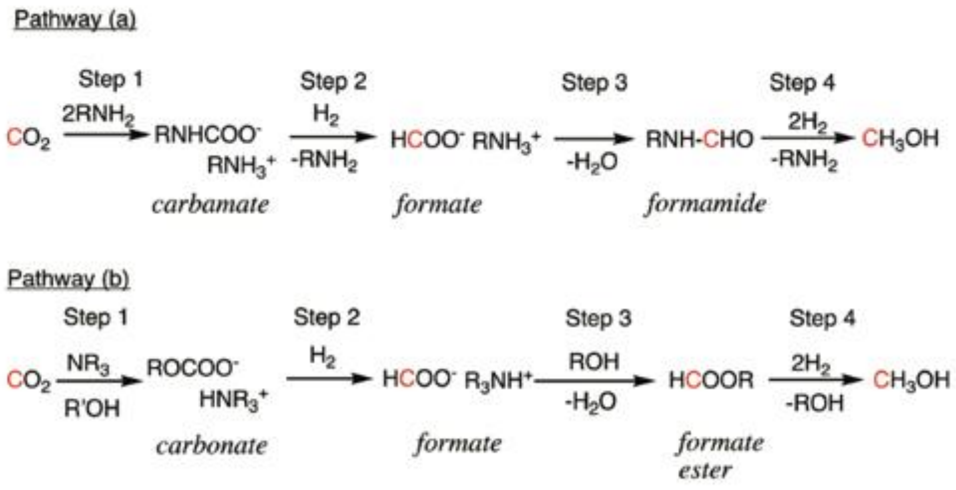
Some CO2 Chemistries—Solvents/Absorbents

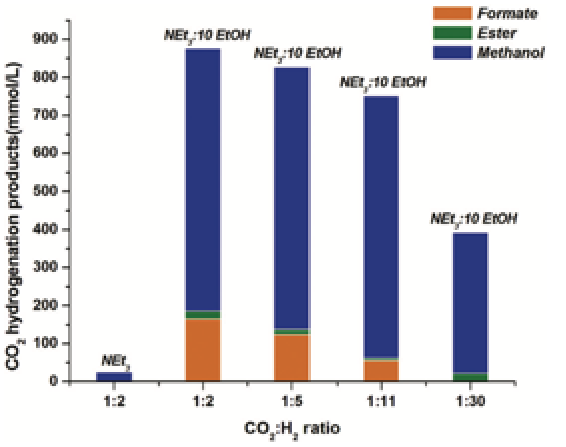


Adapted from: CO2 Capture and *in situ* Catalytic Transformation
Fu et al. Frontiers in Chemistry, 2019
https://www.frontiersin.org/articles/10.3389/fchem.2019.00525/full

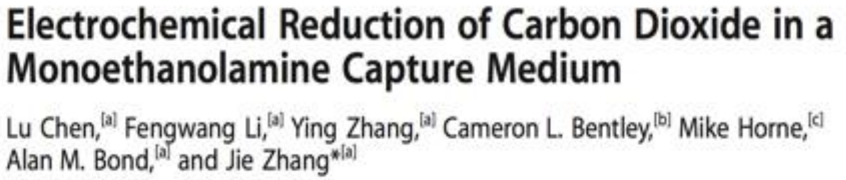
Adsorbents—CO2 bound to solids, pores
Membranes—CO2 in a matrix, pores

Reductions in MEA Media





Kothandaraman, Heldebrant, Green Chem 2020, 22, 828–8

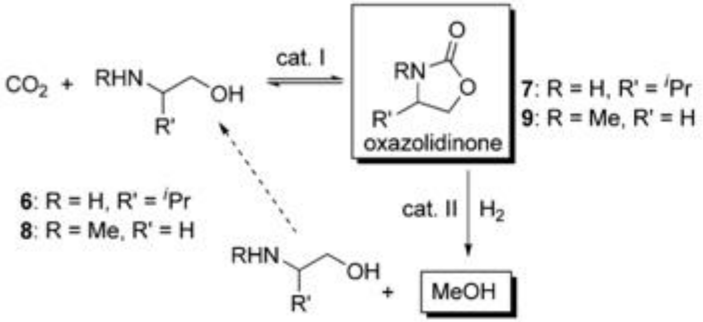


Electrochemical Reduction of Carbon Dioxide in a Monoethanolamine Capture Medium

Lu Chen,[a] Fengwang Li,[a] Ying Zhang,[a] Cameron L. Bentley,[b] Mike Horne,[c] Alan M. Bond,[a] and Jie Zhang*[a]

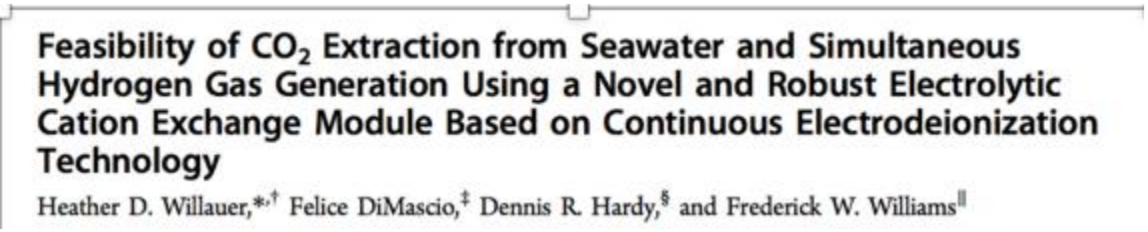
ChemSusChem 2017, 10, 4109 – 4118

Scheme 3. Proposed Scheme for Selective CO_2 Capture and Conversion to MeOH



Milstein ACS Catal. 2015, 5, 2416−2422

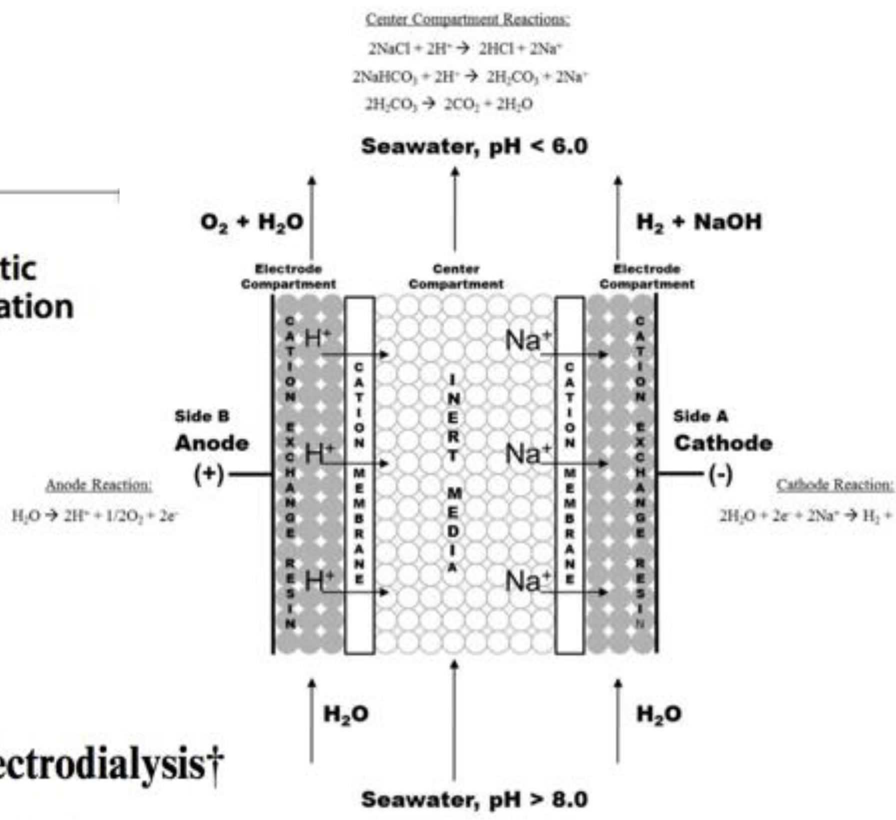
Electrochemical Separations



Feasibility of CO_2 Extraction from Seawater and Simultaneous Hydrogen Gas Generation Using a Novel and Robust Electrolytic Cation Exchange Module Based on Continuous Electrodeionization Technology

Heather D. Willauer,*[†] Felice DiMascio,[‡] Dennis R. Hardy,[§] and Frederick W. Williams[‖]

I&EC 2014



Center Compartment Reactions:

$2NaCl + 2H^+ \rightarrow 2HCl + 2Na^+$

$2NaHCO_3 + 2H^+ \rightarrow 2H_2CO_3 + 2Na^+$

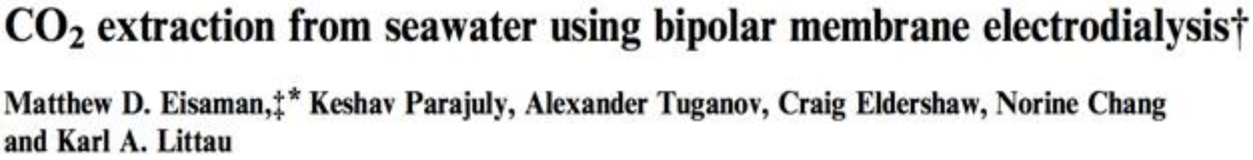
$2H_2CO_3 \rightarrow 2CO_2 + 2H_2O$

Anode Reaction:

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

Cathode Reaction:

$2H_2O + 2e^- + 2Na^+ \rightarrow H_2 +$



CO_2 extraction from seawater using bipolar membrane electrodialysis†

Matthew D. Eisaman,‡* Keshav Parajuly, Alexander Tuganov, Craig Eldershaw, Norine Chang and Karl A. Littau

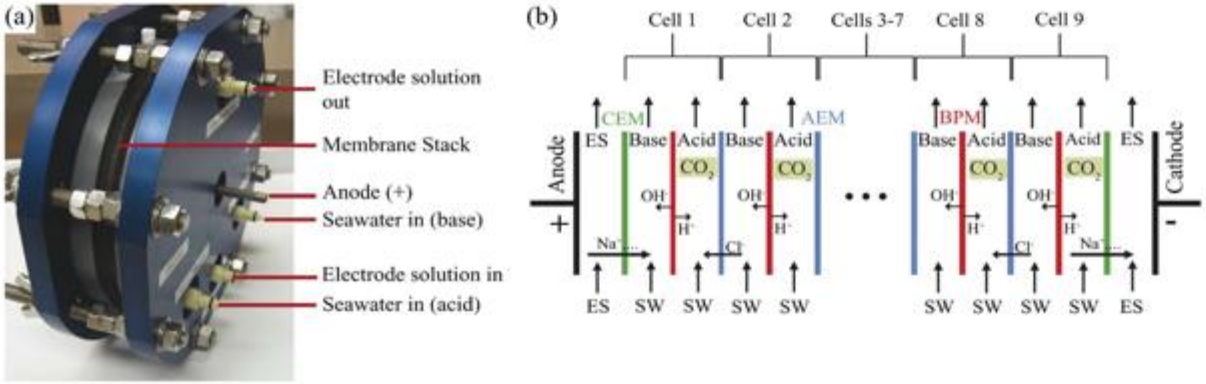


Fig. 2 (a) Picture and (b) schematic of the CO_2-from-seawater BPMED unit. ES = electrode solution, SW = seawater, CEM = cation exchange membrane, AEM = anion exchange membrane, BPM = bipolar membrane. In panel (a), the opposite side of the unit that is not visible contains the cathode (−), Electrode solution in and out for the cathode, Seawater out (acid), and Seawater out (base).

Energy Environ. Sci., 2012, 5, 7346

Google-X
PARC

Foghorn Project
Seawater to Fuel

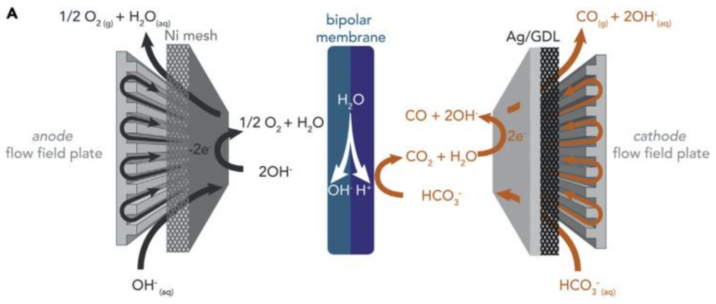
Electrochemical Upgrading of CO_2 Capture Solution

Scientific Approach

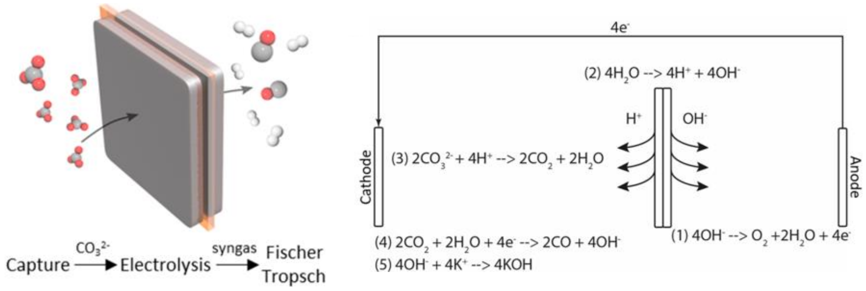
- CO_2 is captured in KOH solution to form (bi)carbonate ions
- Carbonate is fed to the cation conducting side of a bipolar membrane based CO_2 electrolyzer
- Protons supplied by the bipolar membrane generate CO_2 from carbonate
- CO_2 is reduced to CO, at its point of generation from CO_3^{2-}, which also regenerates the hydroxide for further capture
- H_2 is also produced so pure syngas is the cathode product

Significance and Impact

- Combined capture and conversion demonstration at a relevant current density – 150 mA/cm^2
- Energy efficiency ~35%
- Stable operation over 145 hours
- Near 100 % carbon utilization – no need to remove CO_2 from product stream



Joule 3, 1487–1497, June 19, 2019



ACS Energy Lett. 2019, 4, 1427−1431

Electrochemical Capture

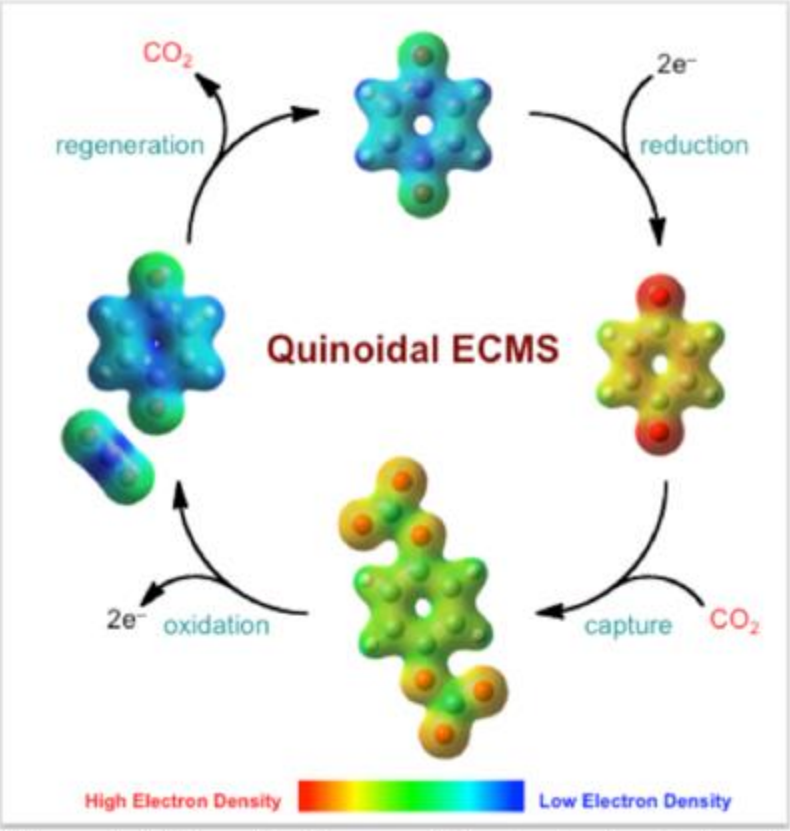
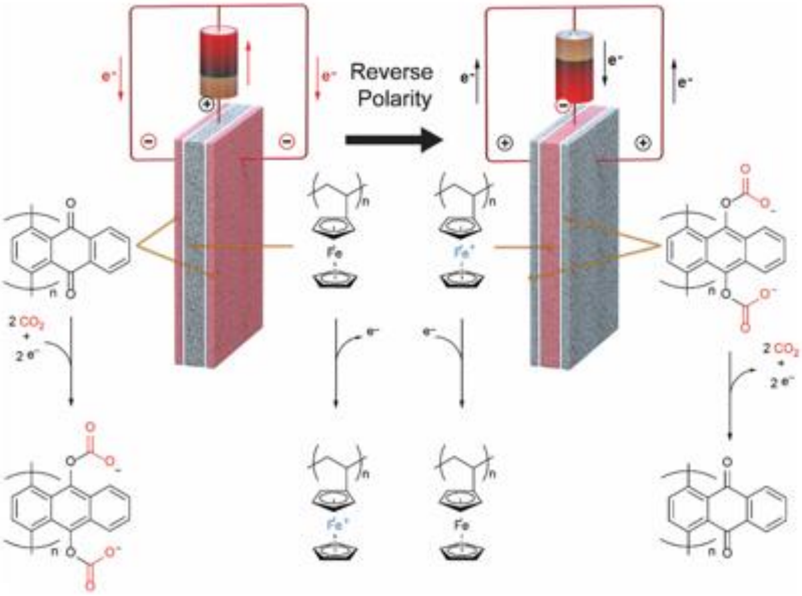


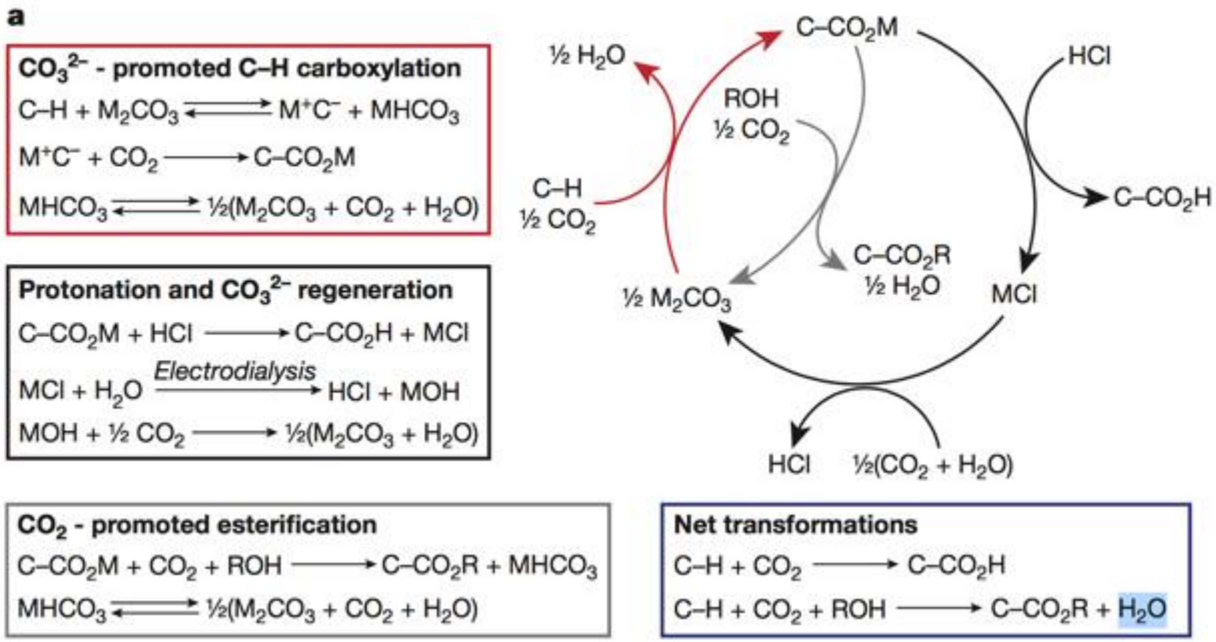
Figure 1. Schematic diagram of the electrochemical cycle of 1,4-benzoquinone during CO_2 capture and regeneration.



Wrighton, Mizen 1989

Voskian, Hatton *Energy Environ. Sci.*, 2019, 12, 3530

Molten Salts



CO_3^{2-} - promoted C–H carboxylation

$$C\text{–}H + M_2CO_3 \rightleftharpoons M^+C^- + MHCO_3$$

$$M^+C^- + CO_2 \longrightarrow C\text{–}CO_2M$$

$$MHCO_3 \rightleftharpoons \tfrac{1}{2}(M_2CO_3 + CO_2 + H_2O)$$

Protonation and CO_3^{2-} regeneration

$$C\text{–}CO_2M + HCl \longrightarrow C\text{–}CO_2H + MCl$$

$$MCl + H_2O \xrightarrow{\textit{Electrodialysis}} HCl + MOH$$

$$MOH + \tfrac{1}{2}\,CO_2 \longrightarrow \tfrac{1}{2}(M_2CO_3 + H_2O)$$

CO_2 - promoted esterification

$$C\text{–}CO_2M + CO_2 + ROH \longrightarrow C\text{–}CO_2R + MHCO_3$$

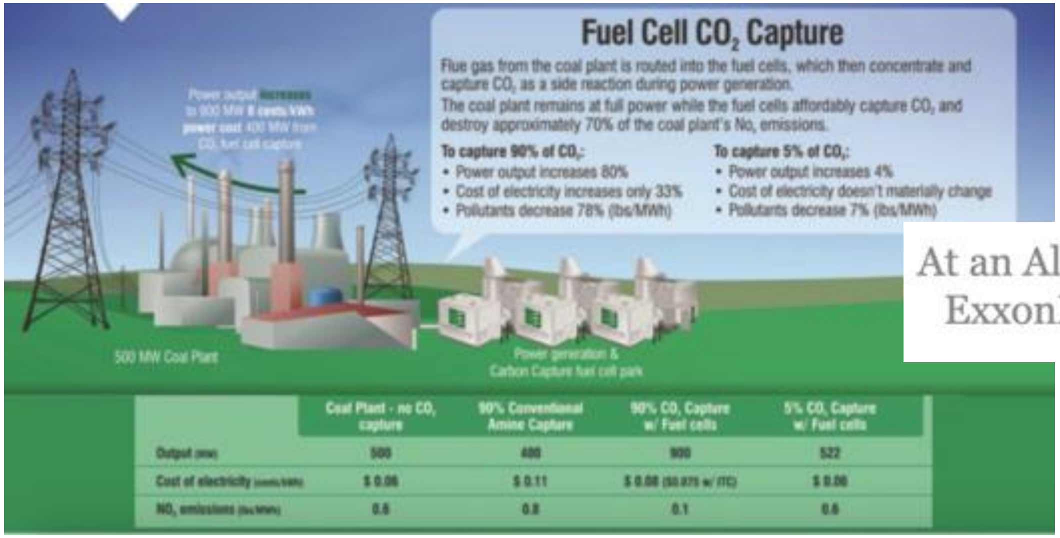
$$MHCO_3 \rightleftharpoons \tfrac{1}{2}(M_2CO_3 + CO_2 + H_2O)$$

Net transformations

$$C\text{–}H + CO_2 \longrightarrow C\text{–}CO_2H$$

$$C\text{–}H + CO_2 + ROH \longrightarrow C\text{–}CO_2R + H_2O$$

Banerjee et al. Nature 531, 215 (2016)



Fuel Cell CO_2 Capture

Flue gas from the coal plant is routed into the fuel cells, which then concentrate and capture CO_2 as a side reaction during power generation.

The coal plant remains at full power while the fuel cells affordably capture CO_2 and destroy approximately 70% of the coal plant's No_x emissions.

To capture 90% of CO_2:
- Power output increases 80%
- Cost of electricity increases only 33%
- Pollutants decrease 78% (lbs/MWh)

To capture 5% of CO_2:
- Power output increases 4%
- Cost of electricity doesn't materially change
- Pollutants decrease 7% (lbs/MWh)

	Coal Plant - no CO_2 capture	90% Conventional Amine Capture	90% CO_2 Capture w/ Fuel cells	5% CO_2 Capture w/ Fuel cells
Output (MW)	500	400	900	522
Cost of electricity (cents/kWh)	\$ 0.06	\$ 0.11	\$ 0.08 (\$0.075 w/ ITC)	\$ 0.06
NO_x emissions (lbs/MWh)	0.6	0.8	0.1	0.6

At an Alabama power plant, FuelCell Energy and ExxonMobil aim to capture 90 percent of CO_2

https://spectrum.ieee.org/green-tech/fuel-cells/fuel-cells-finally-find-a-killer-app-carbon-capture

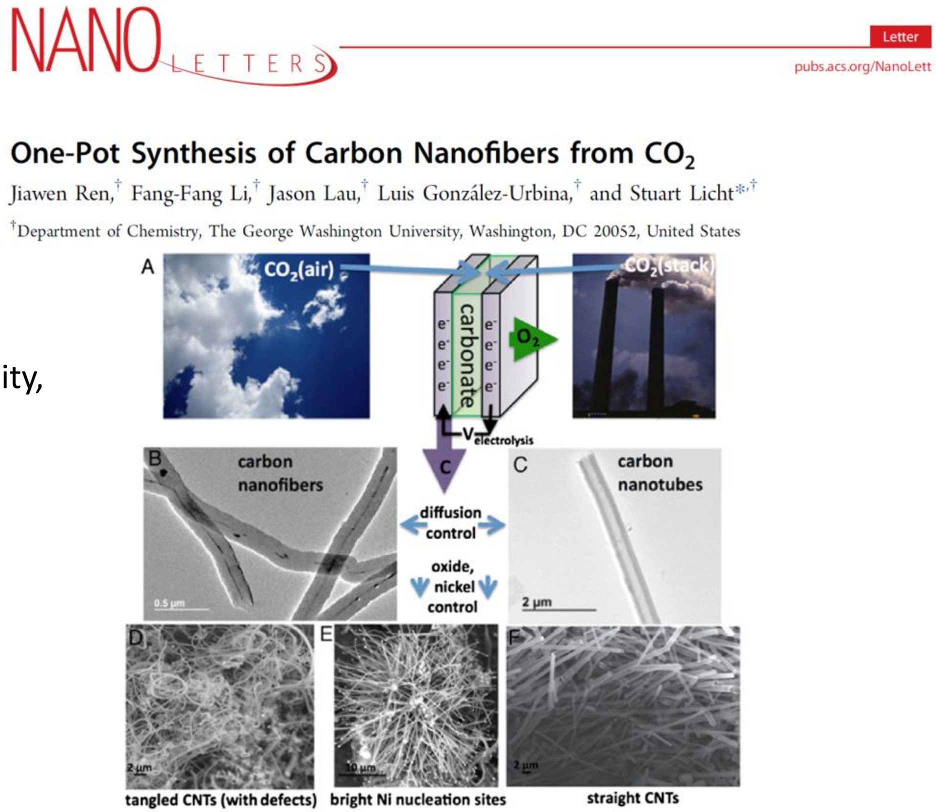
Carbon Nanotubes via Molten Carbonate Electrolyzers

Scientific Approach

- Molten carbonate electrolyzer
- Governing reactions:
  - (1) $CO_2\ (g) + Li_2O \rightarrow Li_2CO_3$
  - (2) $Li_2CO_3 \rightarrow C\ (s) + Li_2O + O_2\ (g)$
  - (Net) $CO_2 \rightarrow C + O_2$
- Control carbon nanofiber morphology via current density, electrolyte (Li-K-Na), and electrolytic temperature

Significance and Impact

- Potential for high coulombic and carbon efficiencies if Li_2CO_3 is not consumed during the reaction and is continuously regenerated from CO_2
- High-value product
- Leverages atmospheric CO_2



NANO LETTERS

Letter

pubs.acs.org/NanoLett

One-Pot Synthesis of Carbon Nanofibers from CO_2

Jiawen Ren,[†] Fang-Fang Li,[†] Jason Lau,[†] Luis González-Urbina,[†] and Stuart Licht*[,†]

[†] Department of Chemistry, The George Washington University, Washington, DC 20052, United States

Nano Lett. 2015, 15, 6142-6148; Energy Conversion and Management 2016, 122, 400-410

Summary: CCU

Electrification of our Economy

- High penetration needs flexible grid and **ENERGY STORAGE**
- Transportation, industrial processes, buildings
- SYSTEMS APPROACH; synergy with CCUS

Hydrogen can play a significant role : $H_2O \rightarrow 2H^+ + 2e^-$

- H2 at Scale—beyond the automobile
- Energy carrier / storage/ catalytic transformations

CO_2 Utilization can have multiple impacts: f(t)

- Commerce / markets
- Energy storage (Beyond Batteries)—hydrogen or ***electricity carrier (fuels)***
- Climate change mitigation

Innovation for CO_2 Utilization is needed

- C-1 vs. C-C bonded products
  SELECTIVITY, efficiency, …
- Electrolysis; Artificial Photosynthesis
- Hybrid concepts
- Integrated processes (C/U Integration)

C/U Integration

- Kind s of Reaction Media
    - - solvents, sorbents (surfaces), membranes (matrices)
- Reduction/chemistry in CO2 capture solvents
    - e.g. MEA reduction- carbamates
    - Make or deliver H2/e- to reaction media
    - Phase-separable catalysis
- Electrochemical separation and reduction
    - - Bipolar membranes
    - - echem control of pH (re-generation of H+)
    - - Seawater
- Sorbents
    - - incorporation of catalysis
    - - MOFs and hierarchical structures
- Membranes
    - Membrane-bound reaction centers; hybrid systems (e.g. IL membranes)
- Molten Carbonates
    - - Feed flue gas directly
    - - Capture and chemical transformations
    - - Solid oxide fuel cells/electrolyzers

Biology
- - Feed flue gas directly
- - algae, cyanobacteria, engineered organisms

Effects of contaminants, control of reaction conditions selectivity, throughput (STY matching), durability, ….

C/U Integration

What are the benchmarks?

What are the metrics? Performance, cost

Timeframe?

Where are the asymptotes/limits to current techs vs. new concepts?

Where will or should the CO_2 come from?

What should we make and why?

Finance, business models, deployment concepts?

R&D agenda; Needs and opportunities

(Some) Key Technical Challenges

Electrochemistry/Electrocatalysis/Solar Fuels

- New ways to use electric potential to deliver high concentrations of reagents
- Self healing catalysts, membranes, systems
- Coupling membranes and catalysis, new GDE concepts
- ***Selective C-C Bond formation catalysis***

Nexus of catalysis/electrocatalysis and biology:

- Linking high efficiency abiotic reducing agents with biocatalysts and microbes
- ***Matching energetics and kinetics; Productivity;*** Mechanisms
- Understanding the bioenergetics to create higher flux in microbes
- Enhance CO_2 and H_2 uptake by synthetic microbes
- Control and design of metabolic pathways

Novel reaction and reactor engineering for tandem/hybrid concepts

- ***Coupling CO_2 capture with reactions***, CO_2 reduction in capture media, reactive separations
- Multiphase flow, electrochemical and electrode engineering
- New precursors and processing science for polymers and materials: ***Beyond drop-in replacements***
- Low temperature, selective catalysis in water and complex media and fit-for-purpose water***; Downstream selective catalytic conversions***
- Incorporating heteroatoms; ***Nitrogen reduction***