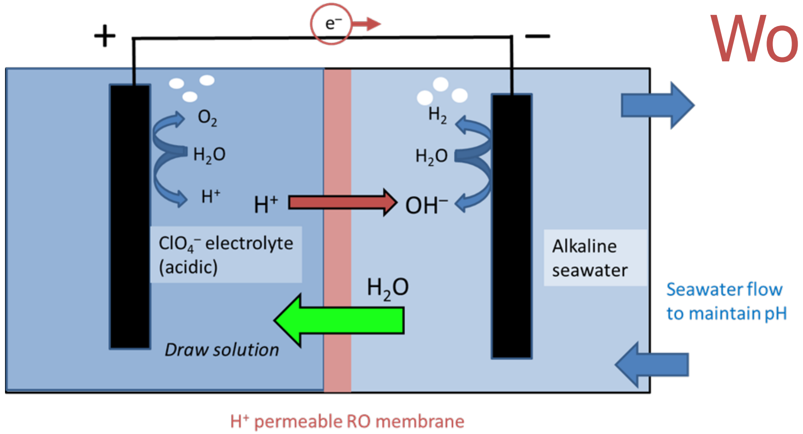
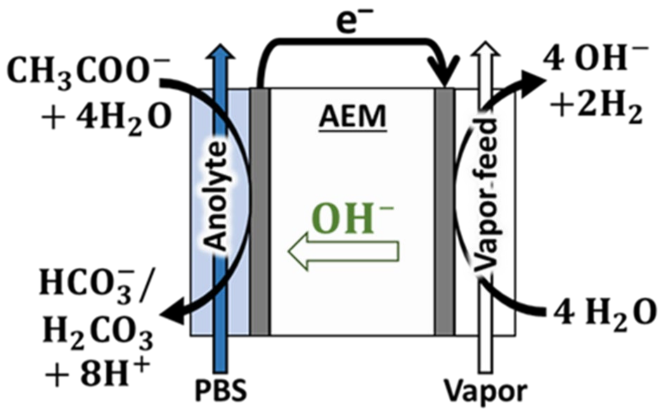
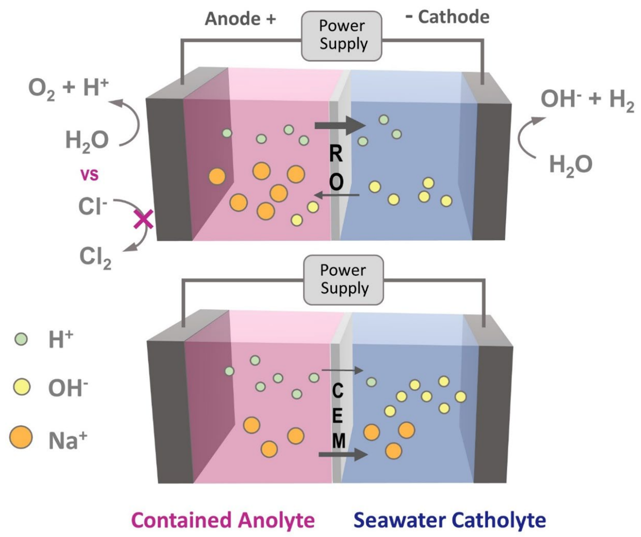
Green Hydrogen using Novel Water Electrolyzers and next-generation Microbial Electrolysis Cells

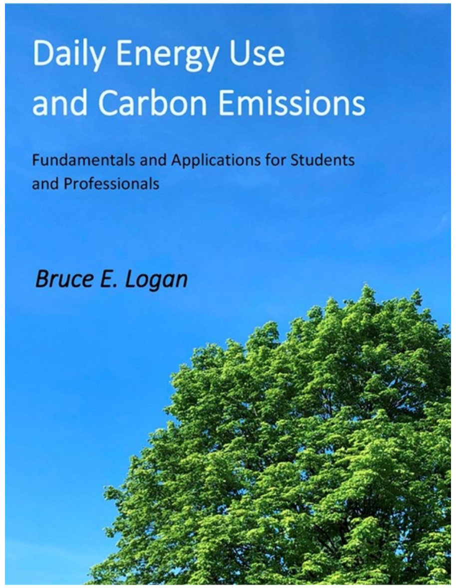


World Hydrogen Energy Conference
June 27, 2022

Bruce E. Logan
Penn State University, blogan@psu.edu



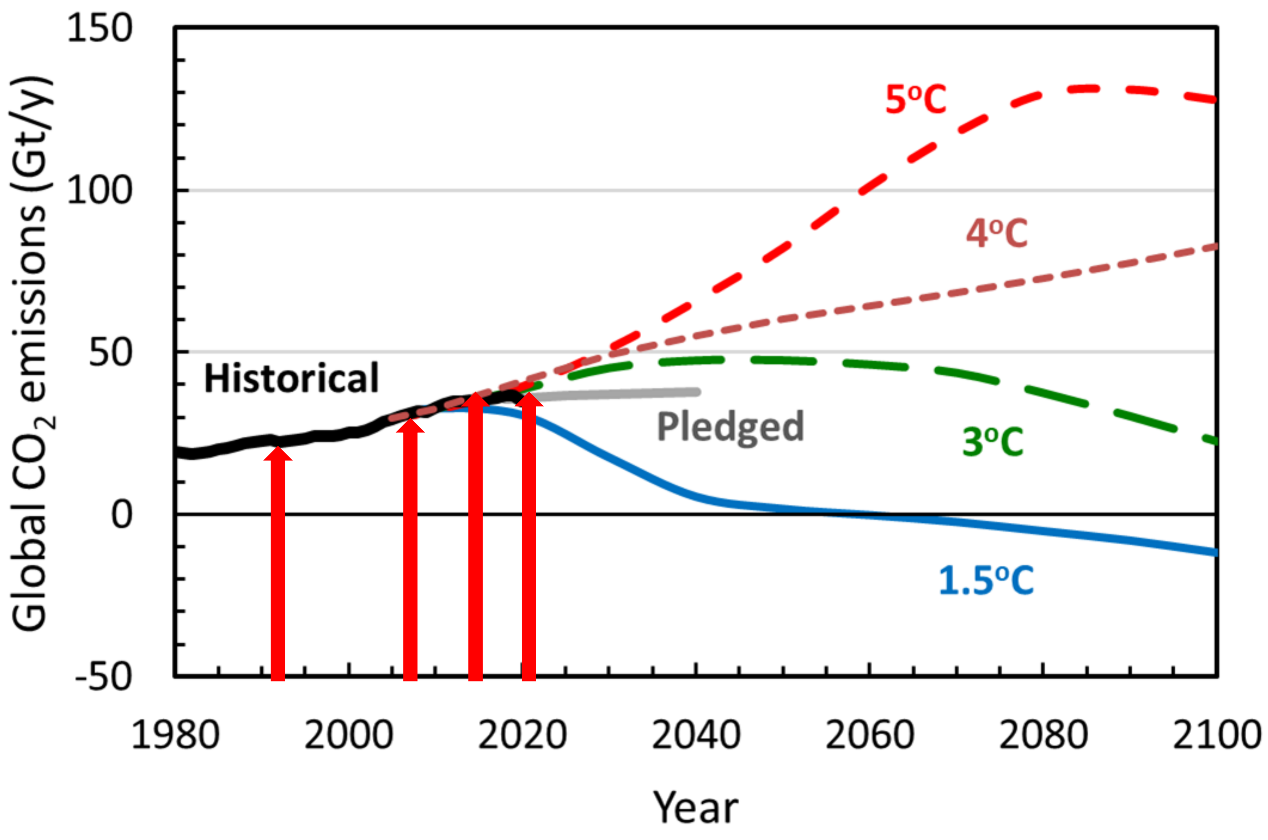


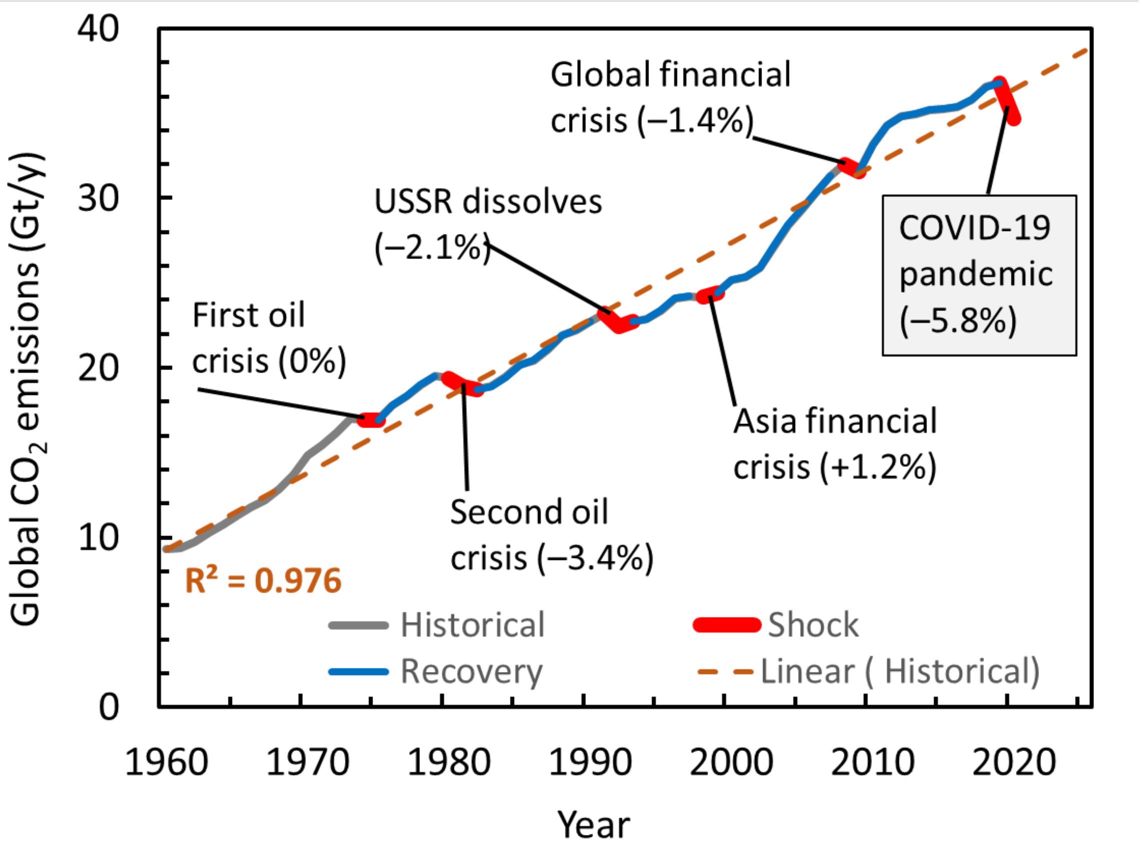


ENERGY earthshots U.S. DEPARTMENT OF ENERGY | Hydrogen

PennState

The global challenge of CO_2 emissions





International treaties of UNFCCC (1992), Kyoto (2007), and the Paris Agreement (2015) did not stop the trend in increased CO_2 emissions: Will COP 26 be different?
Global disruptions have not produced long-term increases in emissions

B.E. Logan. (2022): *Daily Energy Use and Carbon Emissions*, Publisher: John Wiley

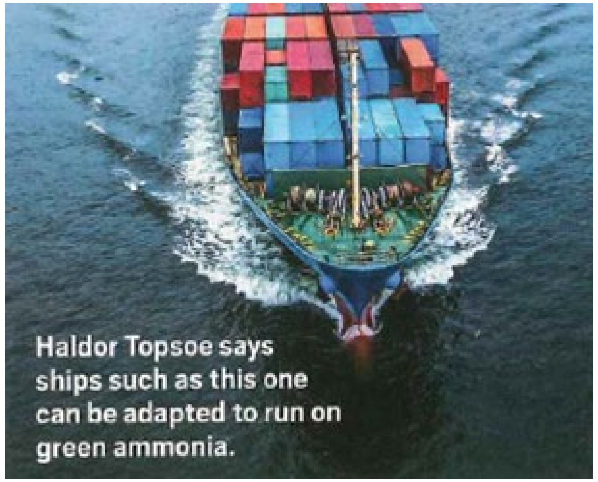
Why H_2? Heavy hauling transportation

Consider Energy Densities:

Method	Density (kWh/kg)	Gas greater by
Gasoline	12.4	---
H_2 tank (car)	33	0.38 x
Battery (Tesla)	0.16	77 x

- Fuel: percentage of total weight:
  - Car (gasoline): 2%
  - Airplane (jet fuel): 26-45%
- Batteries for
  - Electric vehicle (Tesla) weight = 27%
  - Batteries for large airplanes? They can't take off…

(737 fuel = 40,000 lb, Full = 175,000 lb; battery =3.1 million lb)



PennState

H_2 from water

Netherlands

Nouryon and partners are building an electrolyzer facility to produce green hydrogen at this site in Delfzijl, the Netherlands.

HYDROGEN POWER

Making green hydrogen work

Decarbonizing hydrogen will take time, thought, and investment, but Europe's industry says it is committed

VANESSA ZAINZINGER, SPECIAL TO C&EN

for green hydrogen, predicts Grzegorz Pawelec, research, innovation, and funding manager with the trade association Hydrogen Europe. At first glance, this seems unlikely: falling oil and gas prices are working

Spain

ENVIRONMENT

Spanish to make fertilizer from green hydrogen

Project will cut CO_2 emissions by 39,000 metric tons

Two Spanish companies, the fertilizer producer Fertiberia and the energy firm Iberdrola, plan to build Europe's largest plant making green hydrogen for industrial use—ammonia production in this case. The companies will build a facility with capacity to produ... year of green hy... ammonia plant ... km south of Ma... the project will ... tovoltaic plant ... to power electr... into oxygen and ... combine the hy... form ammonia.

Fertiberia wi... erated oxygen a... acid, which it al...

The partners aim to bring the facility online in 2021, supplementing H_2 production from natural gas. Although the green H_2 plant will be one of the largest in Europe, it will enable Fertiberia to reduce its natural gas consumption only by about 10%.

...nates that ...izer plant's ...,000 t per ...ria a refer... ...ulture and ...'s energy ...Javier Goñi ...urrent price ...on's Emis...

Green hydrogen in Puertollano

- **\$174 million:** Cost of the project
- **100 MW:** Size of solar power plant
- **720 metric tons (t):** H_2 the plant will produce annually
- **39,000 t:** Annual reduction in CO_2 emissions
- **2021:** Planned start-up date

Source: Fertiberia.

they received EU funding for the project. The EU disclosed recently that it will co-fund at least 6 GW of renewable H_2 electrolyzers and the production of up to 1 million t of H_2 in Europe through 2024.

About 500,000 t per year of hydrogen are produced from fossil fuels in Spain every year for the refining, chemical, and fertili... genera...

Germany

HYDROGEN POWER

Electrolyzer ready for German grid

An alkaline water electrolyzer from the engineering firm Thyssenkrupp has qualified as a secondary power source for the German electric grid. During periods of excess renewable electricity production the electrolyzer can generate hydrogen

Thyssenkrupp says its water electrolyz... will ease adoption of electricity from renewable sources.

Washington State in US

ENERGY

Hydroelectric H_2 comes to Washington

The Douglas County Public Utility District in Washington State has selected the engineering firm Cummins to build an electrolyzer that will use excess electricity from the Wells Dam to produce hydrogen gas. The firm says the 5 MW facility will be the nation's largest H_2 plant based on proton-exchange membranes. Cummins's water-splitting technology comes largely from its \$290 million purchase of the fuel cell and H_2 production technology firm Hydrogenics in 2019.—CRAIG BETTENHAUSEN

Saudi Arabia will build a \$5 Billion H_2 plant:

Wind & Solar energy → H_2 → NH_3 → H_2

Saudi green hydrogen project announced to be largest in world

https://www.hydrogenfuelnews.com/saudi-green-hydrogen-project-announced-to-be-largest-in-world/8540205/?MvBriefArticleId=18039

Tensions arise as clean hydrogen projects spread

Saudi Arabia will build world's largest green hydrogen plant as the UK plans a big blue hydrogen project

Companies have announced two major projects to produce clean hydrogen for fuel and chemical use as debate grows over just what clean hydrogen is.

Air Products is partnering with the Saudi energy firm ACWA Power and the Saudi development agency Neom to build in northwest Saudi Arabia what will be the world's largest facility for green hydrogen—hydrogen made by electrolyzing water with renewable energy.

The partners will use alkaline water electrolyzers produced by the German engineering firm Thyssenkrupp to convert water into oxygen and about 650 metric tons (t) per day of hydrogen. They plan to build 4 GW of solar and wind energy facilities—the world's largest renewable energy

says Ben Gallagher, senior analyst with the consulting firm Wood Mackenzie. He points to layers of uncertainty associated with the project: its massive size, the processing of hydrogen to ammonia and back again, and that some major renewable energy projects in Saudi Arabia have not materialized as announced.

Air Products estimates the project will

largest industrial cluster into its greenest cluster," Al Cook, Equinor's UK manager, says in a statement.

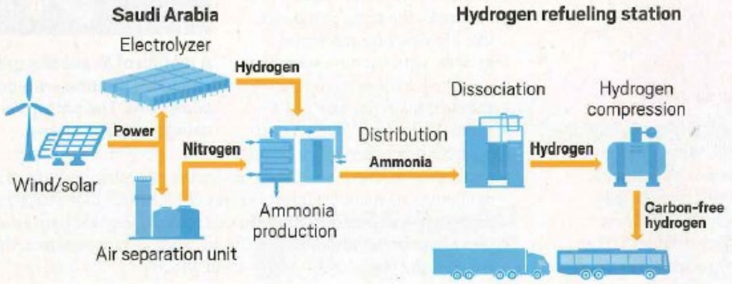
About 100 large-scale hydrogen projects are being planned globally, mostly in Europe, the Asia-Pacific region, and Australia, Gallagher says.

The European Commission has set a target for hydrogen to meet 14% of Europe's energy needs by 2050. To help reach this goal, the EC is gearing up to spend billions of dollars in a post-COVID-19 economic stimulus package that it hopes will attract private investment to create a combined fund of \$200 billion.

The EC proposes cofunding any blue hydrogen project in which roughly 90% of the CO_2 is captured and

Big H_2 plans

Air Products and partners will make green hydrogen in Saudi Arabia, combine it with nitrogen to form ammonia, ship the ammonia around the world, and then extract the hydrogen for use as a vehicle fuel.



1

Department of Energy

DOE Establishes Bipartisan Infrastructure Law's $9.5 Billion Clean Hydrogen Initiatives

FEBRUARY 15, 2022

DOE Seeks Public Input on New Hydrogen Hubs, Clean Hydrogen Manufacturing Programs to Decarbonize Industry, Transportation Sectors and Provide Healthier Air for All

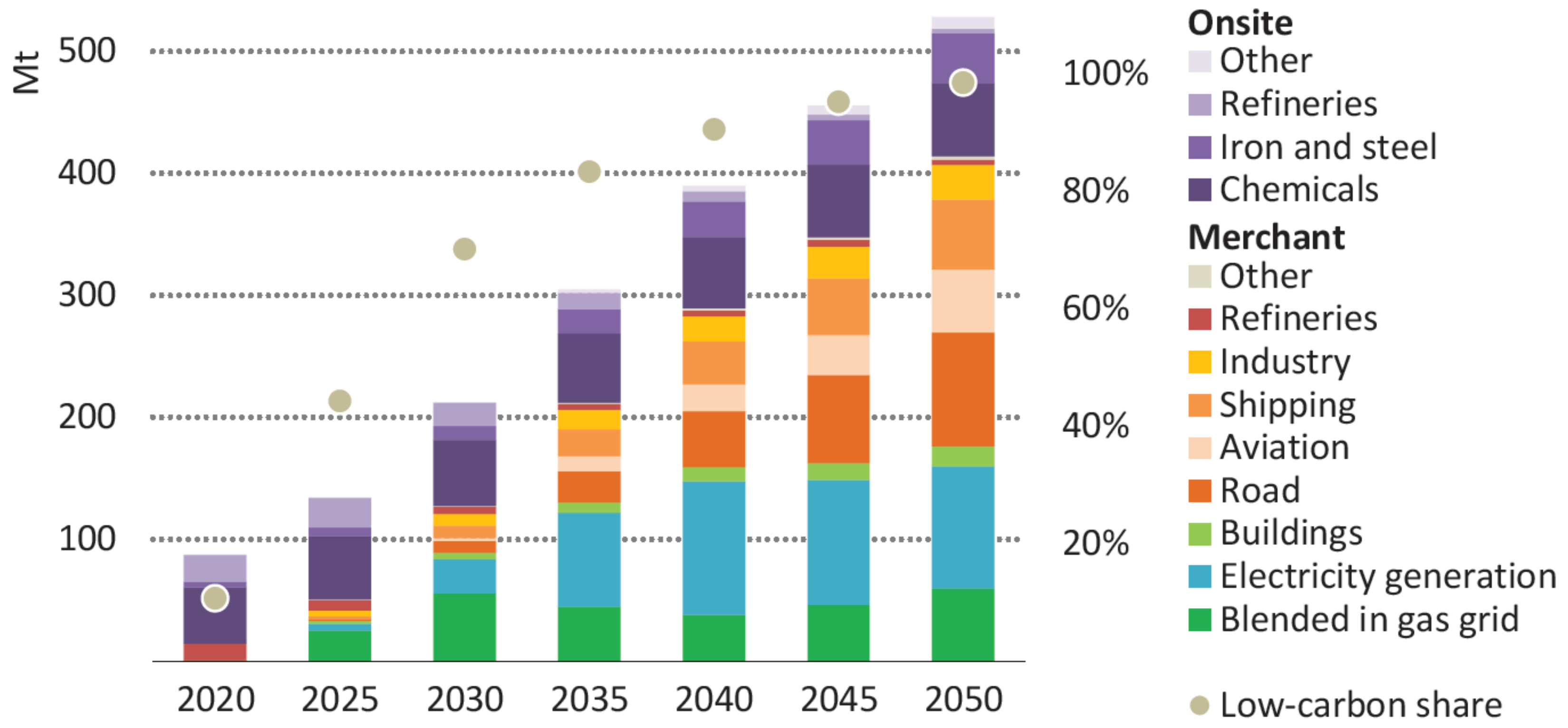
WASHINGTON, D.C. — The U.S. Department of Energy (DOE) today announced two Requests for Information (RFI) to collect feedback from stakeholders to inform the implementation and design of the Bipartisan Infrastructure Law's Regional Hydrogen Hub and the Electrolysis and Clean Hydrogen Manufacturing and Recycling Programs. This request will help accelerate progress,

Getting to the Future with H_2: IEA 2021 Report

- **2020-2030:** Focus on "low hanging fruit": fossil fuels to low-carbon H2 for industry, refineries, powerplants, blending with natural gas. (report p.75)
- **Invest** in H_2 technologies increases from \$1B to \$40B annually by 2030. (p.17)
- **Heavy Industry**: Reductions in CO_2 by ~50% due to H_2 + carbon capture and storage (CCS). (p.99)
- **Transportation**: By 2050, H_2 is fuel for:
  - 33% heavy trucks, 33% aviation, 60% shipping
  - H_2 + grid electricity = 95% for rail. (p.138)
- **Electricity**: Provide a low-carbon source of dispatchable power and <u>seasonal</u> storage. (p.108)

Key Challenges: Inexpensive, GREEN H_2

Figure 2.19 ▷ Global hydrogen and hydrogen-based fuel use in the NZE

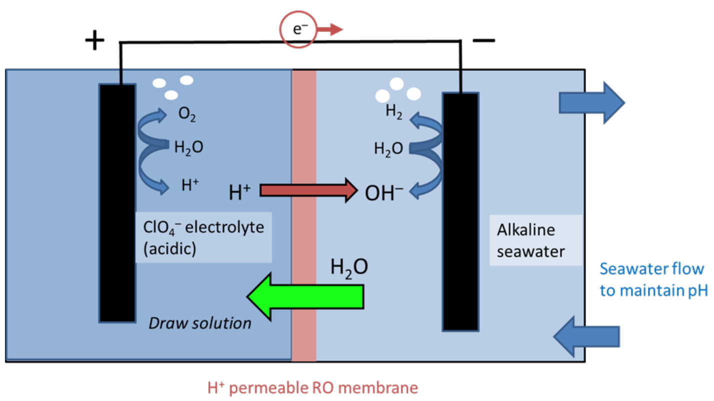


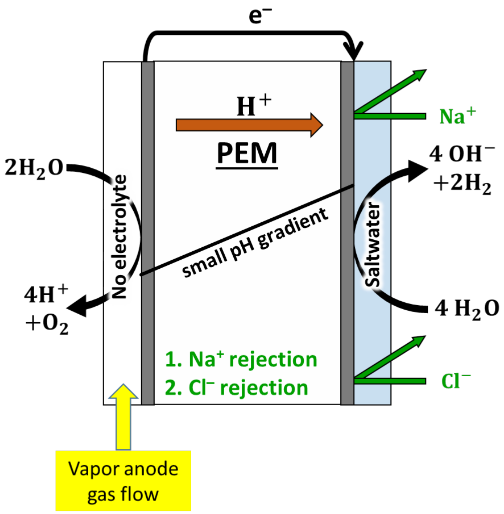
Topics for this presentation on Green H_2

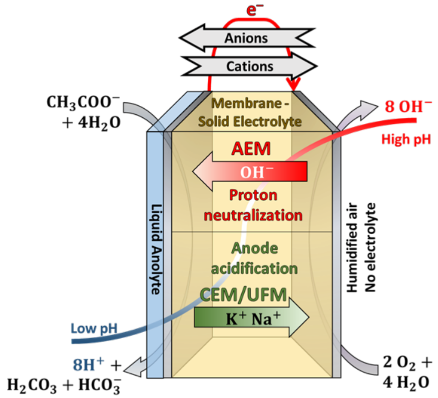
- Hydrogen gas-
  - Why is it important? (Done)
  - Global interest & the US DOE 1:1:1 program
  - Why "blue H_2" made with CH_4 has challenges
- H_2 from water electrolyzers
  - Research at Penn State using RO membranes
  - Vapor-fed anolytes in PEM-based WE

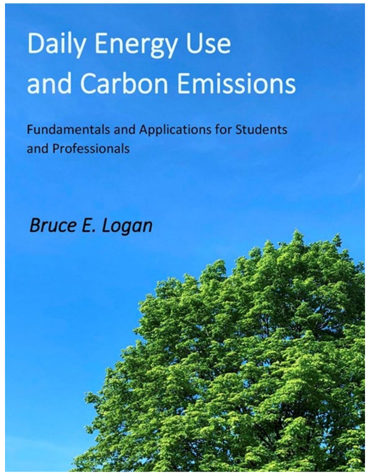
- Making H_2 gas using Microbial Electrolysis Cells (MECs)
  - Increasing rates using novel designs

- Energy education
  - Climate change is impacting the world, and things have to change
  - The benefits of green H2 need to be more effectively communicated to the public.









PennState

1 1 1 "H_2 shot": $1 for 1 kg in 1 decade

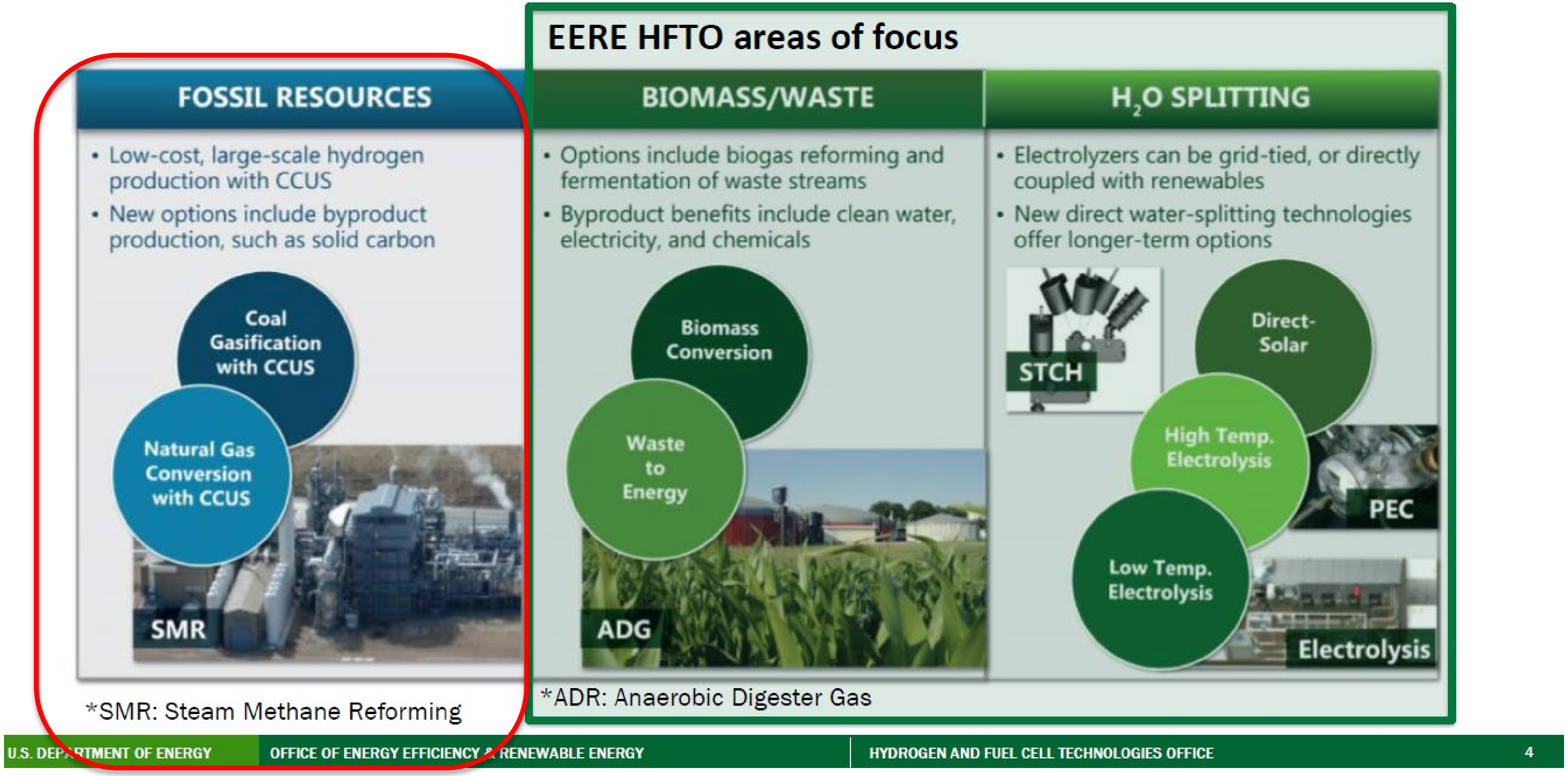
ENERGY earthshots U.S. DEPARTMENT OF ENERGY | Hydrogen

The U.S. Department of Energy (DOE) **Hydrogen Shot Summit** will convene thousands of stakeholders online to introduce the Hydrogen Shot, solicit dialogue, and rally the global community on the urgency of tackling the climate crisis through concrete actions and innovation. The Hydrogen Shot Summit will be held virtually August 31 and September 1, 2021.

DOE will share results from the recent Request for Information and obtain feedback on pathways to achieving the Hydrogen Shot's "1 1 1" goal of $1 for 1 kg of clean hydrogen in 1 decade. Breakout sessions on various clean hydrogen production pathways as well as deployment and financing will help identify key challenges and potential strategies to address them.

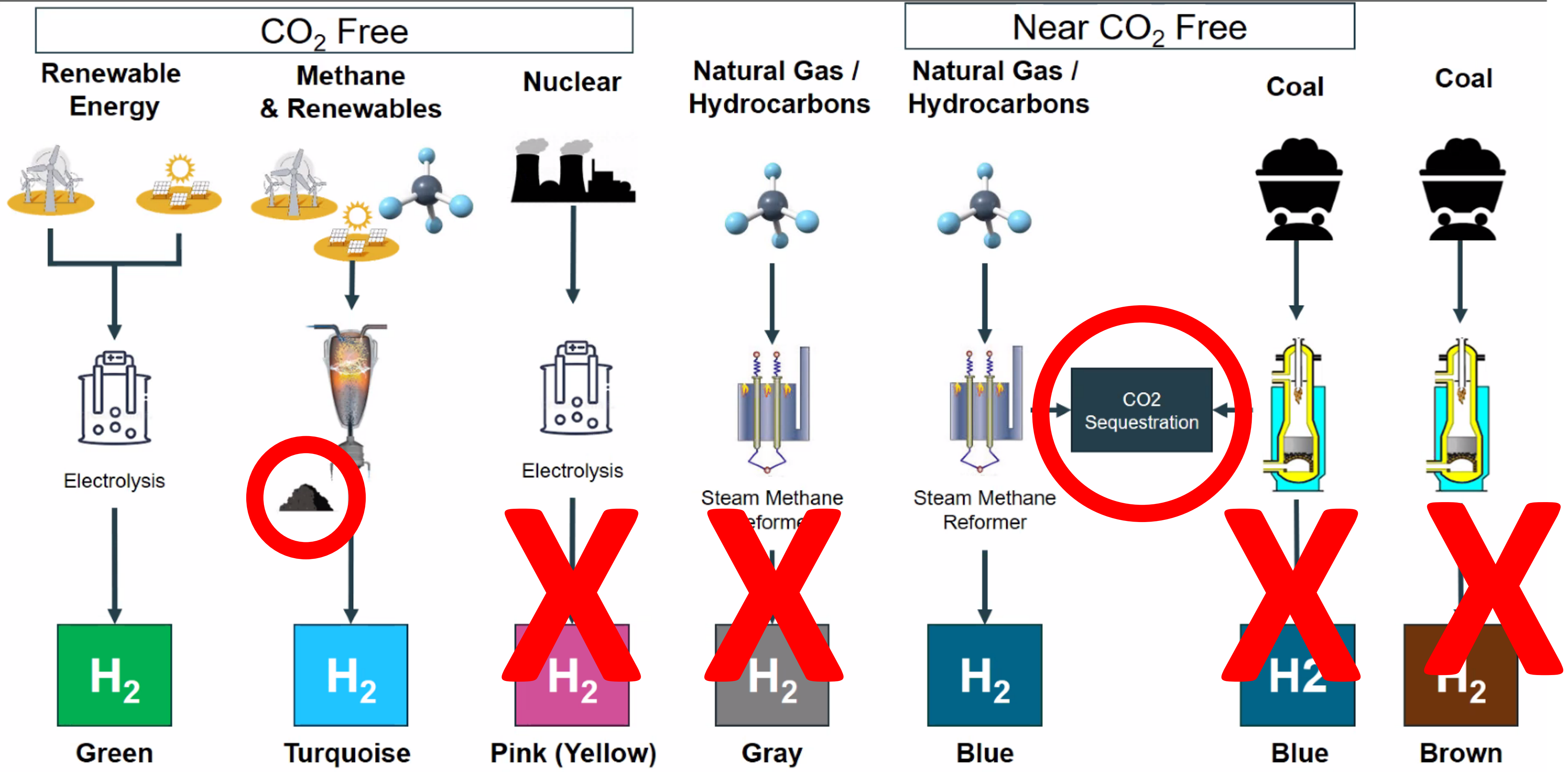
Relevance to US DOE HFTO and Hydrogen Shot

Portfolio Includes Hydrogen Production from Diverse Sources and Pathways



*Sourced from March 11, 2021, Sustainable Energy Council (SEC) World Hydrogen Summit by Dr. Sunita Satyapal

Colors of Hydrogen



Blue H_2: How much net CO_2 release if the captured CO_2 is used for further oil extraction?

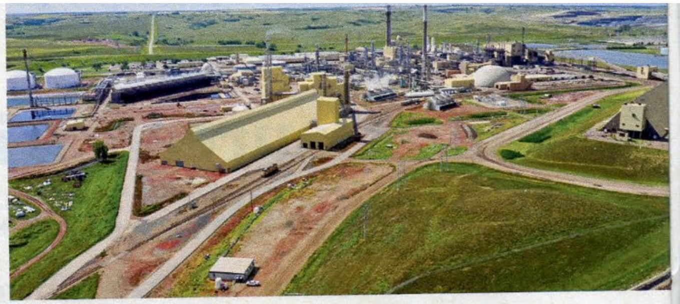
"where it assists in oil recovery"

Business Concentrates

HYDROGEN POWER

Blue hydrogen investment planned

Projects in Alberta and North Dakota aim to create low-carbon hydrogen from natural gas



Mitsubishi Power may redevelop the Dakota Gasification plant in Beulah, North Dakota.

Blue hydrogen is taking a big step forward in North America as Air Products and Chemicals and Mitsubishi Power unveil ambitious projects in Canada and the US, respectively.

Air Products plans to spend $1.1 billion to build a complex in Edmonton, Alberta, that makes blue hydrogen, so-called because by-product carbon dioxide is captured and stored.

Officials say the facility, which will open in 2024, will be the first of its kind in Canada. The technology is based on a reformer that makes hydrogen from natural gas. Some 95% of the CO_2 will be captured and sent to the Alberta Carbon Trunk Line. This network already gathers CO_2 from emitters such as the fertilizer maker Nutrien and sends it to oil fields, where it assists in oil recovery and is stored underground.

Air Products will construct a hydrogen liquefaction facility to supply industrial customers and operators of hydrogen-powered trucks and buses. The firm will also build a hydrogen-based power plant.

At a press conference with local officials, Air Products CEO Seifi Ghasemi said this is only the "first phase" of the company's plans for Edmonton, and that Air Products intends more hydrogen projects there and elsewhere in Canada. More broadly, Air Products has been trying to cultivate a business in low-carbon hydrogen for fuel. It is already involved in a $5 billion alternative energy complex in Saudi Arabia that will make green hydrogen for ammonia by splitting water using renewable energy.

"We are the leading producer of hydrogen worldwide," Ghasemi said. "And we intend to be the leading producer in blue hydrogen and also in green hydrogen."

The US may get a blue hydrogen hub as well. Mitsubishi Power and the oil and gas firm Bakken Energy are contemplating buying and redeveloping the Dakota Gasification plant near Beulah, North Dakota, to make hydrogen.

Run by the Basin Electric Power Cooperative, Dakota Gasification is a unique operation that gasifies coal and converts it into natural gas, nitrogen fertilizers, and petrochemical feedstocks. The facility has struggled because of low commodity prices in recent years, and operators have been considering eliminating coal gasification. The plant already captures 2 million metric tons of CO_2 per year, which is sent via pipeline to Saskatchewan for oil recovery. Project details remain confidential while due diligence is conducted, Mitsubishi says.—ALEX TULLO

PennState

There are also substantial natural gas leaks prior to use

What percentage of natural gas is lost?

- US EPA: 1.4%
- Alvarez et al.: 2.3%

Science

REPORTS

Cite as: R. A. Alvarez *et al.*, *Science* 10.1126/science.aar7204 (2018).

Assessment of methane emissions from the U.S. oil and gas supply chain

Ramón A. Alvarez[1*], Daniel Zavala-Araiza[1], David R. Lyon[1], David T. Allen[2], Zachary R. Barkley[3], Adam R. Brandt[4], Kenneth J. Davis[3], Scott C. Herndon[5], Daniel J. Jacob[6], Anna Karion[7], Eric A. Kort[8], Brian K. Lamb[9], Thomas Lauvaux[3], Joannes D. Maasakkers[6], Anthony J. Marchese[10], Mark Omara[1], Stephen W. Pacala[11], Jeff Peischl[12,13], Allen L. Robinson[14], Paul B. Shepson[15], Colm Sweeney[13], Amy Townsend-Small[16], Steven C. Wofsy[6], Steven P. Hamburg[1]

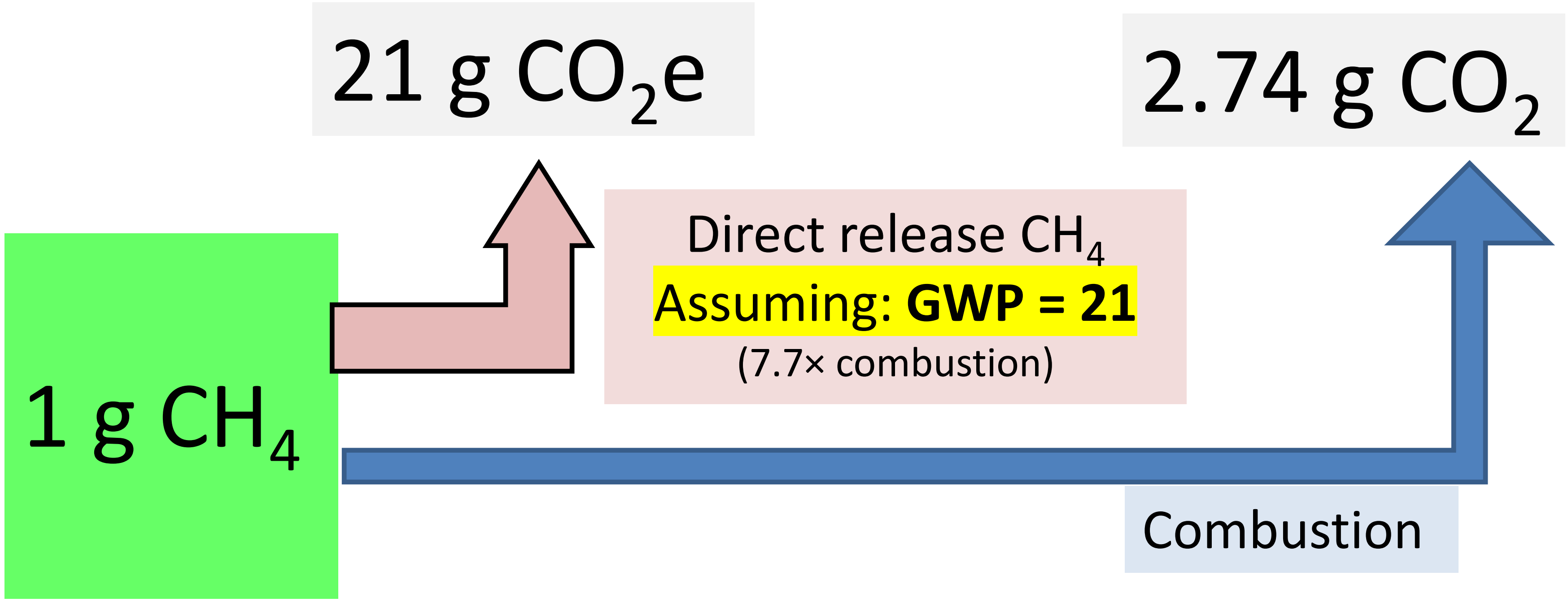
[1]Environmental Defense Fund, Austin, TX, USA. [2]University of Texas at Austin, Austin, TX, USA. [3]The Pennsylvania State University, University Park, PA, USA. [4]Stanford University, Stanford, CA, USA. [5]Aerodyne Research Inc., Billerica, MA, USA. [6]Harvard University, Cambridge, MA, USA. [7]National Institute of Standards and Technology, Gaithersburg, MD, USA. [8]University of Michigan, Ann Arbor, MI, USA. [9]Washington State University, Pullman, WA, USA. [10]Colorado State University, Fort Collins, CO, USA. [11]Princeton University, Princeton, NJ, USA. [12]University of Colorado, CIRES, Boulder, CO, USA. [13]NOAA Earth System Research Laboratory, Boulder, CO, USA. [14]Carnegie Mellon University, Pittsburgh, PA, USA. [15]Purdue University, West Lafayette, IN, USA. [16]University of Cincinnati, Cincinnati, OH, USA.

*Corresponding author. E-mail: ralvarez@edf.org

Methane emissions from the U.S. oil and natural gas supply chain were estimated using ground-based, facility-scale measurements and validated with aircraft observations in areas accounting for ~30% of U.S. gas production. When scaled up nationally, our facility-based estimate of 2015 supply chain emissions is 13 ± 2 Tg/y, equivalent to 2.3% of gross U.S. gas production. This value is ~60% higher than the U.S. EPA inventory estimate, likely because existing inventory methods miss emissions released during abnormal operating conditions. Methane emissions of this magnitude, per unit of natural gas consumed, produce radiative forcing over a 20-year time horizon comparable to the CO_2 from natural gas combustion. Significant emission reductions are feasible through rapid detection of the root causes of high emissions and deployment of less failure-prone systems.

Global Warming Potential (GWP) # for CH_4 is changing

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$



Study	GWP
100-y, IPCC 1995	21
IPCC 2014	28
20-y, IPCC 1995	56
20-y, IPCC 2014	85
20-y, Alvarez et al.	96

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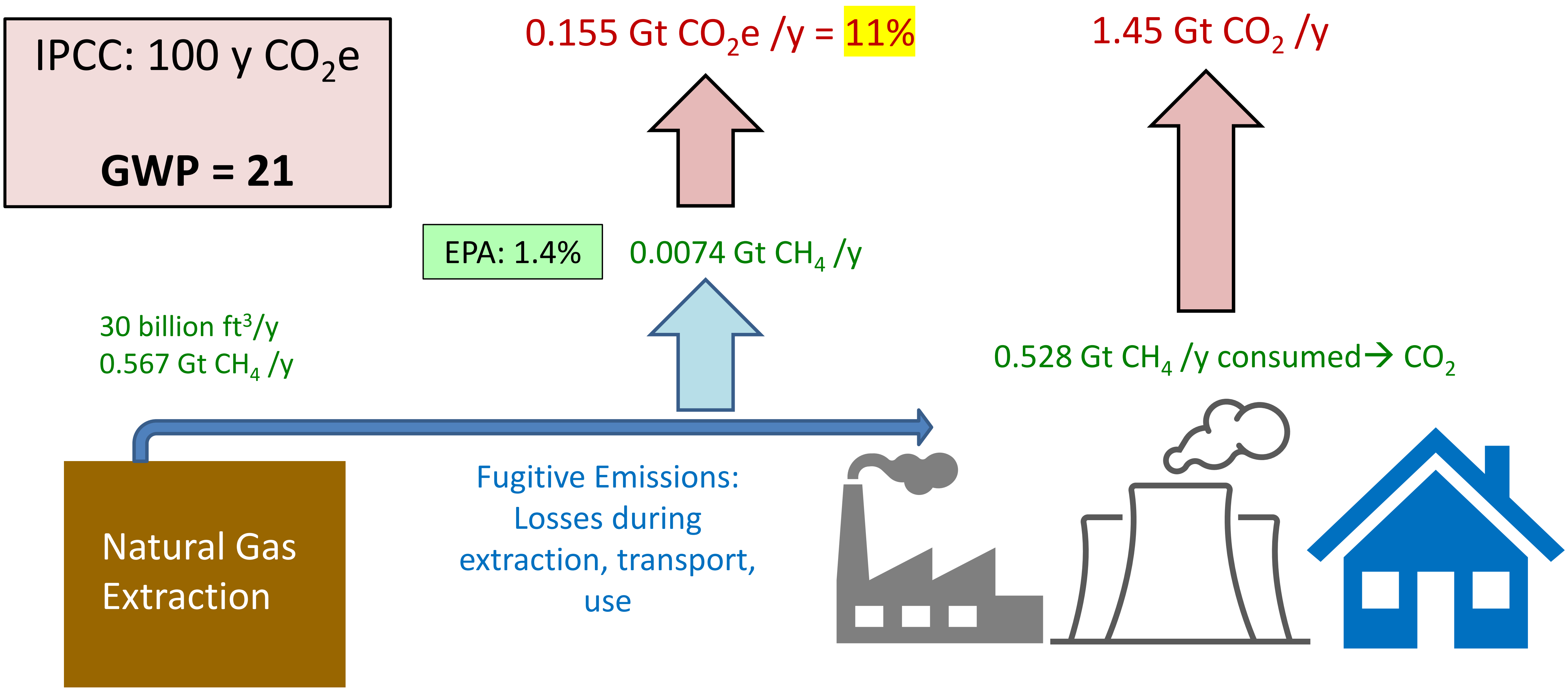
Natural Gas (methane) use and CO_2e emissions



PennState

Natural Gas (methane) use and CO_2e emissions

IPCC: 20 y CO_2e

GWP = 85

1.03 Gt CO_2e /y = 71%

1.45 Gt CO_2 /y

Alvarez et al: 2.3%

0.0121 Gt CH_4 /y

30 billion ft^3/y
0.567 Gt CH_4 /y

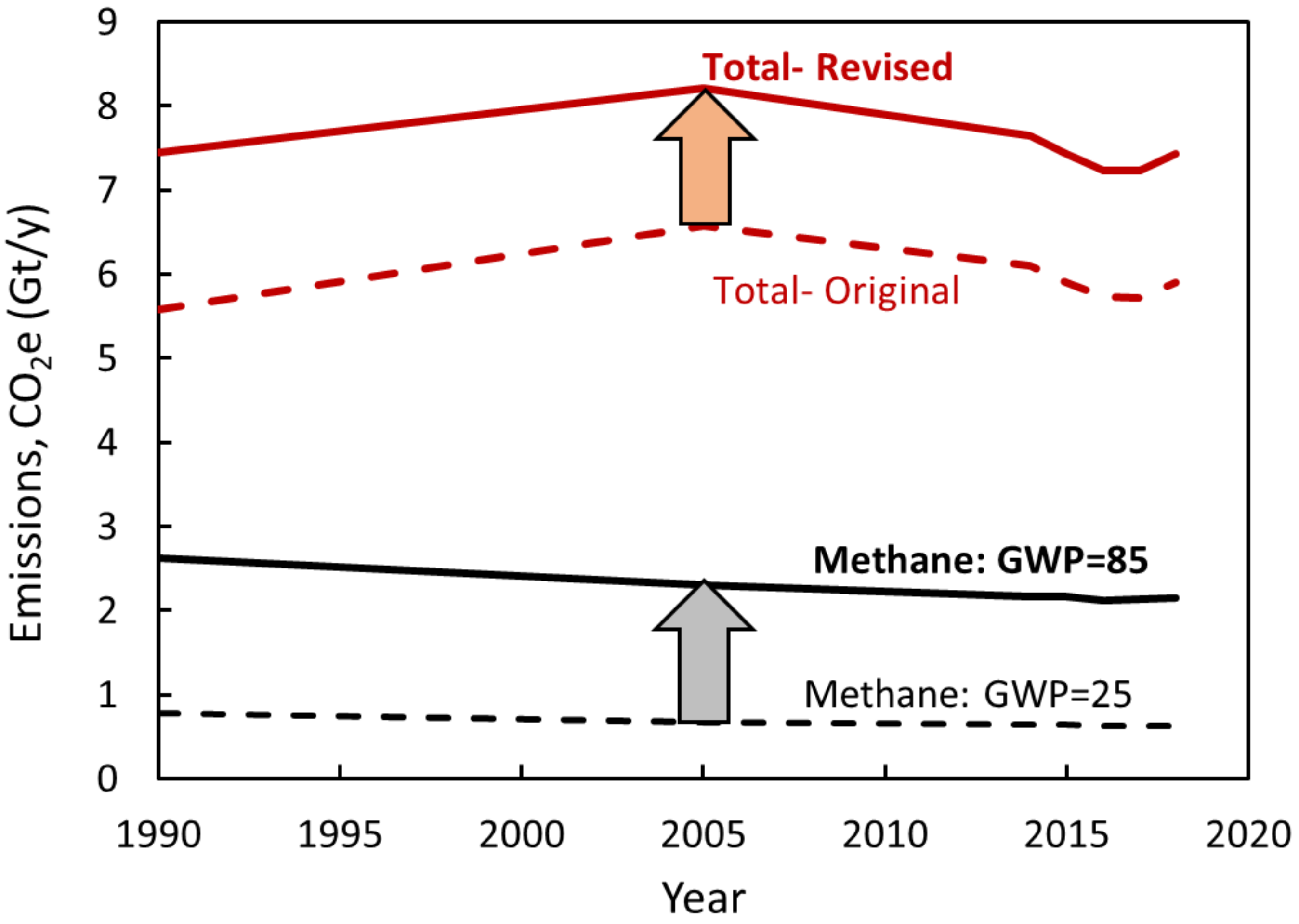
0.528 Gt CH_4 /y consumed → CO_2

Natural Gas Extraction

Fugitive Emissions: Losses during extraction, transport, use

How does a GWP=85 affect total US CO_2e emissions?

- GWP = 25 (100-y)
  - 0.63 Gt CO_2e in 2018 due to methane
  - 5.90 Gt (Total=6.68)
- GWP = 85 (20-yr)
  - 2.2 Gt CO_2e from methane
  - Emissions increase 21% to 7.4 Gt



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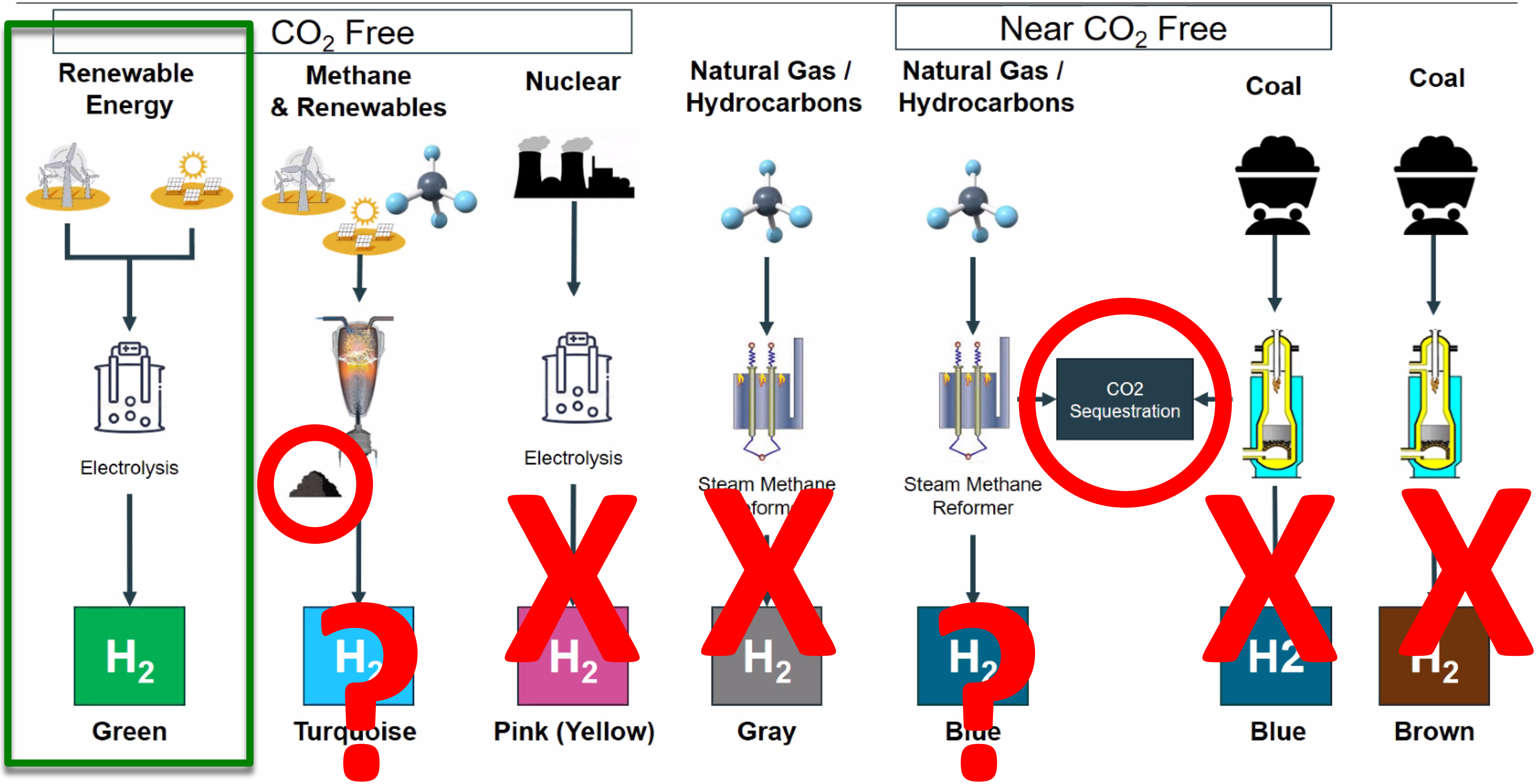
Data from US EPA Report (2019)

Colors of Hydrogen

MITSUBISHI POWER



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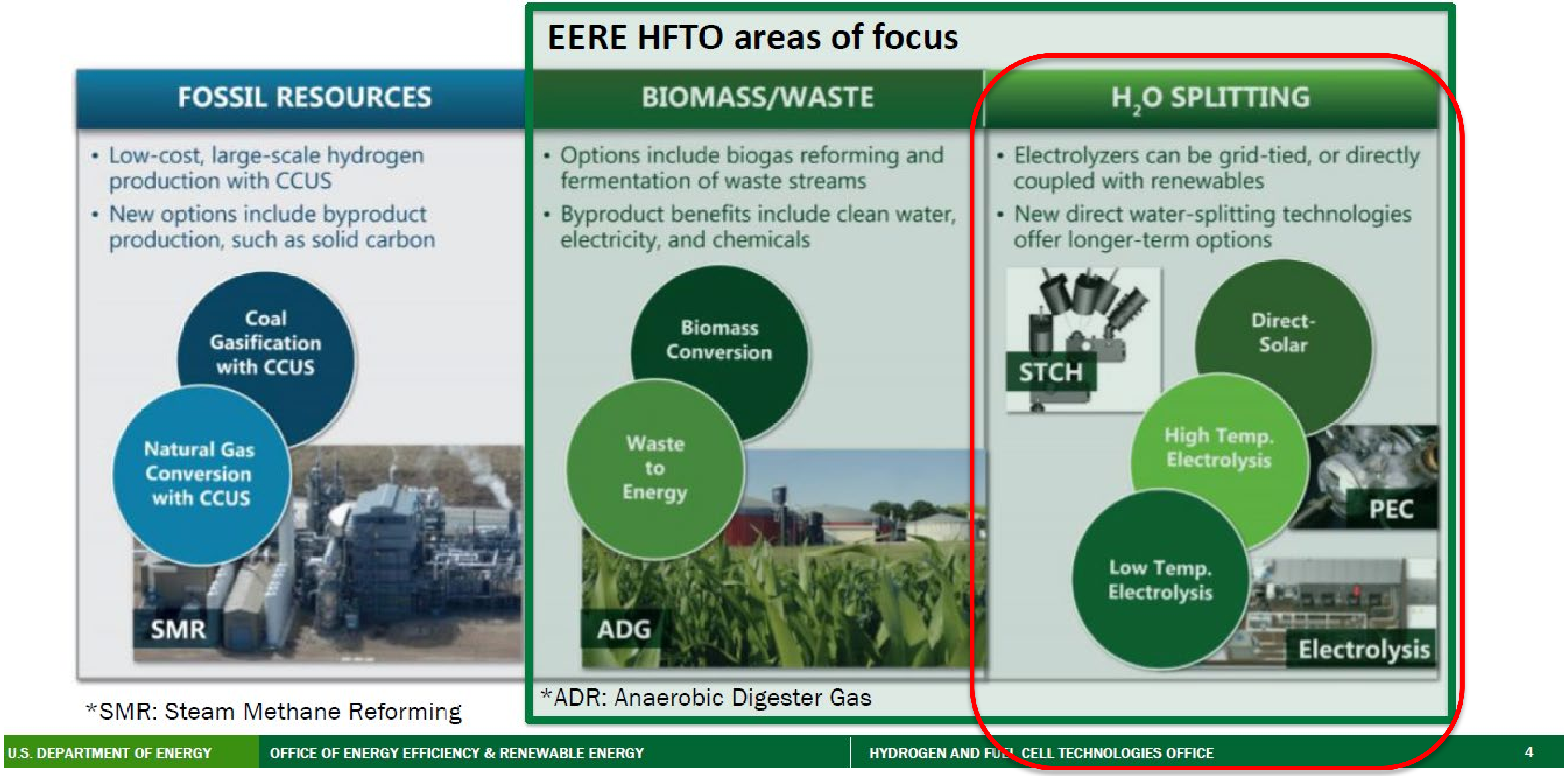
Relevance to US DOE HFTO and Hydrogen Shot

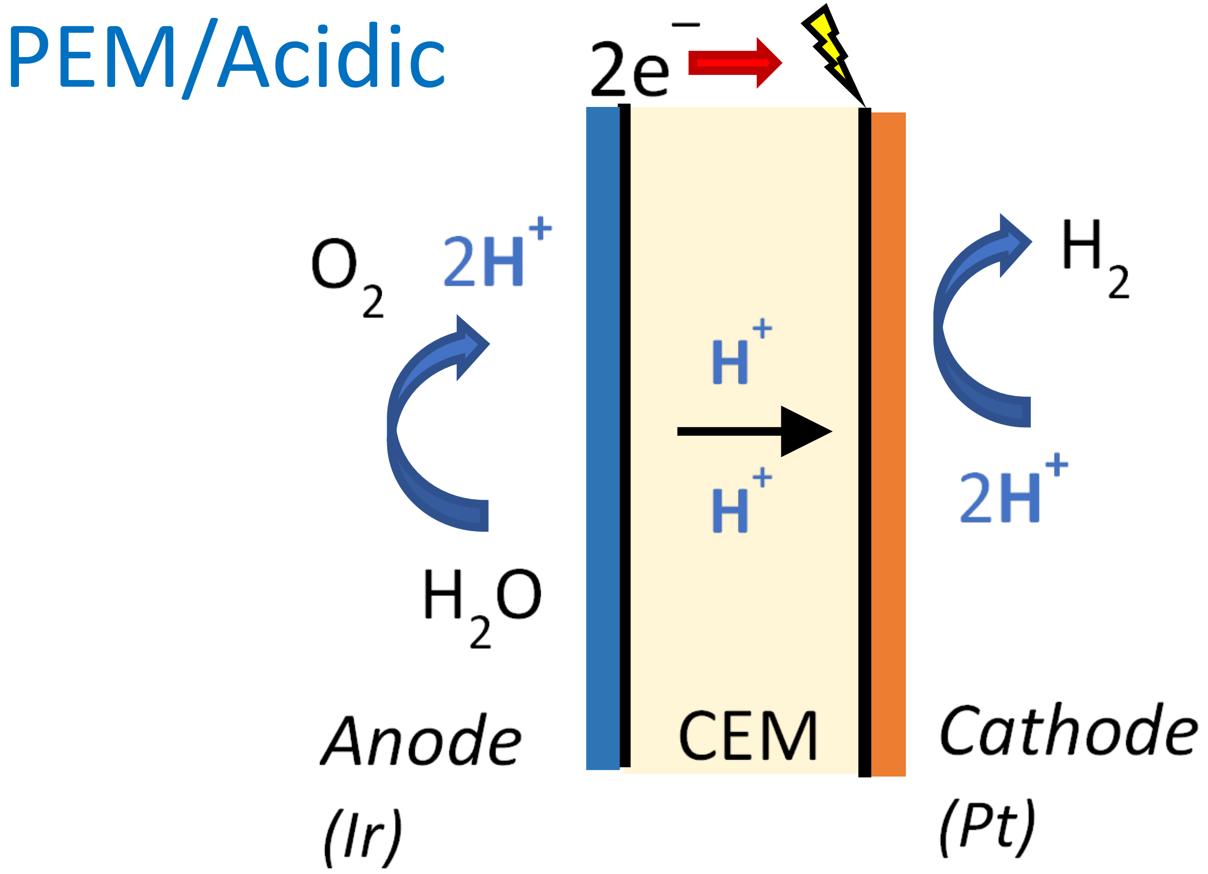
Portfolio Includes Hydrogen Production from Diverse Sources and Pathways

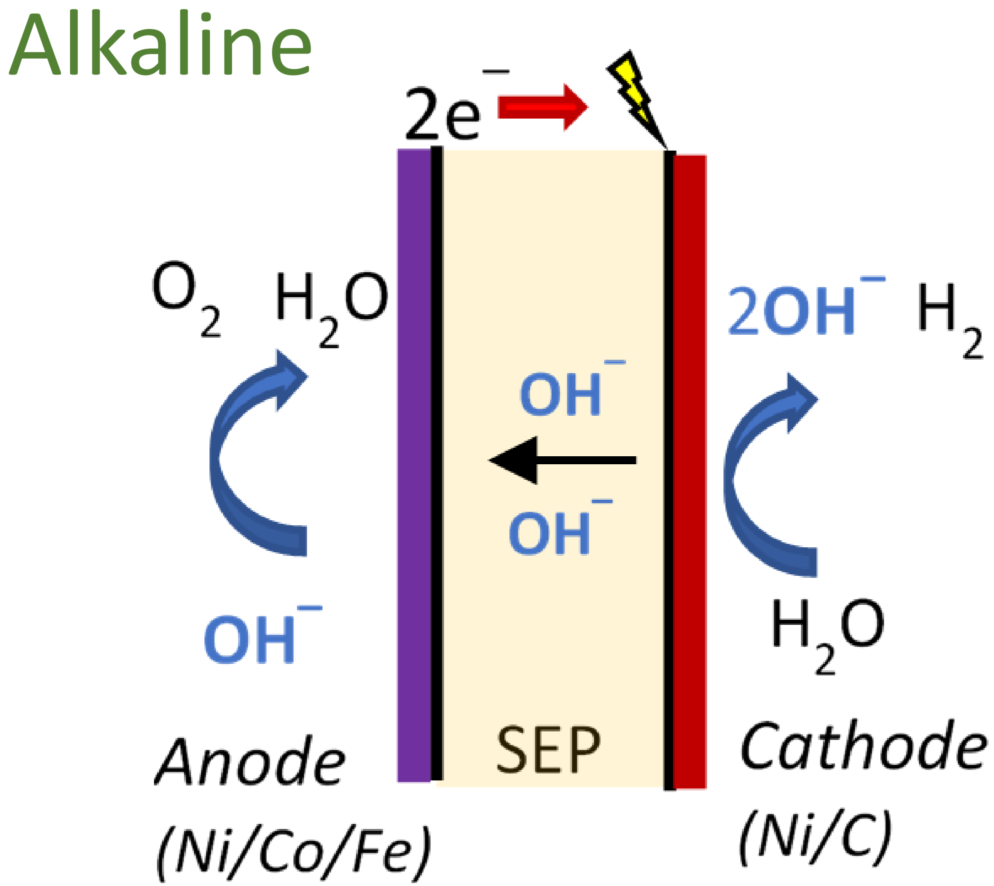


*Sourced from March 11, 2021, Sustainable Energy Council (SEC) World Hydrogen Summit by Dr. Sunita Satyapal

Water Electrolyzers: Two main approaches

Both approaches need ultra-pure (deionized) water





Challenges for Electrochemical H_2 production

- Up to 50% of the cost of water electrolysis (WE) is in membranes and catalysts
- Renewable energy sources offshore (wind) or in arid regions (solar)
- Water source for WE is a concern
- Great interest in using seawater/impaired water

- Need water with no Cl^-
- Presence of Cl^- results in Cl_2 gas evolution instead of water splitting

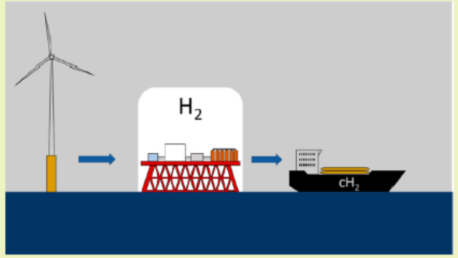
ACS Sustainable Chemistry & Engineering
Perspective
Cite This: ACS Sustainable Chem. Eng. 2019, 7, 8006−8022
pubs.acs.org/journal/ascecg

Sustainable Hydrogen Production from Offshore Marine Renewable Farms: Techno-Energetic Insight on Seawater Electrolysis Technologies

Rafael d'Amore-Domenech*[,†] and Teresa J. Leo[†]

[†]Dept. Arquitectura, Construcción y Sistemas Oceánicos y Navales, ETSI Navales, Universidad Politécnica de Madrid, Avenida de la Memoria 4, Madrid 28040, Spain

ABSTRACT: Hydrogen production with offshore marine renewable energies may have an important role in the future as an energy vector and as a fuel. In this regard, this work reviews all the technologies capable of performing electrolysis at sea. The review includes a thorough description and explanation of all known possible damages to the different electrolysis technologies caused by the impurities that may be present in water sourcing from the sea. In addition, this work studies three different hypothetic plants based on the reviewed technologies, to produce hydrogen at 350 bar for its transportation in compressed state. The study is aimed to make an energetic and environmental comparison. The results show that low-temperature electrolysis technologies are currently the best possible candidates regarding both sustainability and durability, with an estimated specific energy to produce hydrogen at 350 bar of 175 MJ/kg under a steady state operation.



KEYWORDS: Compressed hydrogen, Electrolysis, Green hydrogen, Hydrogen production, Offshore wind, Renewable energy

ACS Energy Letters
Cite This: ACS Energy Lett. 2019, 4, 933−942
http://pubs.acs.org/journal/aelccp
PERSPECTIVE

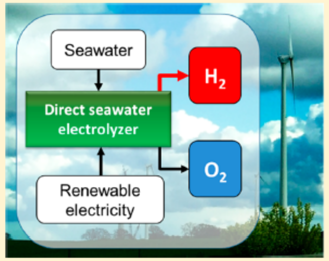
Direct Electrolytic Splitting of Seawater: Opportunities and Challenges

Sören Dresp, Fabio Dionigi, Malte Klingenhof, and Peter Strasser*

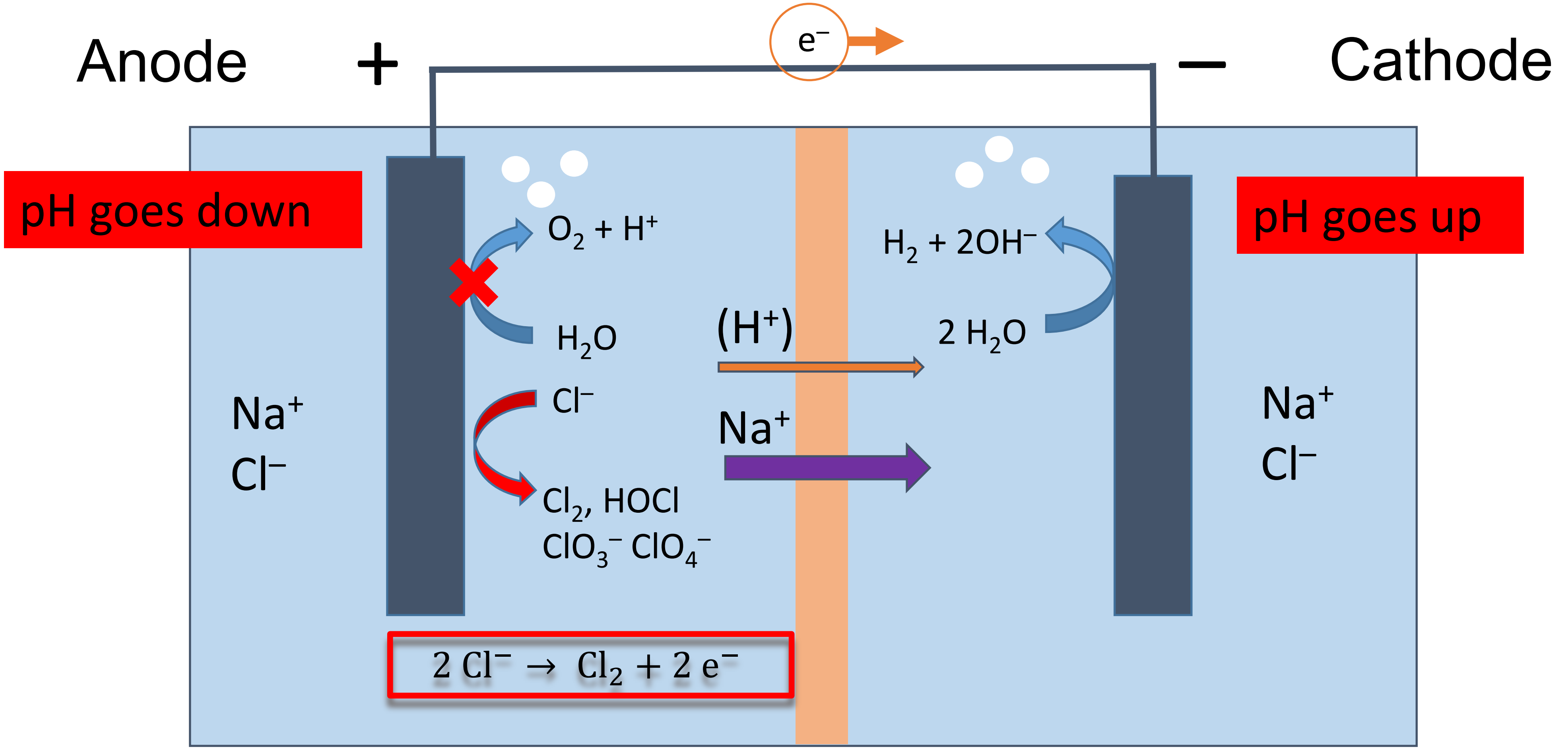
Department of Chemistry, Chemical Engineering Division, Technical University Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany

Supporting Information

ABSTRACT: Hot, coastal, hyper-arid regions with intense solar irradiation and strong on- and off-shore wind patterns are ideal locations for the production of renewable electricity using wind turbines or photovoltaics. Given ample access to seawater and scarce freshwater resources, such regions make the direct and selective electrolytic splitting of seawater into molecular hydrogen and oxygen a potentially attractive technology. The key catalytic challenge consists of the competition between anodic chlorine chemistry and the oxygen evolution reaction (OER). This Perspective addresses some aspects related to direct seawater electrolyzers equipped with selective OER and hydrogen evolution reaction (HER) electrocatalysts. Starting from a historical background to the most recent achievements, it will provide insights into the current state and future perspectives of the topic. This Perspective also addresses prospects of the combination of direct seawater electrolysis with hydrogen fuel cell technology (reversible seawater electrolysis) and discusses its suitability as combined energy conversion−freshwater production technology.



Water Electrolysis: using NaCl?

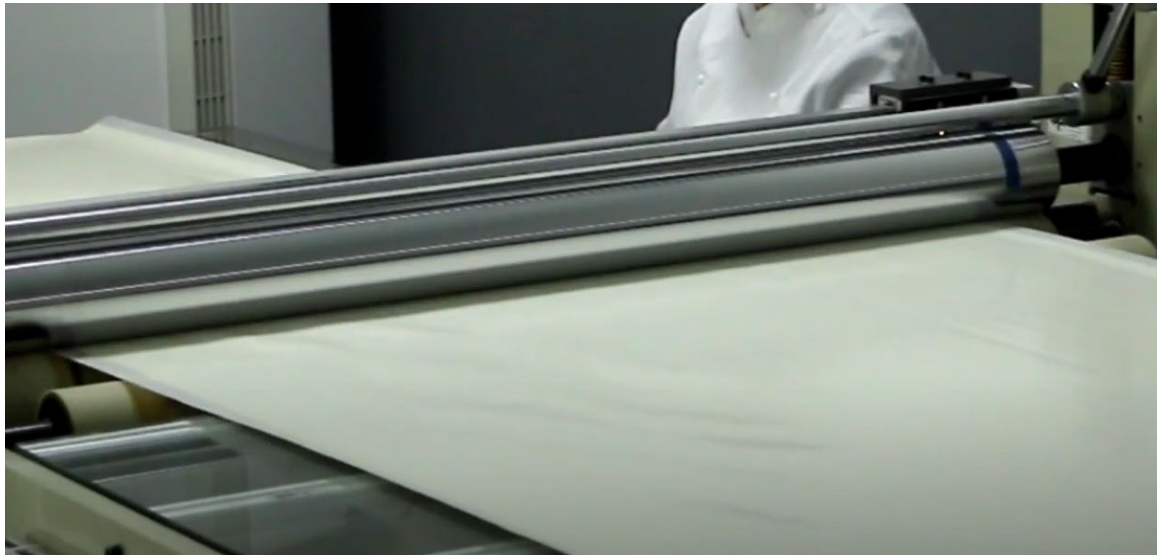


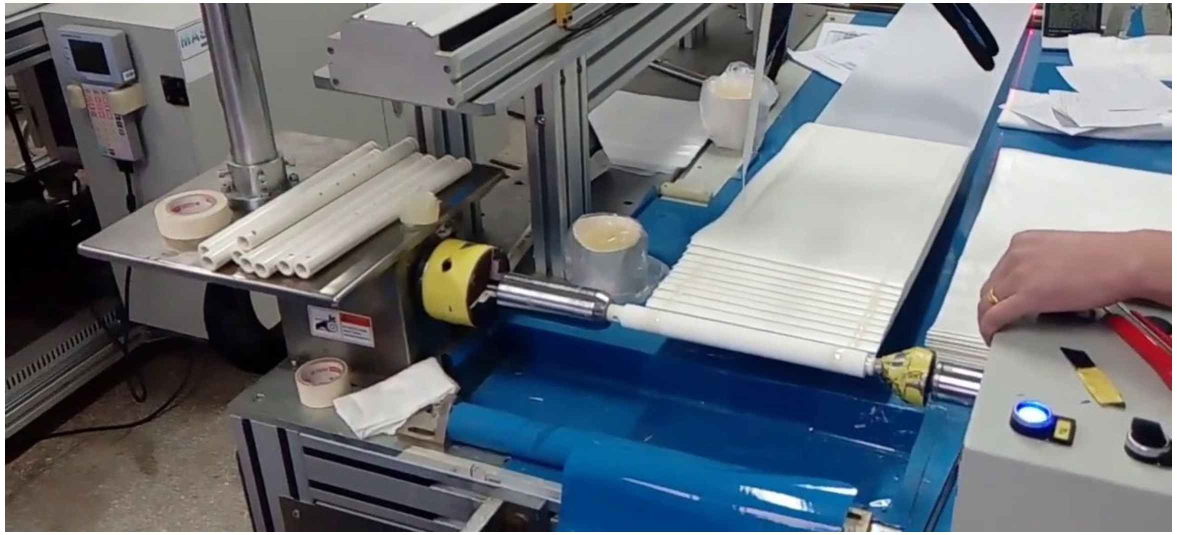
Proton Exchange Membrane (PEM)
Cation Exchange Membrane (CEM)

Reverse Osmosis membranes are "cheap"!

- **Ion Exchange (IX) membranes**
  - Expensive! ~$100 – $1000 /m^2
  - Limited production
  - Use fluorinate compounds (PFAS)
- PEM work well (CEM not clear)

- **Reverse osmosis (RO) membranes**
  - Inexpensive! < ~$10 /m^2
  - Already have mass production
  - Do not use PFAS!
- Can we use RO membranes for WE?





https://www.youtube.com/watch?v=BFjvOyjlU5k

Energy & Environmental Science

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Check for updates

Cite this: *Energy Environ. Sci.*, 2020, **13**, 3138

Using reverse osmosis membranes to control ion transport during water electrolysis†

Le Shi,[a] Ruggero Rossi,[a] Moon Son,[a] Derek M. Hall,[b] Michael A. Hickner,[c] Christopher A. Gorski[a] and Bruce E. Logan *[a]

The decreasing cost of electricity produced using solar and wind and the need to avoid CO_2 emissions from fossil fuels has heightened interest in hydrogen gas production by water electrolysis. Offshore and coastal hydrogen gas production using seawater and renewable electricity is of particular interest, but it is currently economically infeasible due to the high costs of ion exchange membranes and the need to desalinate seawater in existing electrolyzer designs. A new approach is described here that uses relatively inexpensive commercially available membranes developed for reverse osmosis (RO) to selectively transport favorable ions. In an applied electric field, RO membranes have a substantial capacity for proton and hydroxide transport through the active layer while excluding salt anions and cations. A perchlorate salt was used to provide an inert and contained anolyte, with charge balanced by proton and hydroxide ion flow across the RO membrane. Synthetic seawater (NaCl) was used as the catholyte, where it provided continuous hydrogen gas evolution. The RO membrane resistance was 21.7 ± 3.5 Ω cm^2 in 1 M NaCl and the voltages needed to split water in a model electrolysis cell at current densities of 10–40 mA cm^{-2} were comparable to those found when using two commonly used, more expensive ion exchange membranes.

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DOI: 10.1039/d0ee02173c

rsc.li/ees

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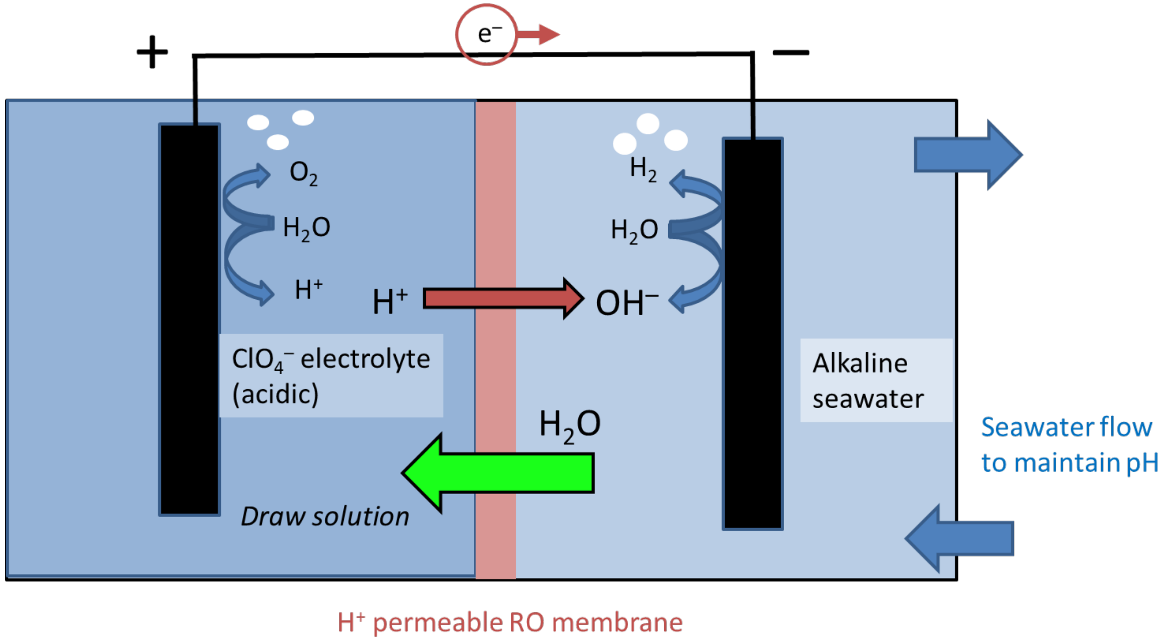
Postdoc, Penn State

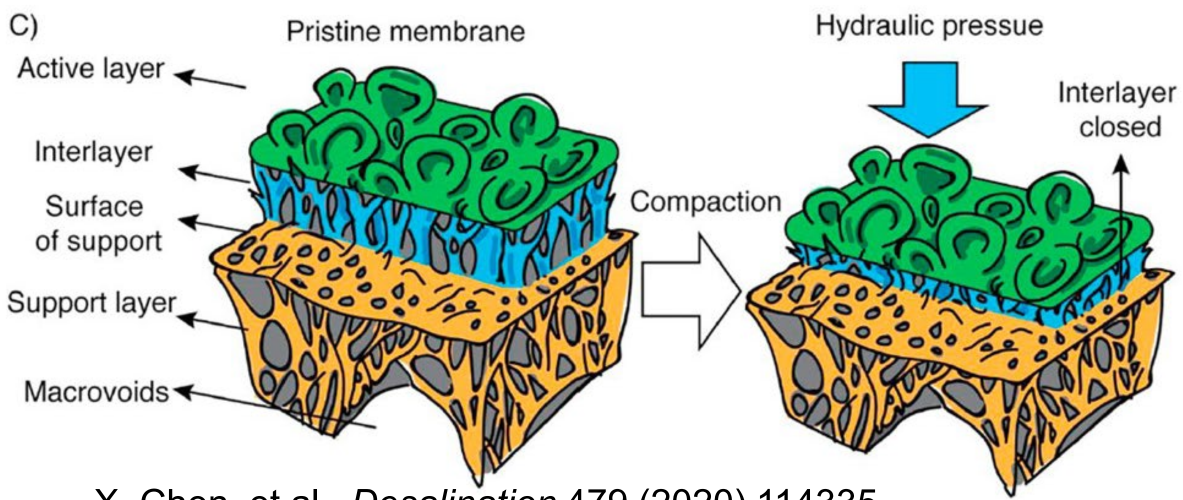
RO membrane must have a sufficient conductivity to sustain ionic current

= Low resistance (Ω m^2)



Shi, Rossi, Son, Hall, Hickner, Gorski, Logan (2021) *Energy Env. Sci.*

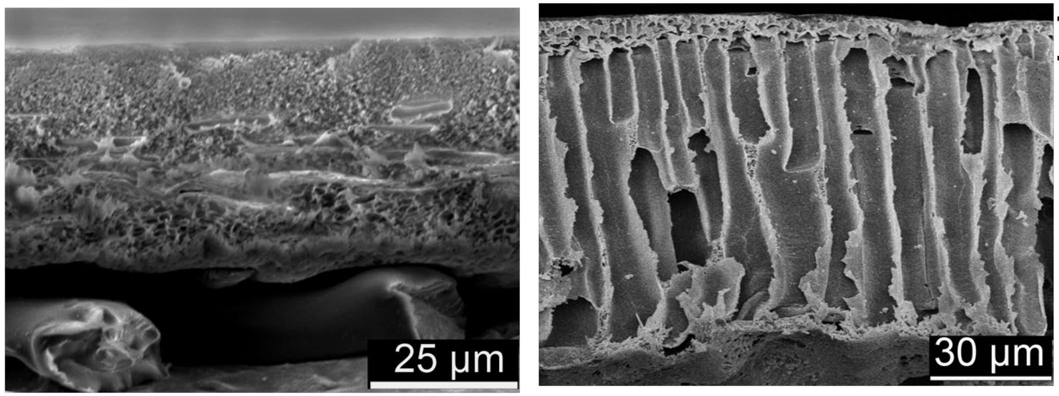
RO membranes



X. Chen, et al., *Desalination* 479 (2020) 114335

TFC-RO

TFC-FO



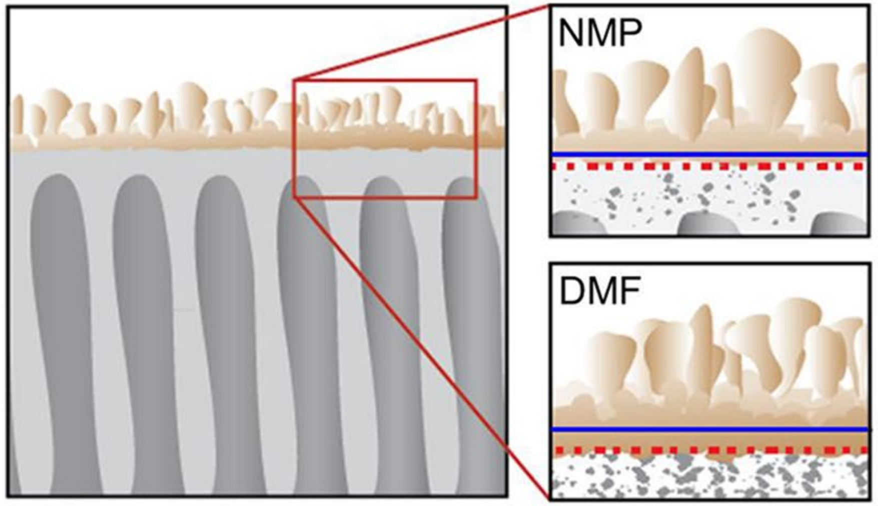
S = 9583 µm

S =492 µm

Yip et al., *Environ. Sci. Technol.*, **44** (2010) 3812–3818.

Active layer of TFC RO membranes ~ 130-300 nm

NMP = 132 ± 28 nm



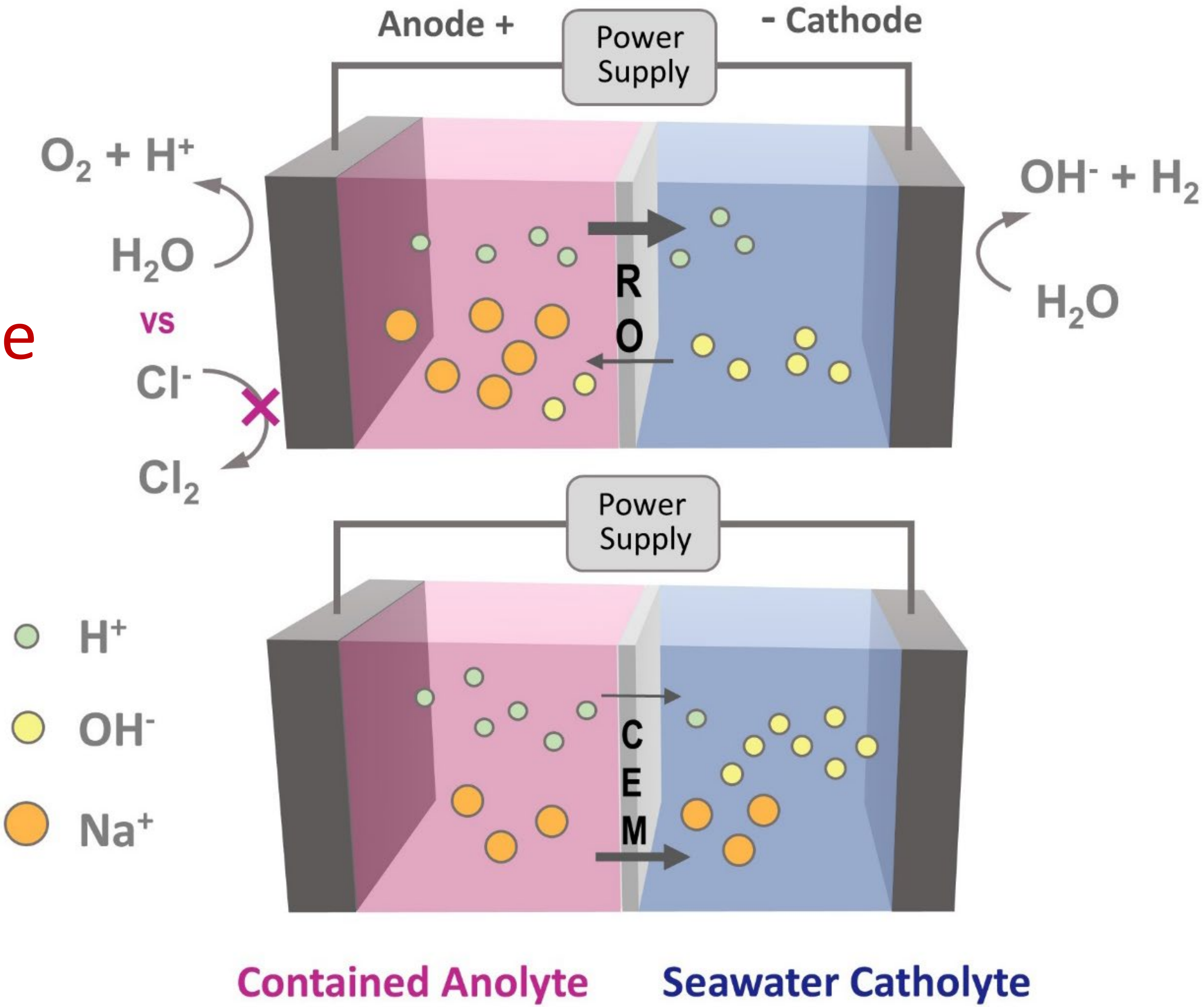
DMF= 171 ± 10 nm

Xinglin Lu, Siamak Nejati, Youngwoo Choo, Chinedum O. Osuji, Jun Ma, Menachem Elimelech. 2015. Elements Provide a Clue: Nanoscale Characterization of Thin-Film Composite Polyamide Membranes. ACS Appl. Mater. Interfaces. 7, 16917−16922

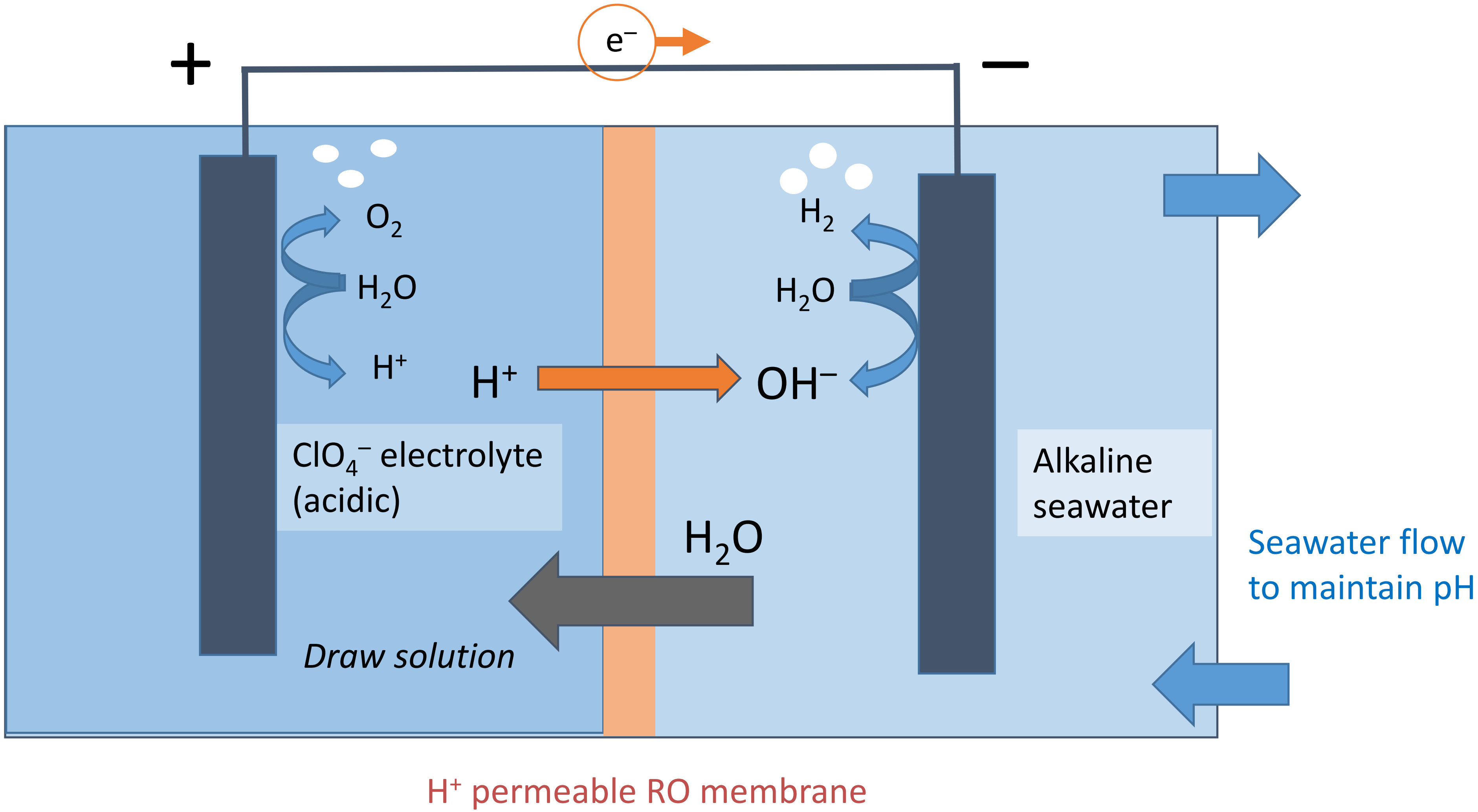
RO

- Low pH anolyte
- Higher pH catholyte (seawater)

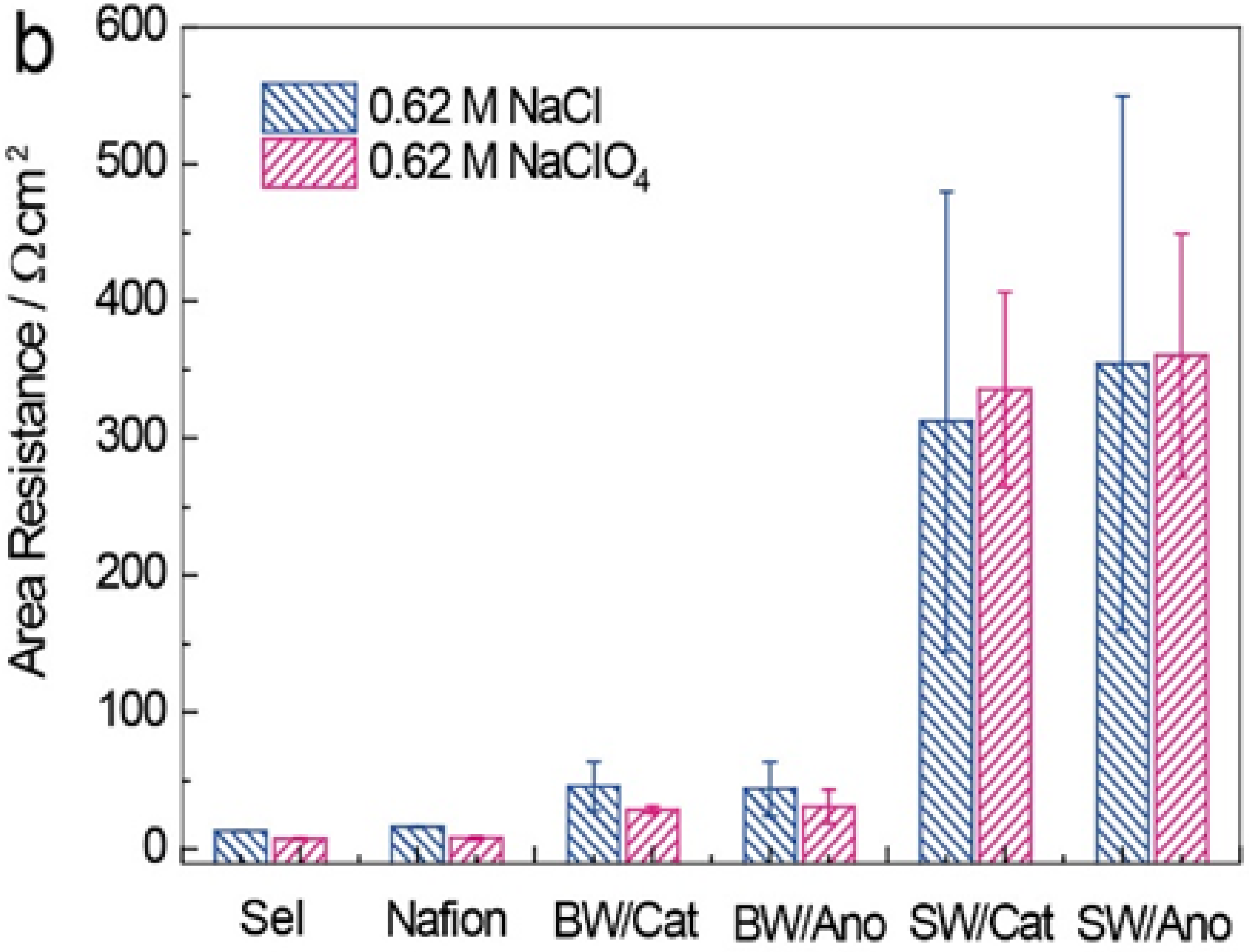
PEM/Acidic

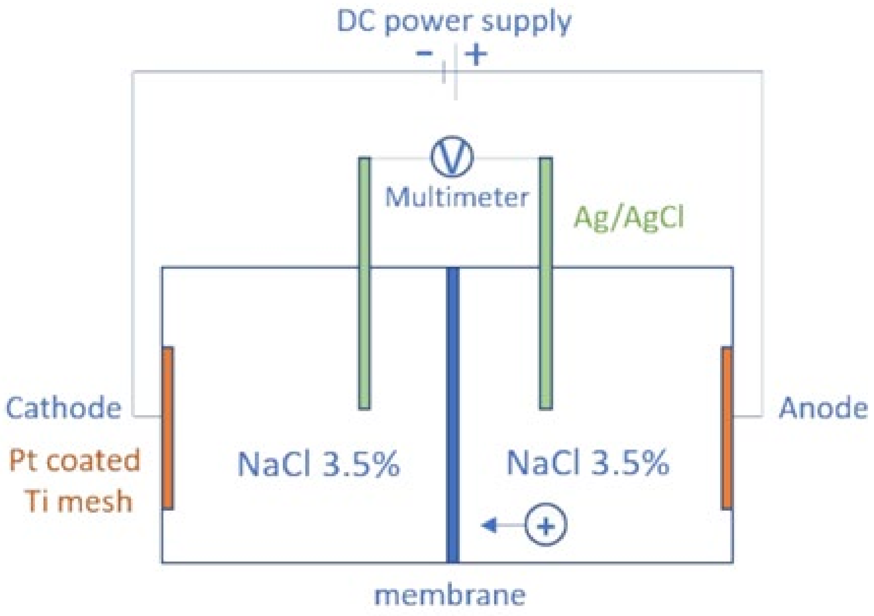


Seawater Electrolysis with a contained anolyte



Area-resistances must be low:
BW-RO membrane vs CEMs (Selemion, Nafion)



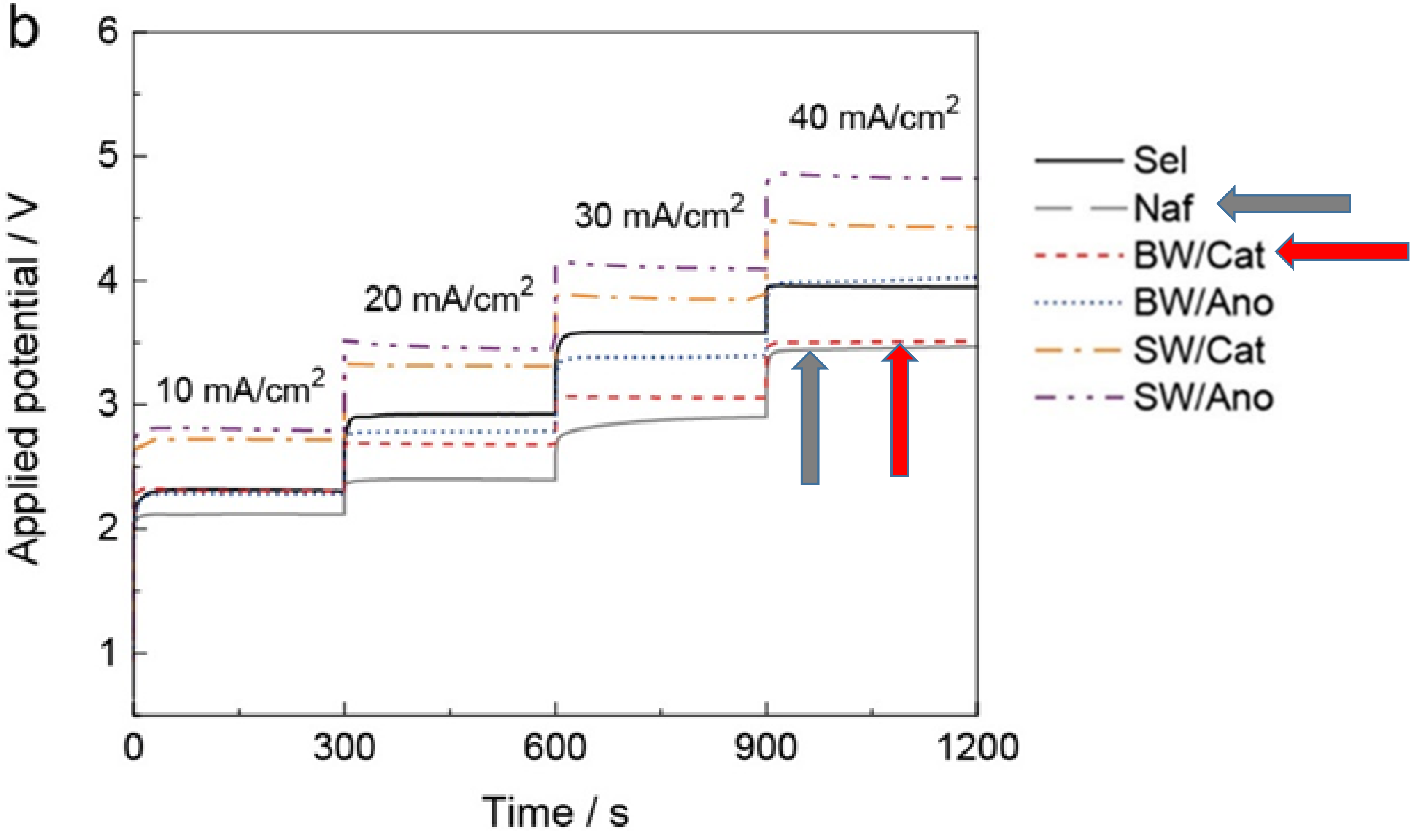


Voltage: $U\ (\mathrm{V}) = I\ \left(\frac{\mathrm{A}}{\mathrm{cm}^2}\right)\ R\ (\Omega\ \mathrm{cm}^2)$

Power: $\mathrm{P}\ \left(\frac{\mathrm{W}}{\mathrm{cm}^2}\right) = I\ \left(\frac{\mathrm{A}}{\mathrm{cm}^2}\right) U\ (\mathrm{V})$

Shi, Rossi, Son, Hall, Hickner, Gorski, Logan (2021) *Energy Env. Sci.*

BW RO membrane can sustain current similar to Nafion (best CEM) with comparable applied voltages



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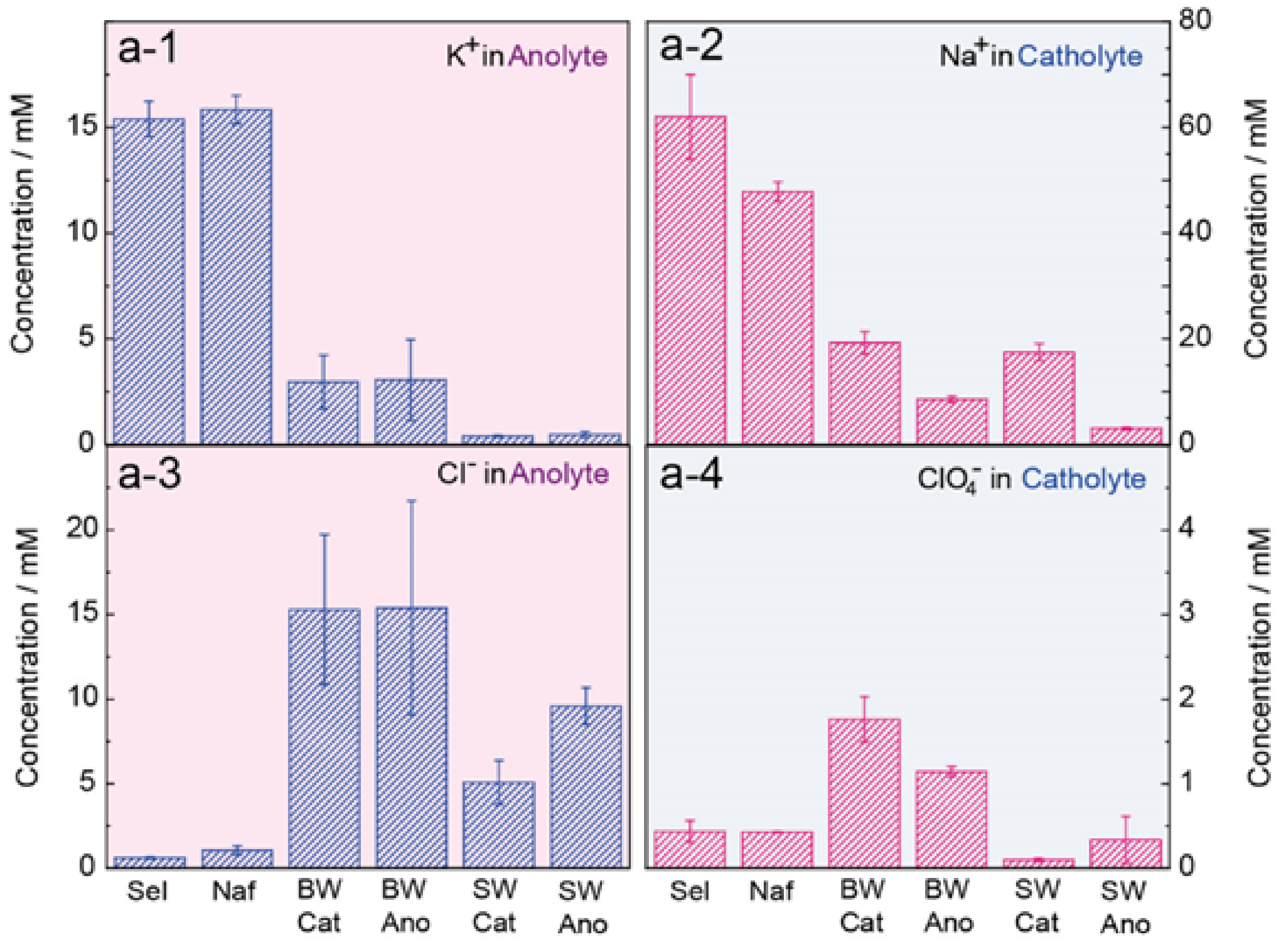
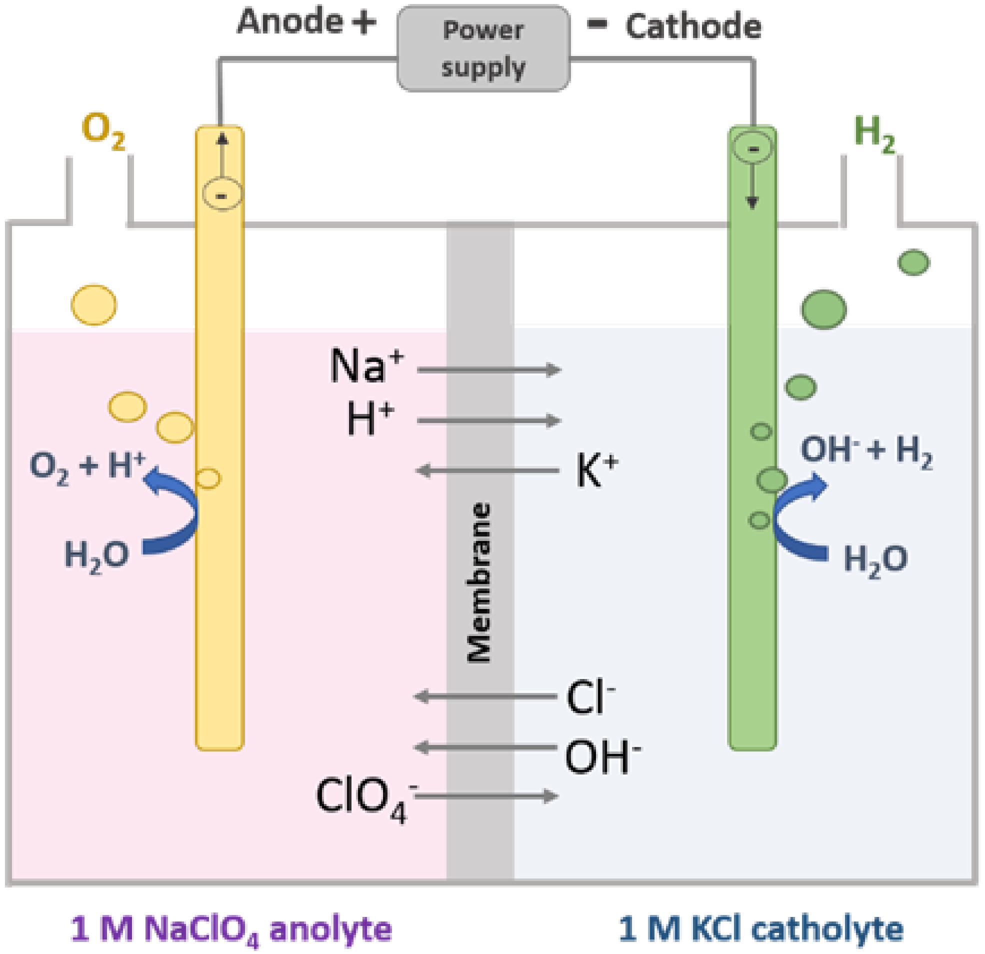
Using different counter ions to measure crossover

Membrane should not have high transport of ions other than H^+ and OH^-



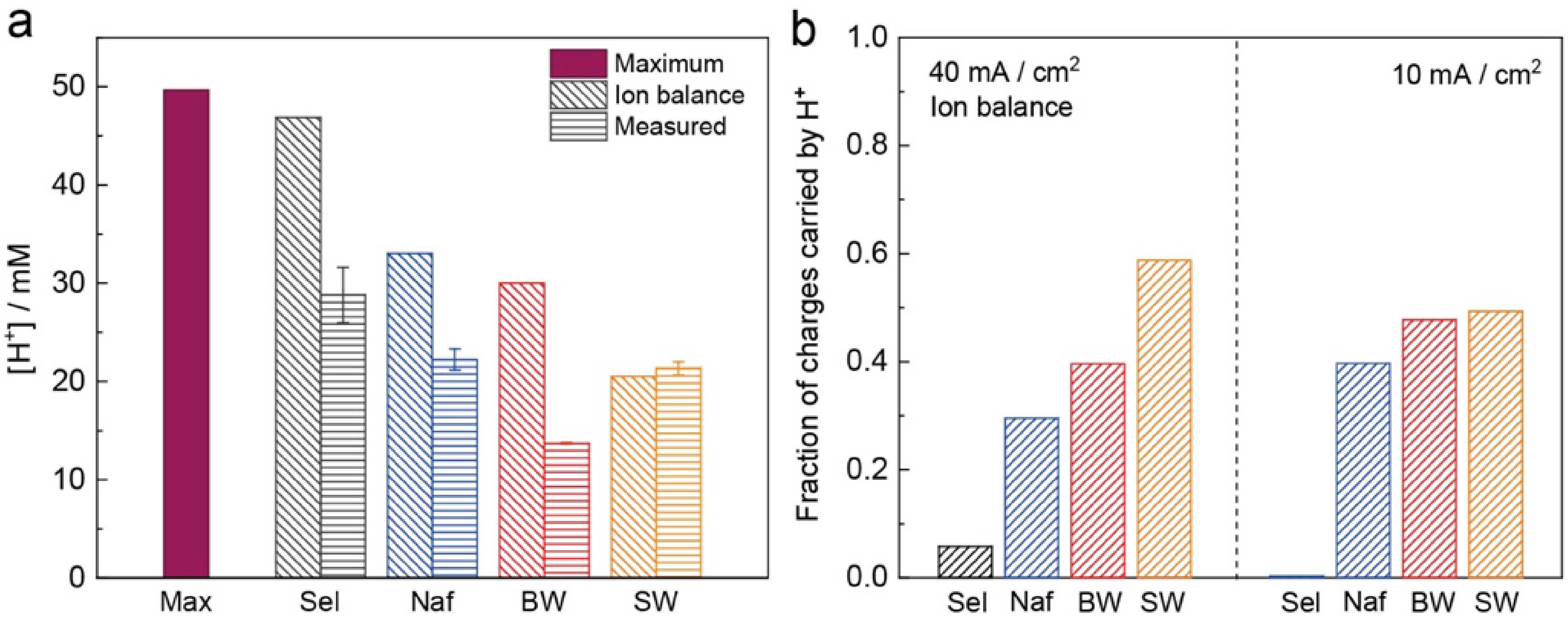


Shi, Rossi, Son, Hall, Hickner, Gorski, Logan (2021) *Energy Env. Sci.*

Comparison of proton transport through membranes to total ion transport

Method: Measure proton concentration (pH) to see how much H+ accumulated versus concentrations of salt ions.

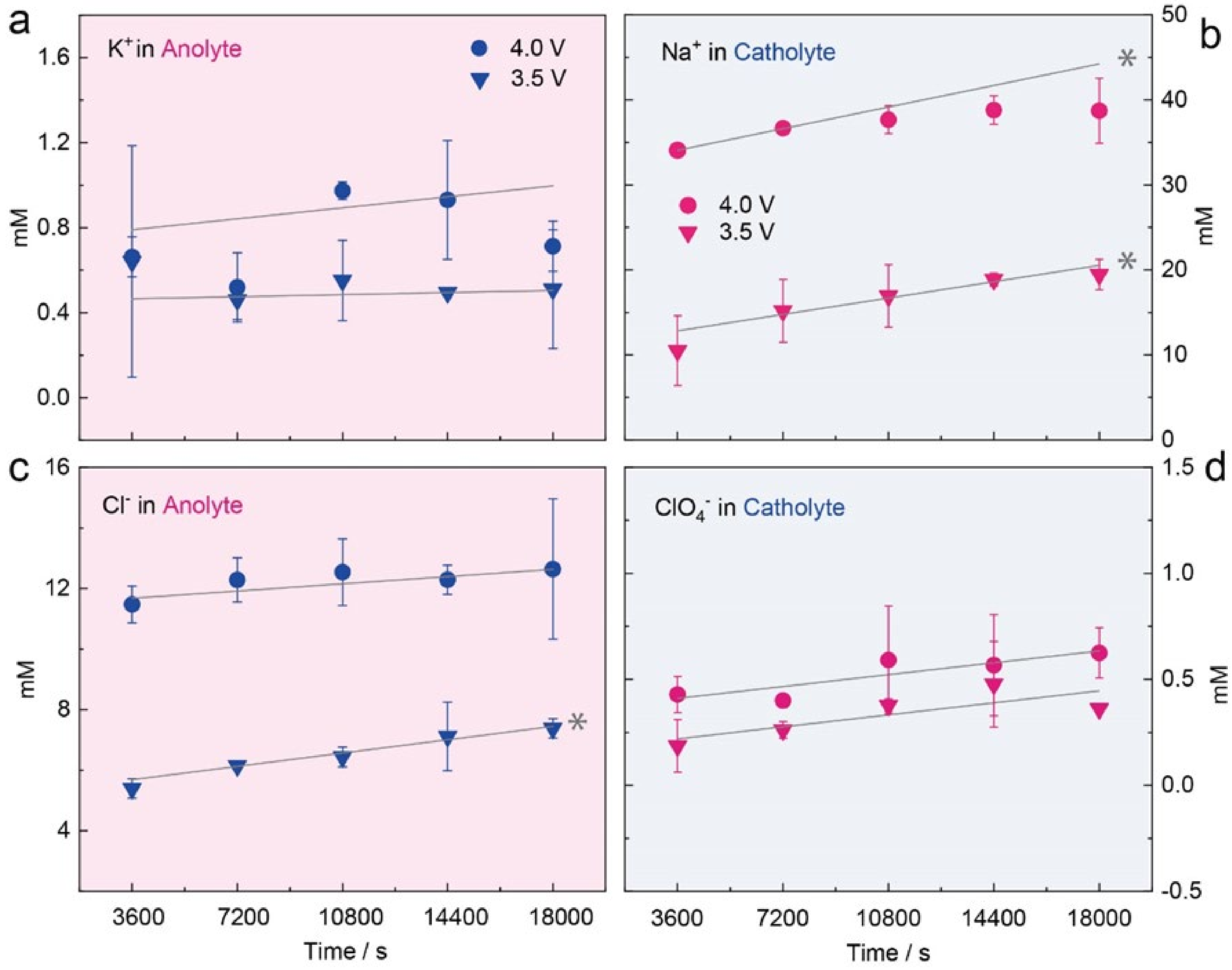
Calculated amount of charge contributed by H^+ compared to other ions.



Shi, Rossi, Son, Hall, Hickner, Gorski, Logan (2021) *Energy Env. Sci.*

Analysis of whether ion transport changes over time

- An increase suggests that the rate of ion transport is increasing.
- That increase could be due to membrane damage



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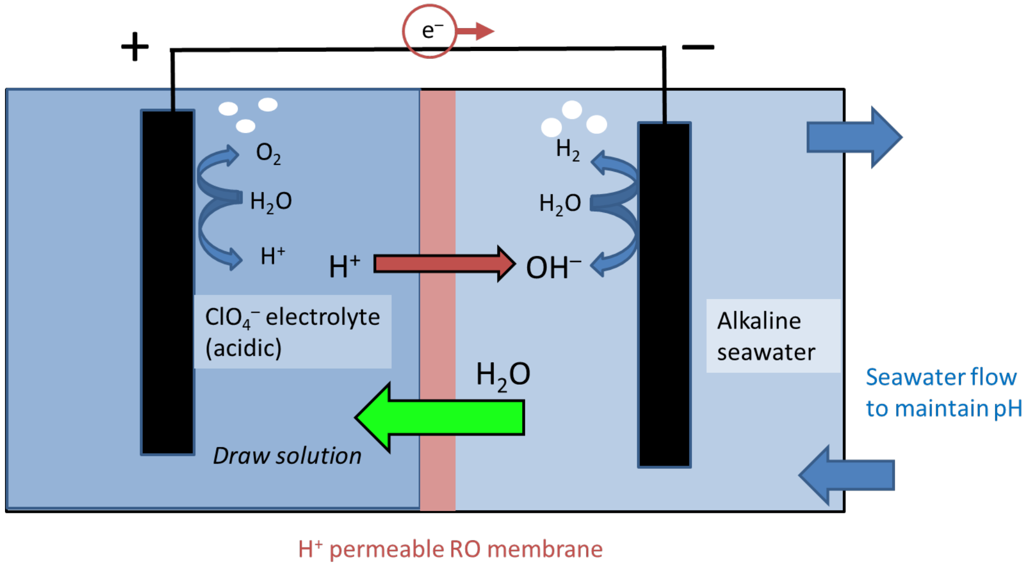
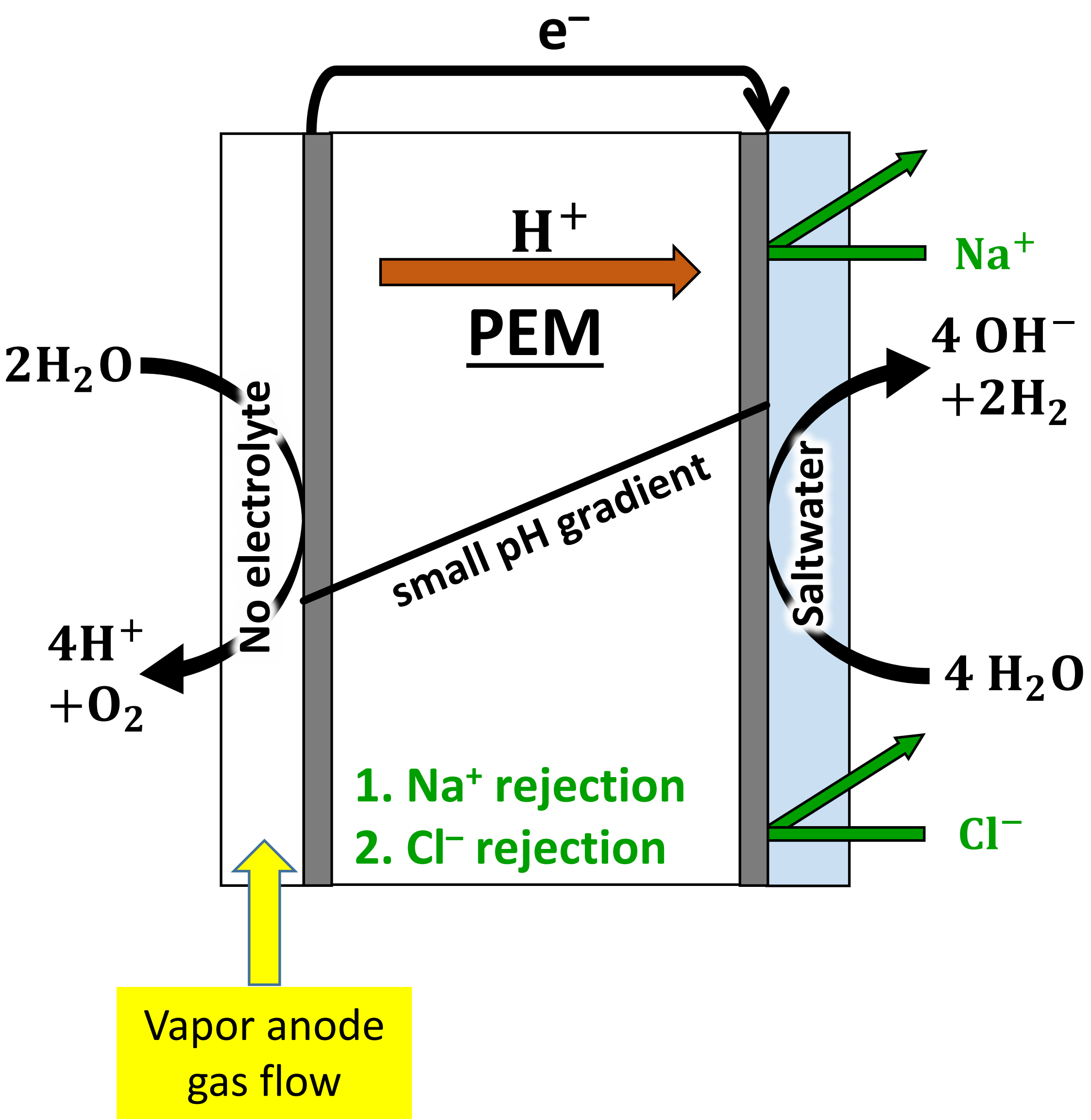
Other Considerations

- Explore inexpensive catalysts:
  - Replace Ir (An) with non-precious metals
- RO membrane has good retention of gases→ pressurized H_2 is important
- Water could be supplied from catholyte to anolyte
  - Pressure: Could adjust pressure to drive water into the anolyte from the catholyte
  - Adjust anolyte concentration to act as a Draw solution (as in Forward Osmosis, FO)



Alternative Water Electrolyzer: Vapor-fed anode



- The PEM rejects the negatively charged Cl^-
- Proton transport is favored to the cathode
- Avoids Na+ ion transport to the anode (no anolyte)

Dr. Ruggero Rossi
Asst. Research Prof. (Penn State)

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Cite this: DOI: 10.1039/d1ee02265b

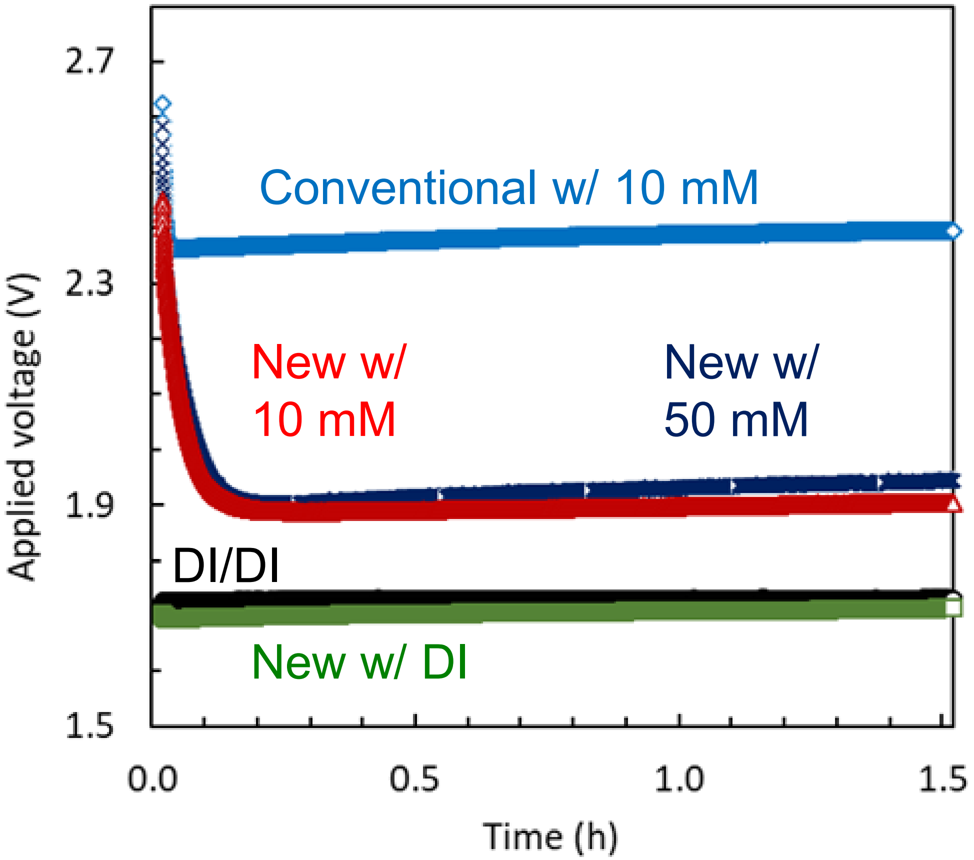
Using a vapor-fed anode and saline catholyte to manage ion transport in a proton exchange membrane electrolyzer†

Ruggero Rossi,[a] Derek M. Hall,[b] Le Shi,[a] Nicholas Cross,[a] Christopher A. Gorski,[a] Michael A. Hickner[c] and Bruce E. Logan[*a]

Rossi, Hall, Shi, Cross, Gorski, Hickner, Logan (2021) *Energy Env. Sci.*

Electrode Overpotentials Using Seawater vs DI

- Costs of ultrapure / deionized (DI) water only part of the H_2 WE Challenge
- Other challenges:
  - Energy use for DI water after RO
  - Brine production
  - Waste production (old modules)
- New approach being developed using CEM membrane, requires low salinity but not DI water



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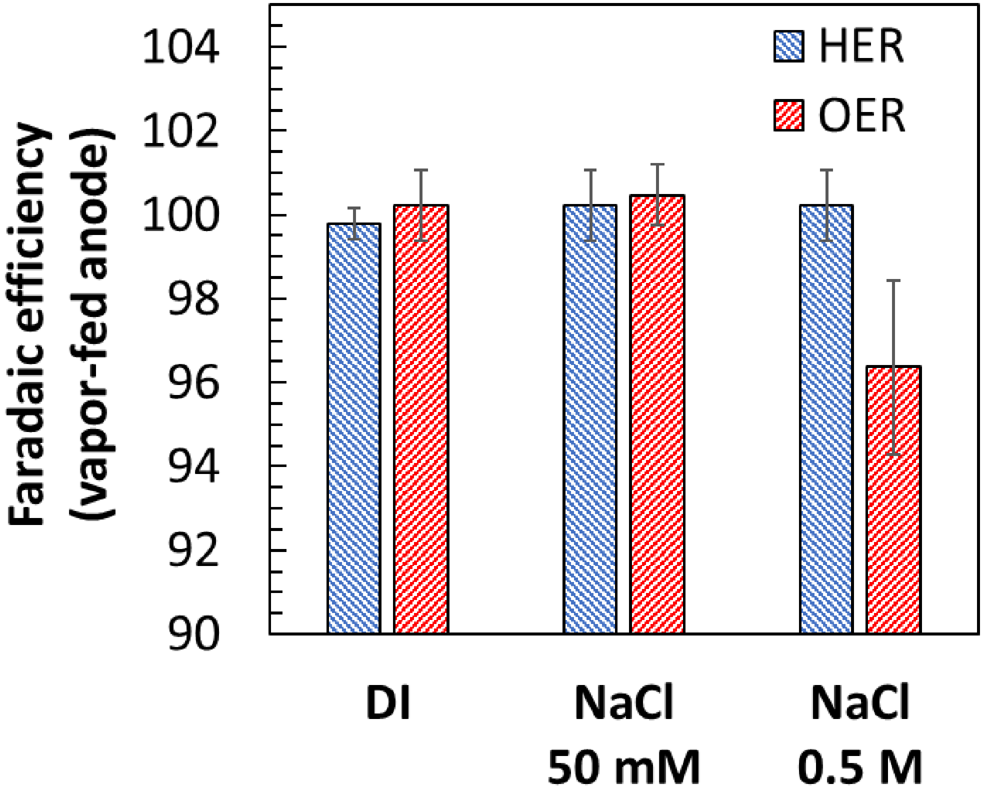
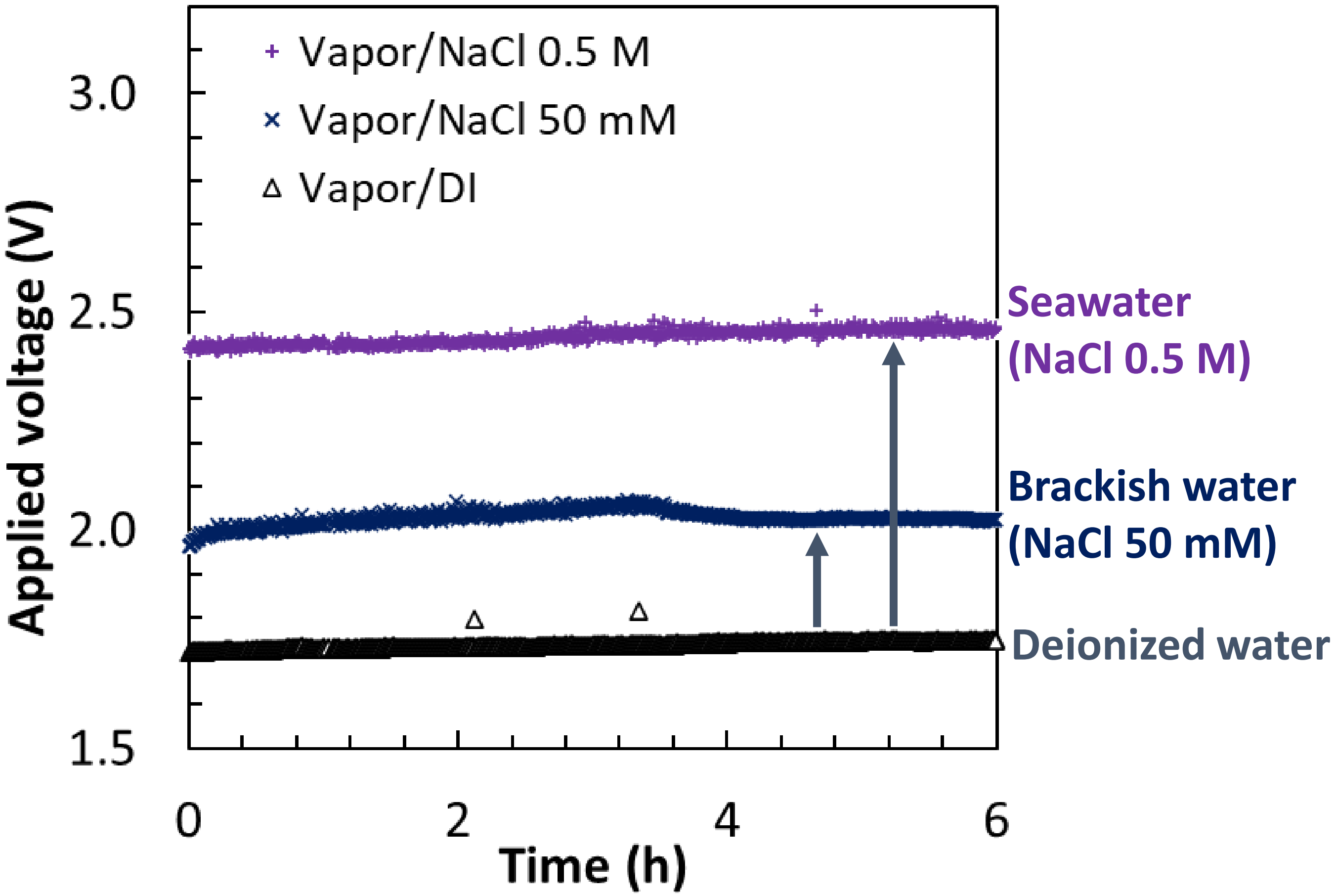
Avoids chlorine evolution with high performance (low overpotential)



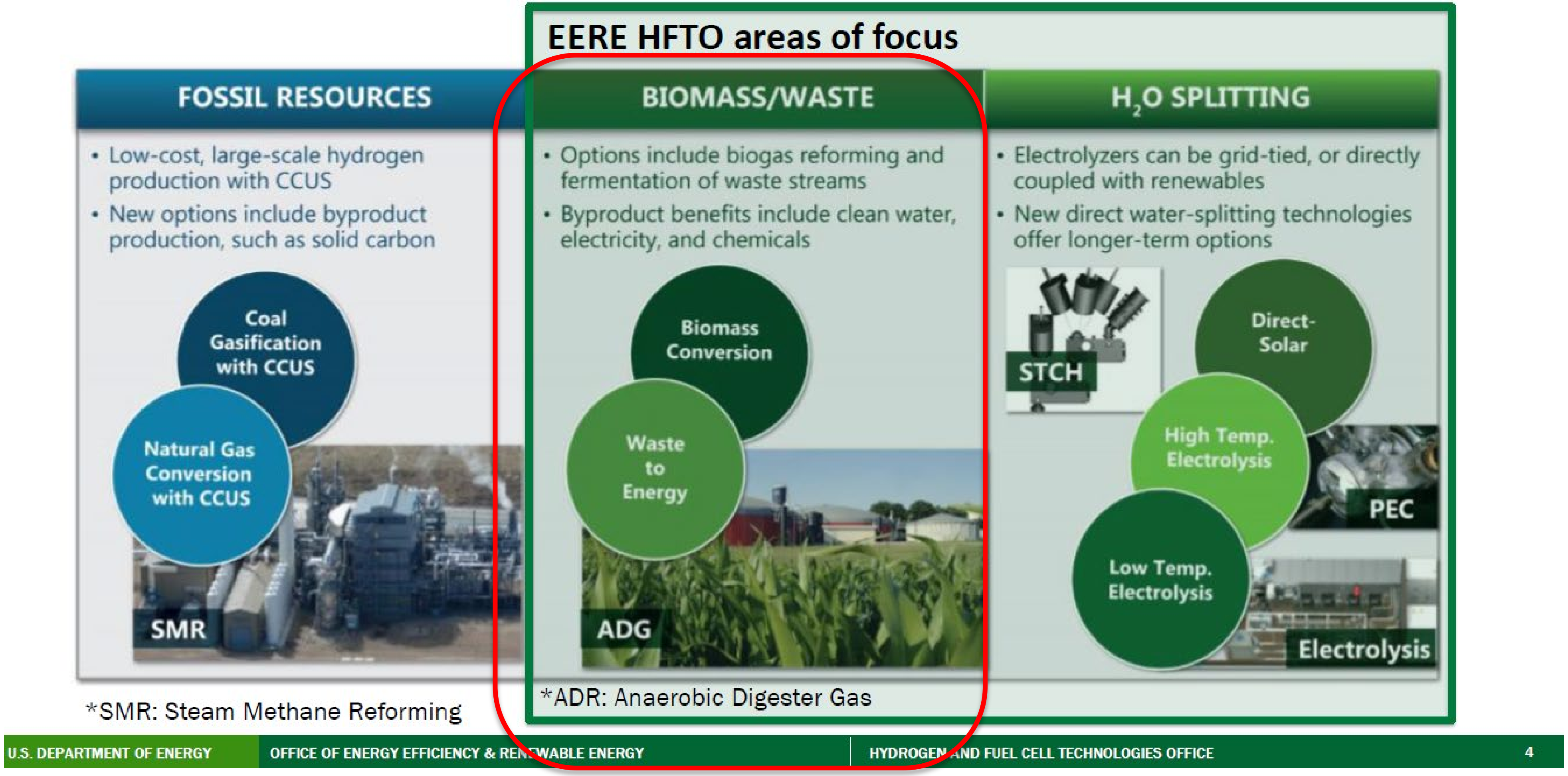
<5% current due to Cl_2 with seawater



Rossi, Hall, Shi, Cross, Gorski, Hickner, Logan (2021) *Energy Env. Sci.*

Relevance to US DOE HFTO and Hydrogen Shot

Portfolio Includes Hydrogen Production from Diverse Sources and Pathways



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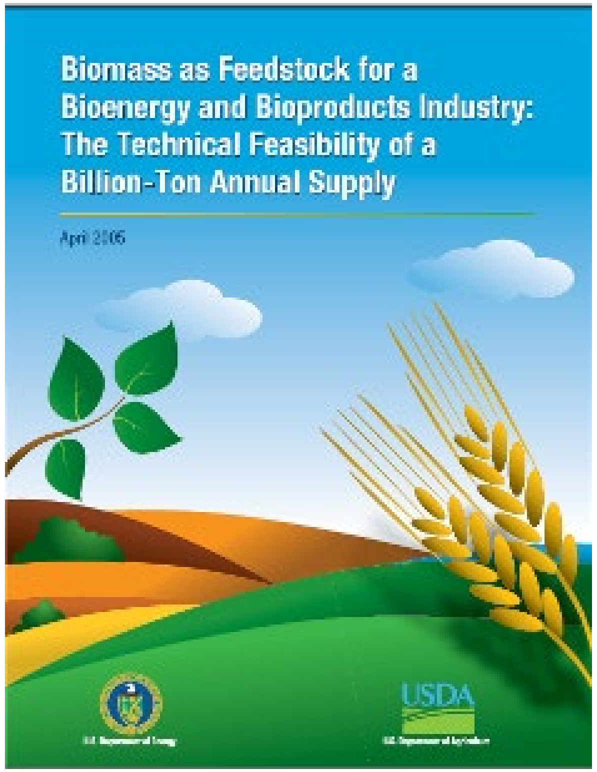
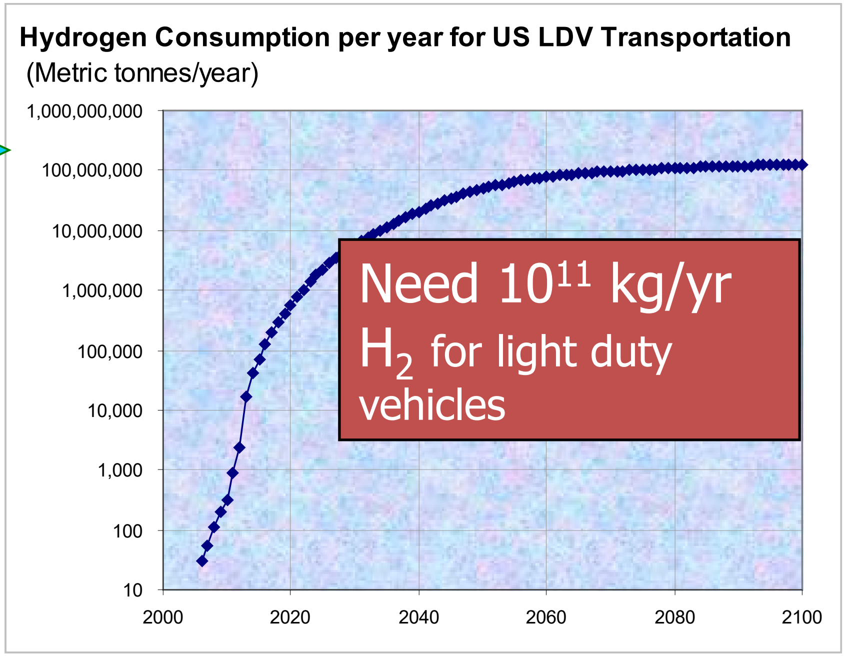
*Sourced from March 11, 2021, Sustainable Energy Council (SEC) World Hydrogen Summit by Dr. Sunita Satyapal

Cellulose to H_2: Getting past the fermentation barrier



In Theory: Cellulose → 12 H_2

1.34/2 billion ton/y of cellulose could produce ~10^{11} kg/yr H_2



The cellulose/biomass "fermentation barrier"

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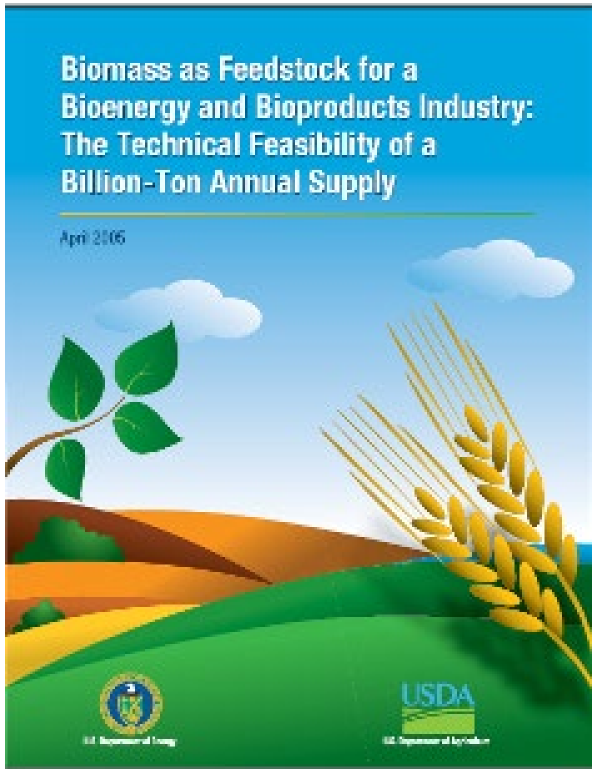
Cellulose to H_2: Getting past the fermentation barrier



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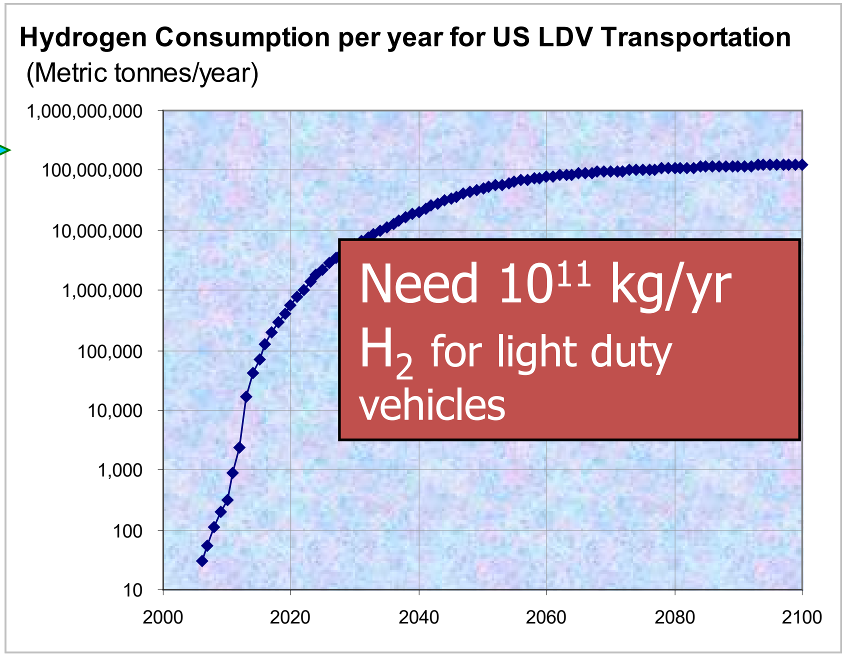

The cellulose/biomass "fermentation barrier"

Cellulose; Wastewaters; *Any biodegradable organic matter*

Fermentation

$$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ C_2H_4O_2 + 2\ CO_2$$

Achieves $\leq$ 4 H_2 (+ 2 Acetate)

Microbial Electrolysis Cells (MECs)

$$2\ C_2H_4O_2 + 2\ H_2O \rightarrow 8\ H_2 + 4\ CO_2$$

Achieves $\leq$ 8H_2 → total possible = 12H_2

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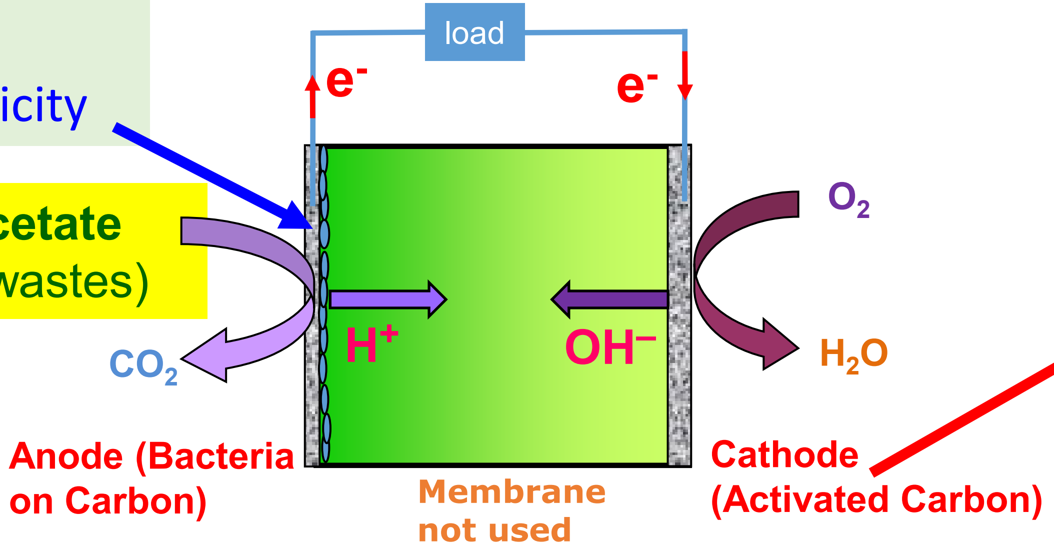
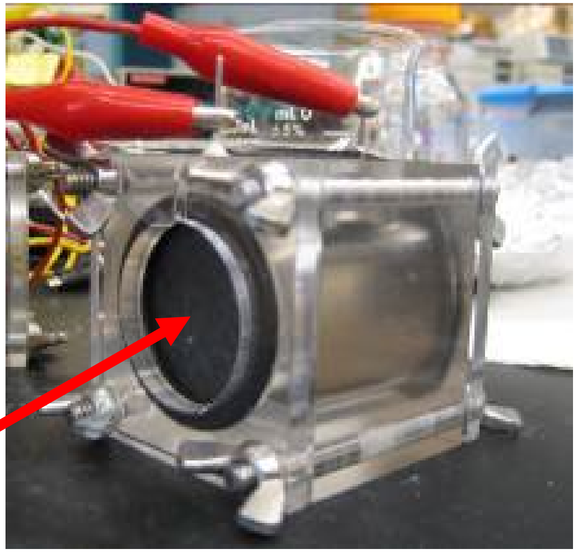
Microbial Fuel Cells (MFCs) make electricity using microorganisms

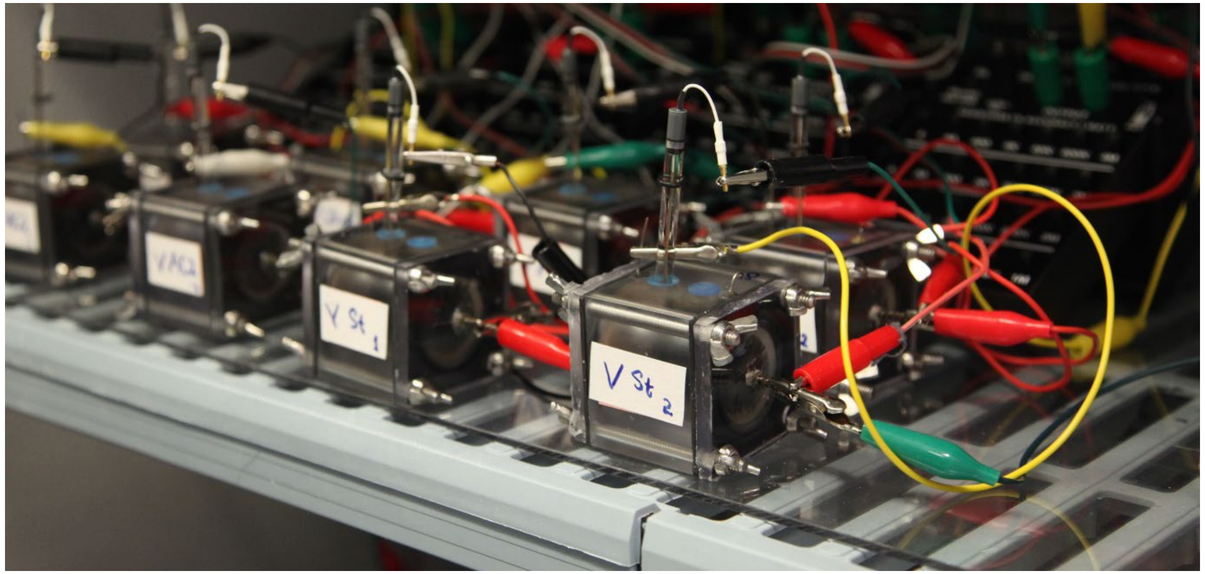
MFCs

Bacteria that produce electricity

Fuel = Acetate
(+organic wastes)







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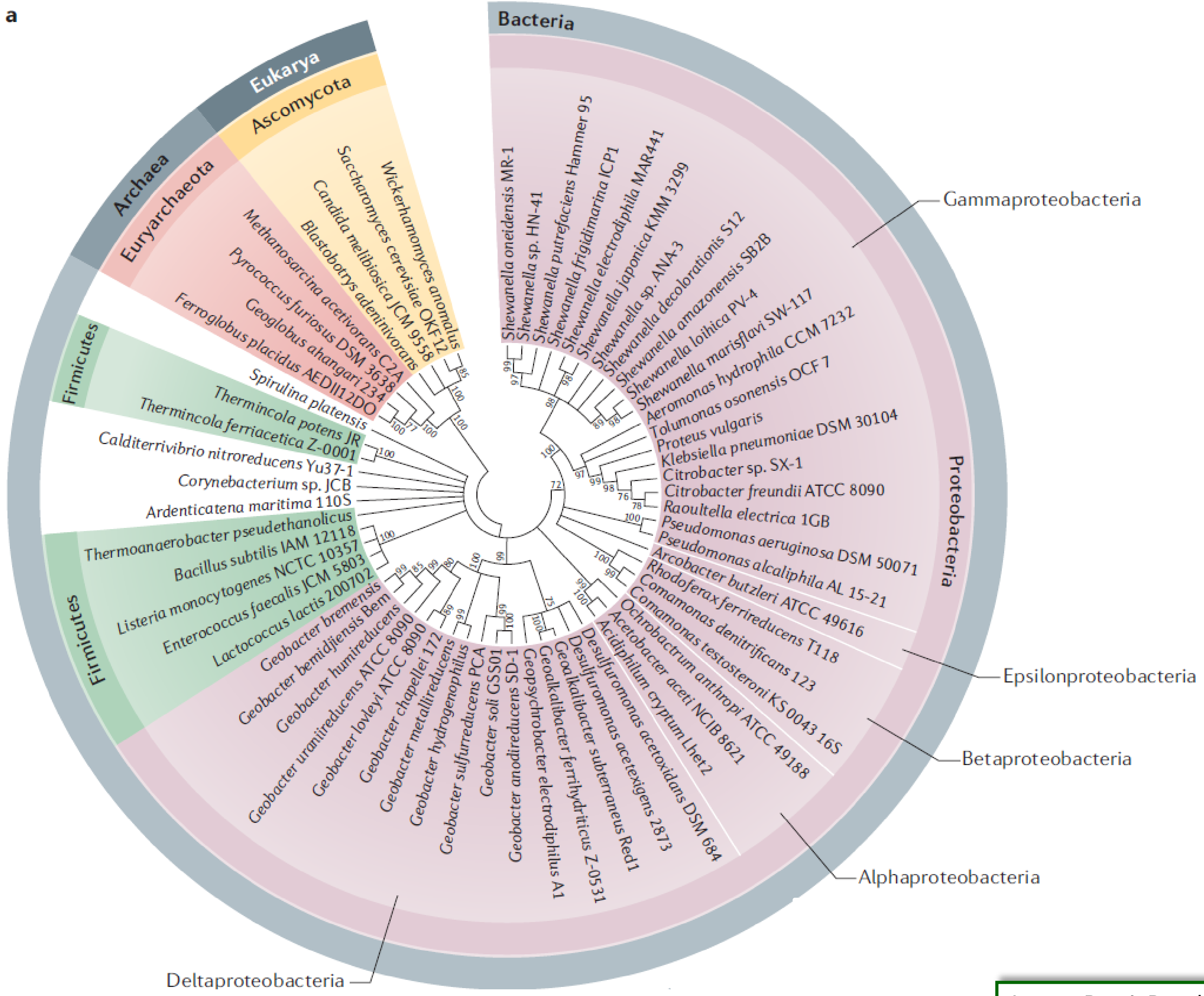
Liu et al. (2004) *Environ. Sci. Technol.*

Exoelectrogenic microorganisms span the 3 domains of life!



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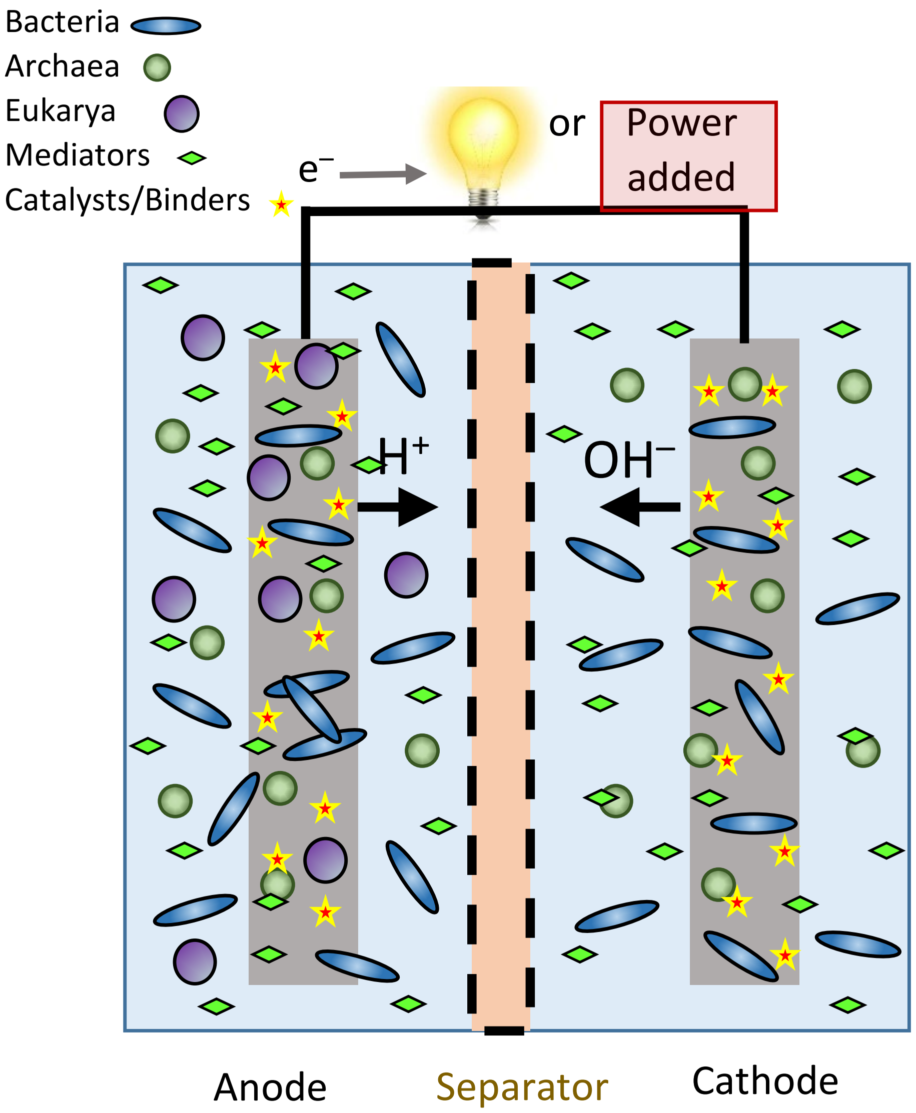
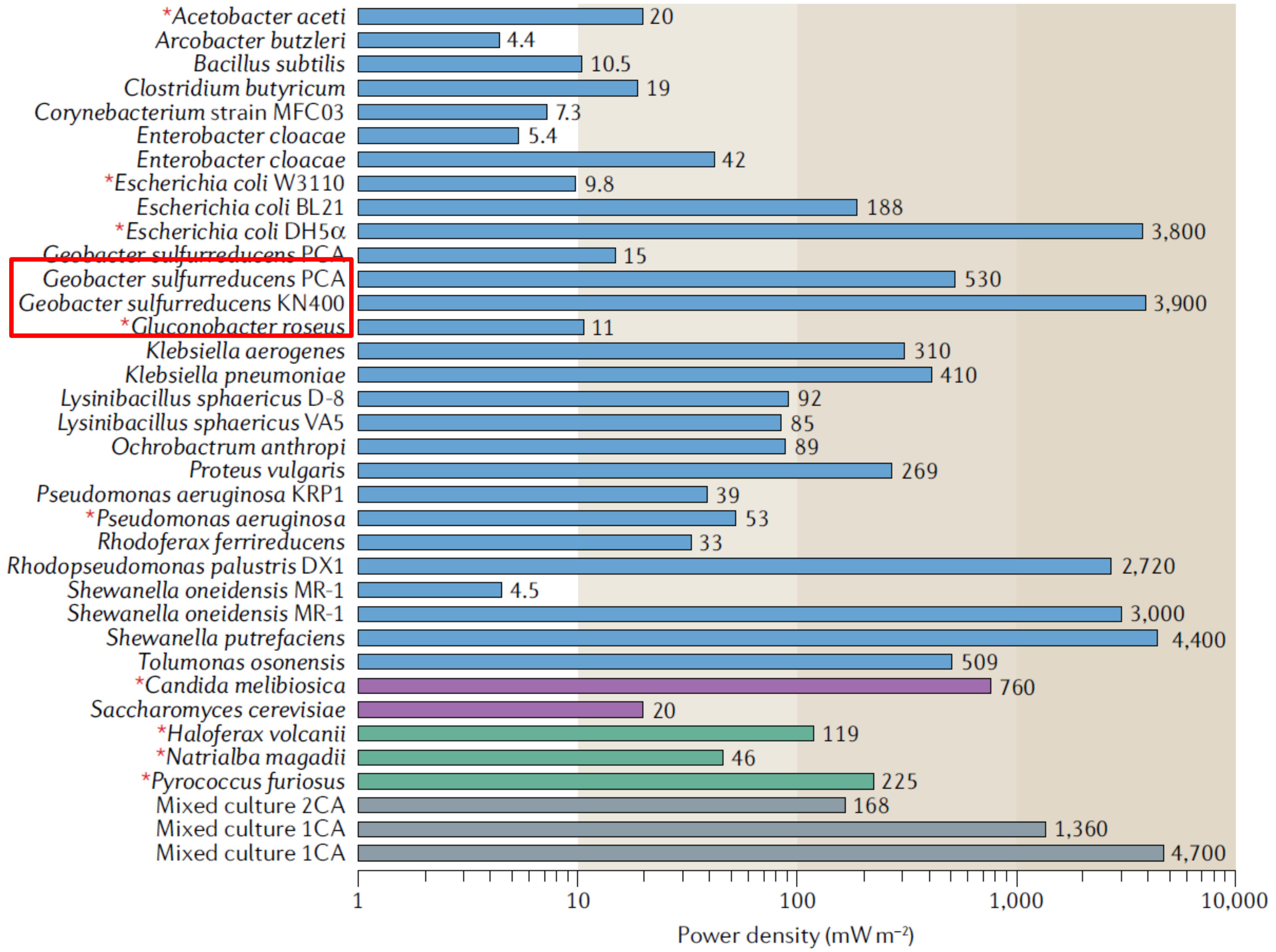
Logan, Rossi, Ragab, Saikaly (2019) *Nature Rev. Microbiol.*

What microorganisms produce current = exoelectrogenic?



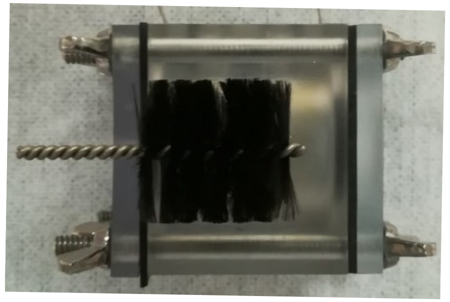


Logan, Rossi, Ragab, Saikaly (2019) *Nature Rev. Microbiol.*

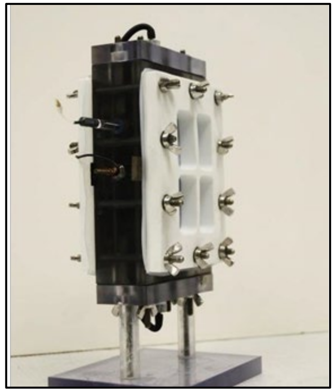
Scaling up MFCs: from laboratory to pilot scale

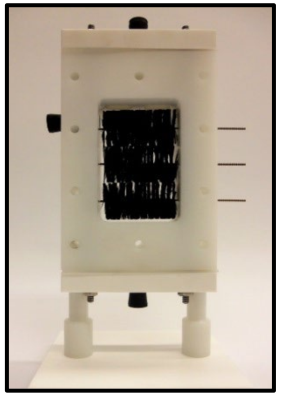
MFCs

Gen 0: 0.025 L, 25 m^2/m^3

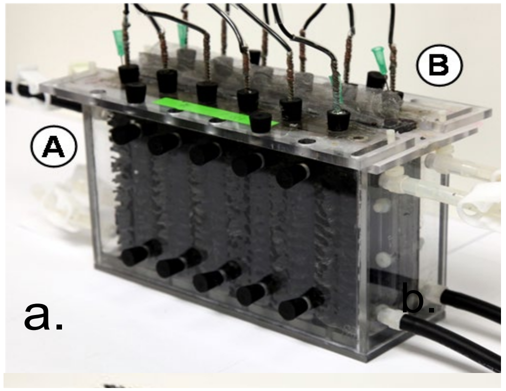


Gen 1: 0.13 L, 25 m^2/m^3

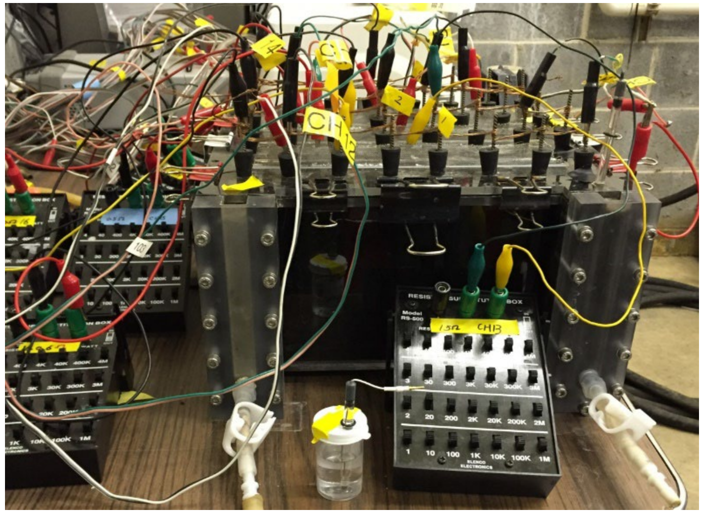




Gen 2: 2 L, 20 m^2/m^3

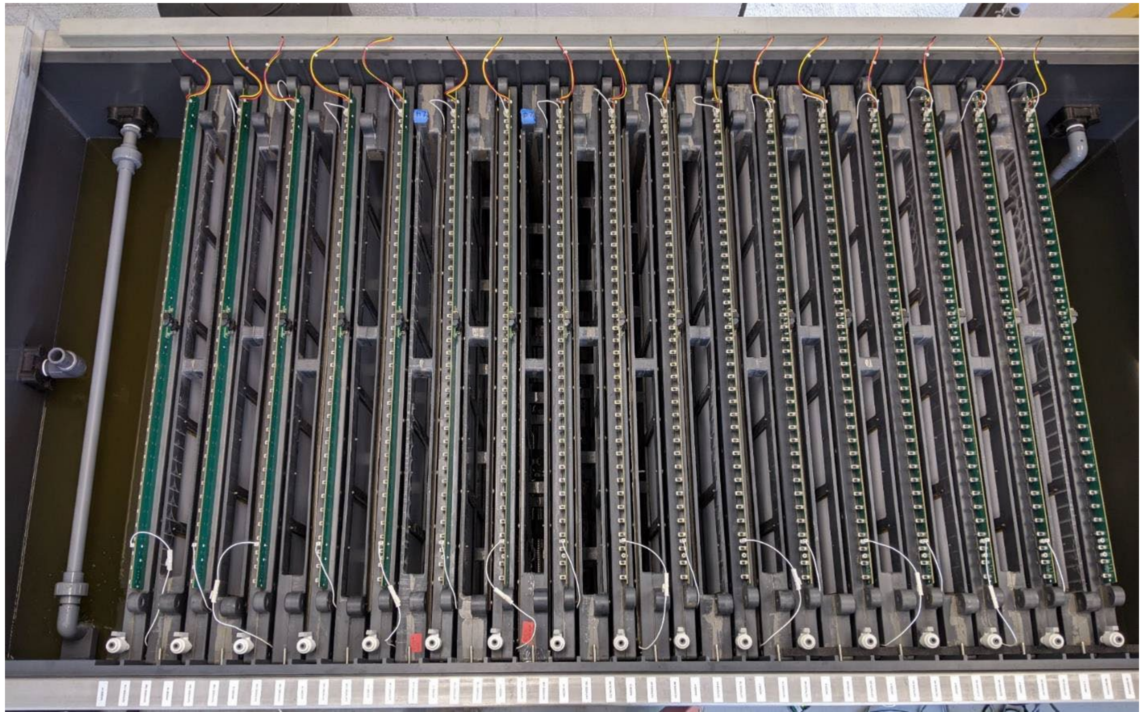


Gen 3: 6.1 L, 20 m^2/m^3



Pilot-Scale MFC:

850 L active volume, 25 m^2/m^3



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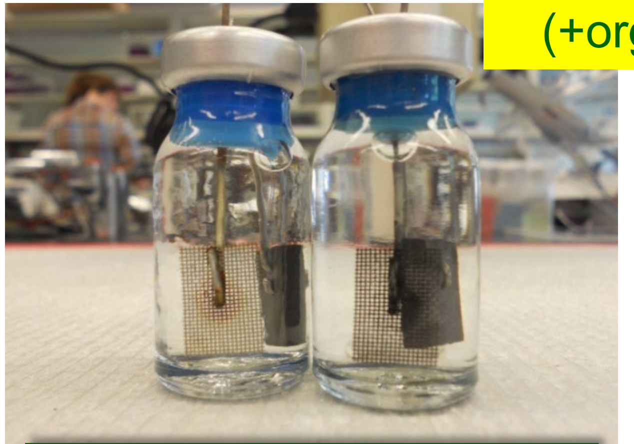
Microbial Electrolysis Cells (MECs) produce H_2

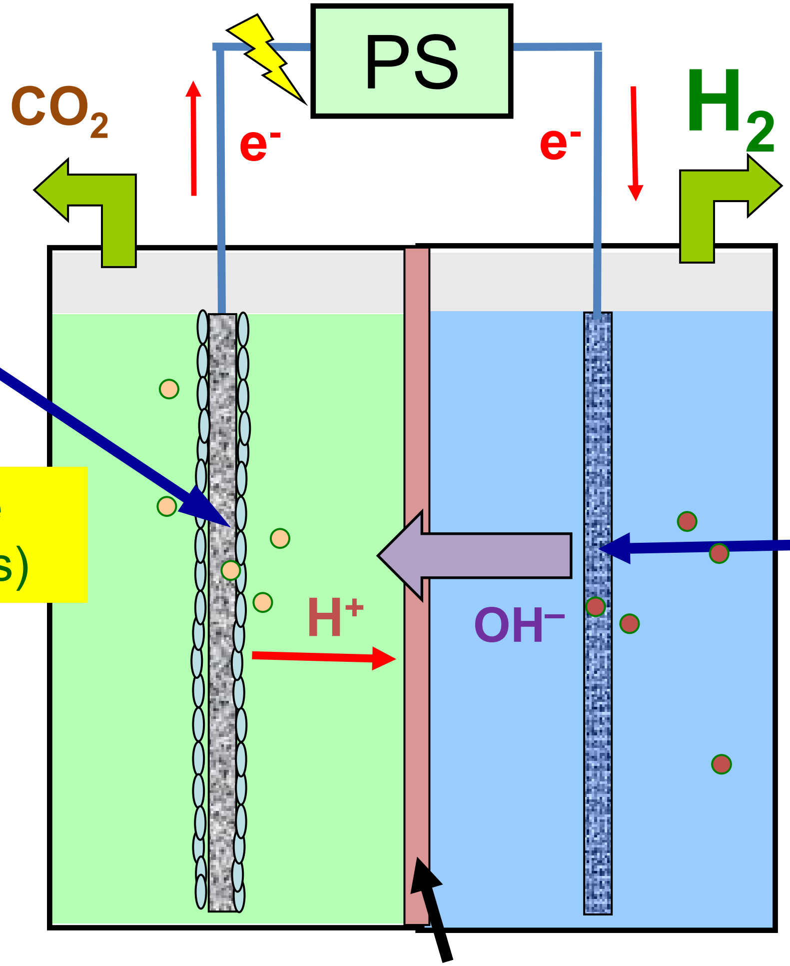
MECs



Call & Logan (2011) *Biosen. Bioelectron.*

Fuel = Acetate
(+organic wastes)

Bacteria (bioanode)



Need >0.11 V
(vs 1.2-1.8 V for water electrolysis)

Cathode
(Pt/Ni/SS catalysts)

No oxygen in cathode chamber

Membrane

Liu, Grot & Logan (2008) *Environ. Sci. Technol.*

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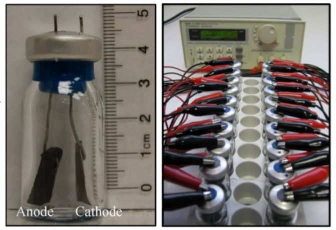
Scaling up MECs: from laboratory to pilot scale: Part I

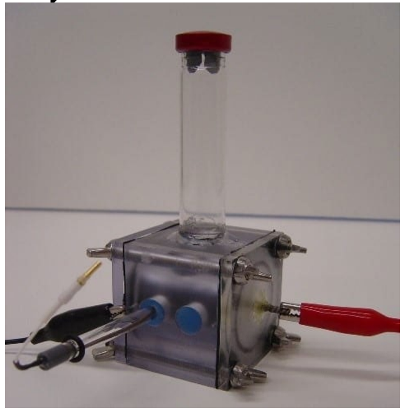
MECs

Single-Chamber MECs: $H_2 \rightarrow CH_4$

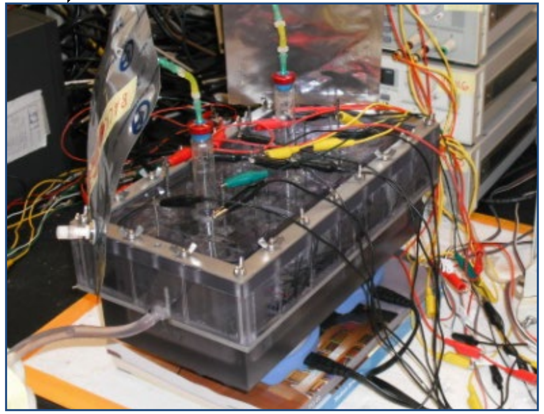
5 mL mini-MEC



28 mL MEC

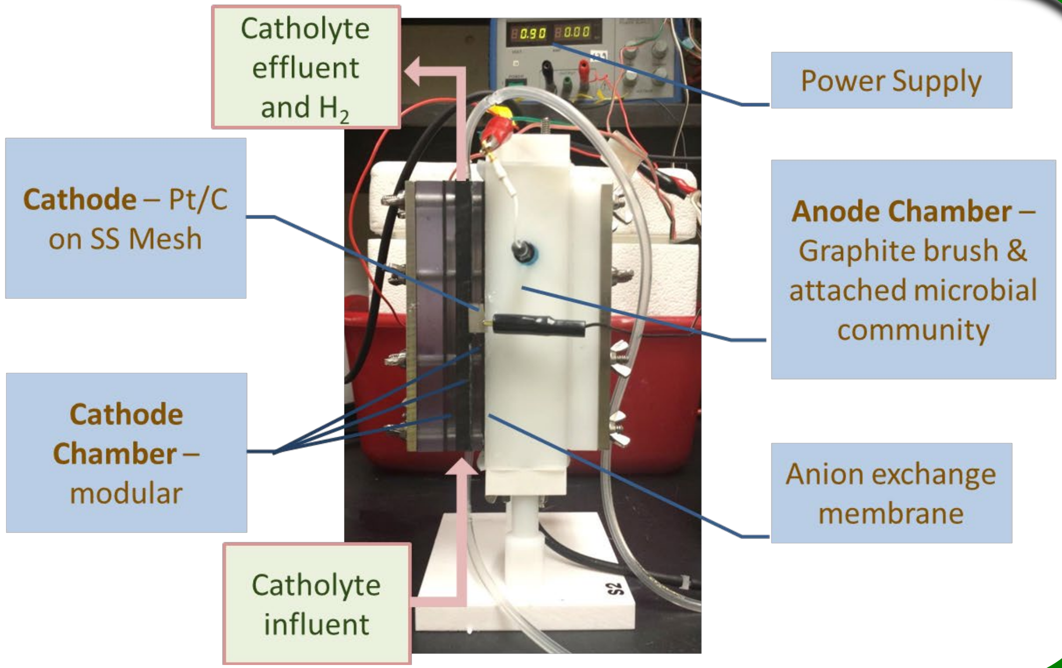


2.5 L MEC



1000 L MEC

Two-Chamber MECs: H_2 recovery



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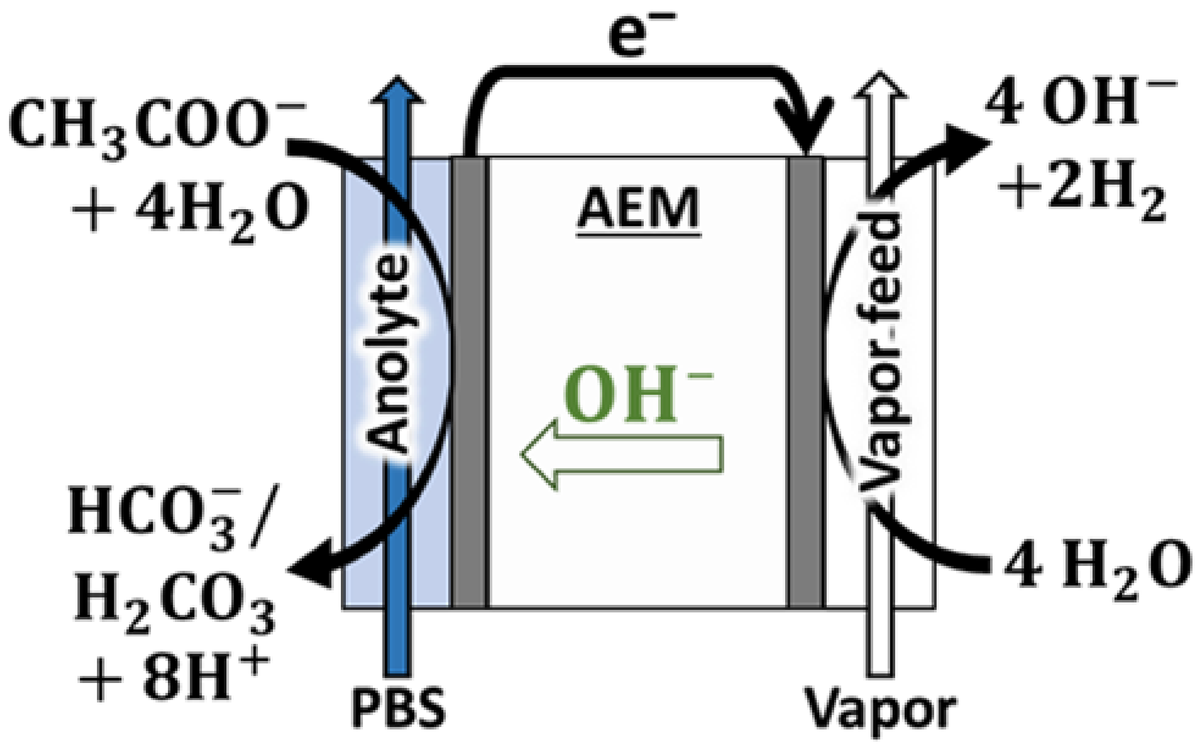
Scaling up MECs: Increasing current and H_2 production rates

NEW Approach: Zero-gap electrode spacing, Vapor-fed cathode

- **No catholyte = no anions other than OH^-**
- AEM facilitates only OH^- transport from catholyte to anolyte
- pH of anode is stabilized

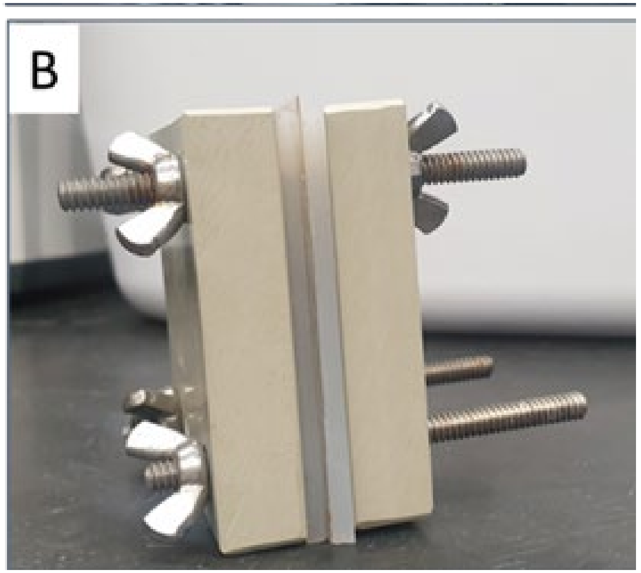


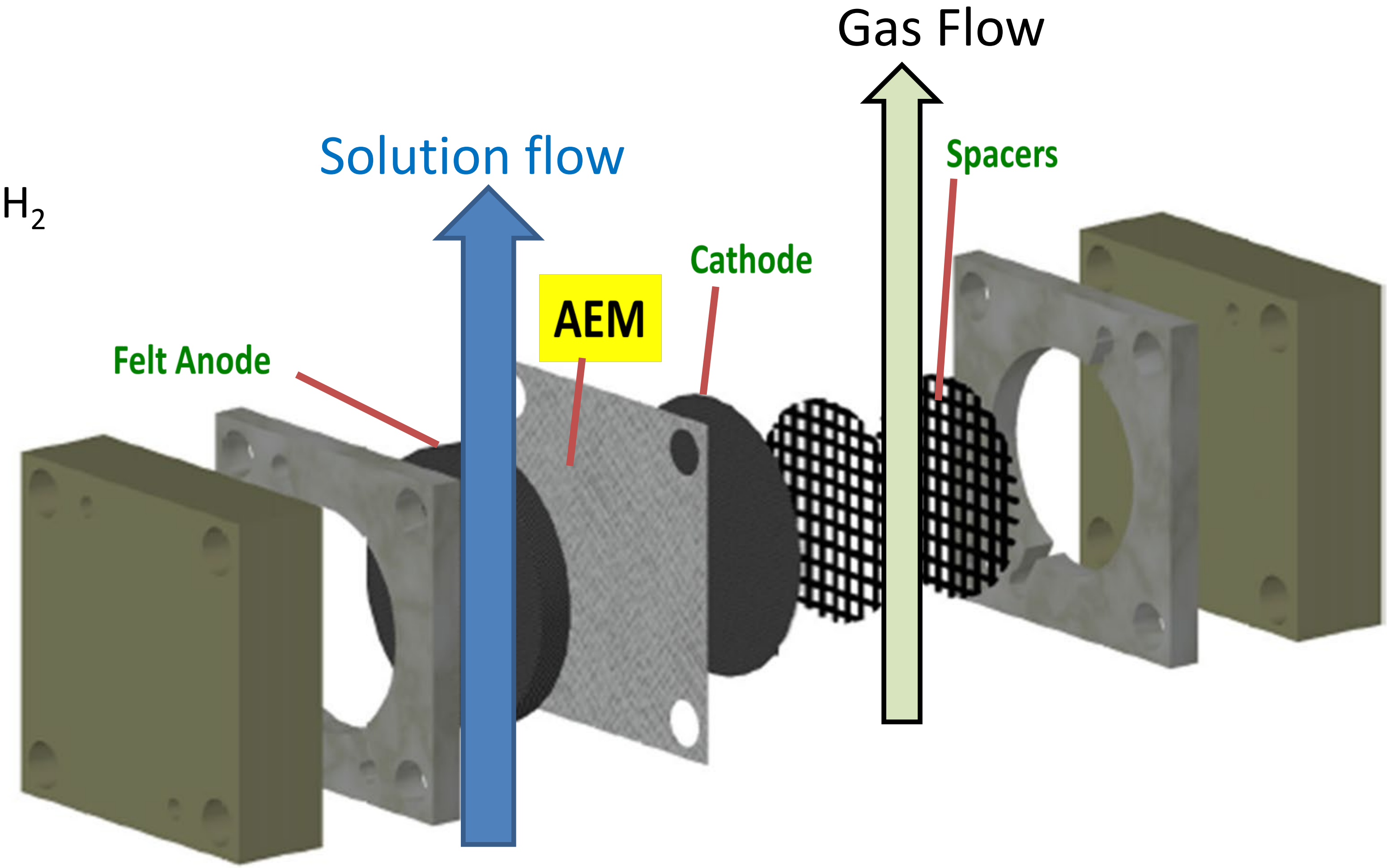
Bacteria on the anode produce current (need neutral pH)

Rossi, Baek, Logan (2022) *Environ. Sci. Technol.*

New type of MEC: Zero gap, gas vapor catholyte

- Electrolyte flow through the anode (carbon felt)
- Anode pressed against the AEM
- AEM pressed against cathode
  (MEA configuration)
- Humidified gas flow past cathode→ H_2



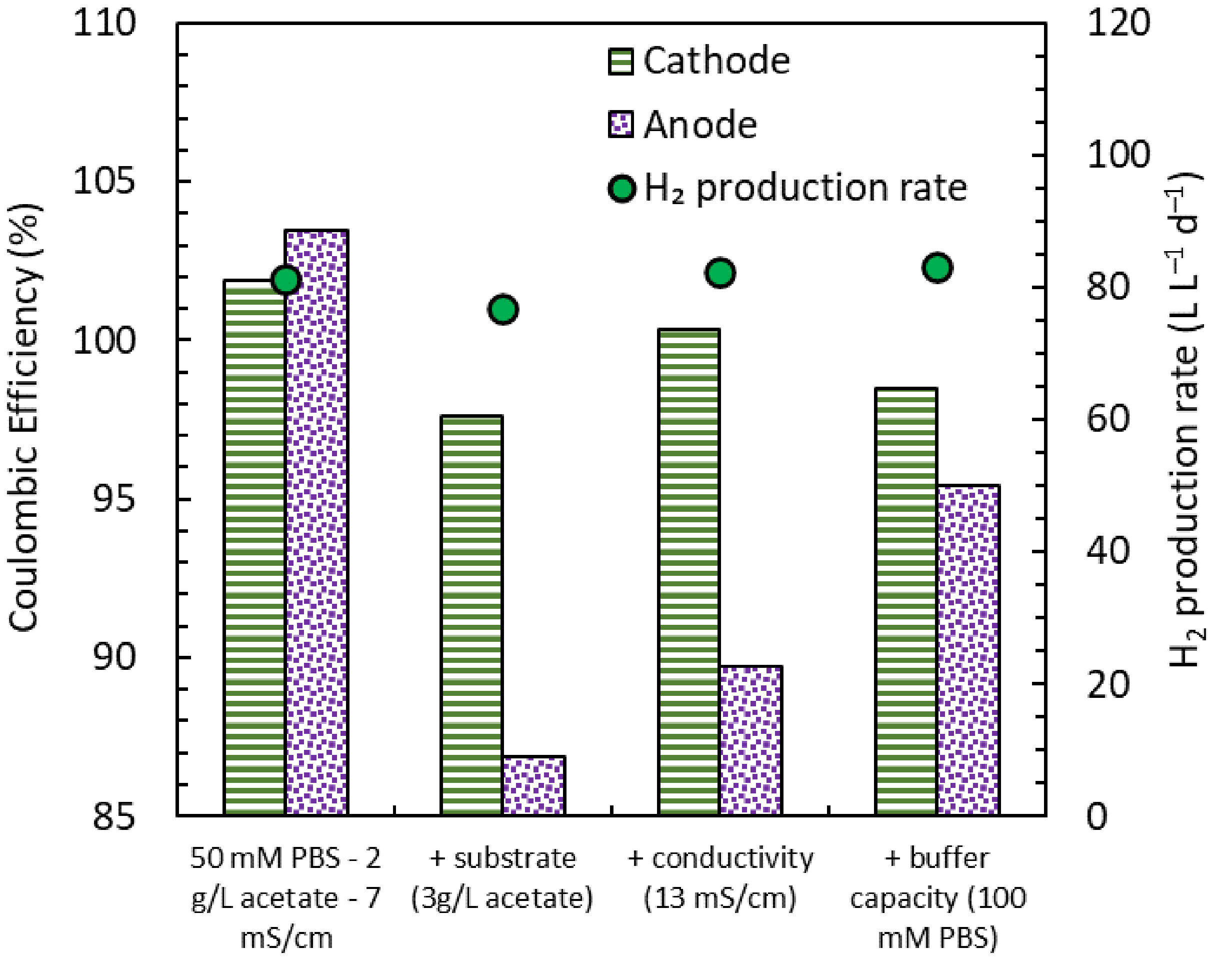


Rossi, Baek, Logan (2022) *Environ. Sci. Technol.*

Scaling up MECs: Increasing current and H_2 production rates

MEC results: 17x increase in performance with Pt cathode, Acetate, PBS:

- 42 A/m^2-d (versus 5 A/m^2)
- 63 L/L-d (versus ~3.8 L/L-d)
- <u>Highest H_2 production rate achieved under these solution conditions</u>



Rossi, Baek, Logan (2022) *Environ. Sci. Technol.*

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Why use biomass (electrolyzers) to achieve $1H$_2$/kg?

- **Water electrolyzers** require 2 steps
  - Water purification (reverse osmosis + deionization)
  - Electrolyzer operation using electrical power
- Electricity use is high
  - Minimum of electrical energy for water splitting is 33 kWh/kg H_2 (thermodynamics)
- $1 kg H_2 requires for electricity:
  - $0.03/kWh for electricity (thermodynamic limit)
  - $0.02/kWh considering current efficiencies (70%)
- Precious metals may be required.
  - PEM uses Ir, Pt; AEM does not (Ni-based)
- Small, compact reactors, high electricity demand

- **Biomass** (with electrolyzers) requires 2 steps
  - Biomass fermentation
    - Fermentation is spontaneous, so no energy input needed during process (neglecting reactor stirring, pumps)
    - Produces 4 moles H_2 per cellulose (of maximum = 12)
  - Microbial electrolysis Cells (MECs)
    - Minimum electrical energy is only 1/10th electrical energy compared to water electrolyzers
- $1 kg H_2 requires for electricity
  - $0.30/kWh for electricity (thermodynamic limit) for 8/12 moles of H_2
  - $0.45/kWh for 12/12 moles of H_2.
- Precious metals not required.
- Large reactors used, need transport of biomass, low electricity demand

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Final Thoughts: Energy, Environment & Climate Change

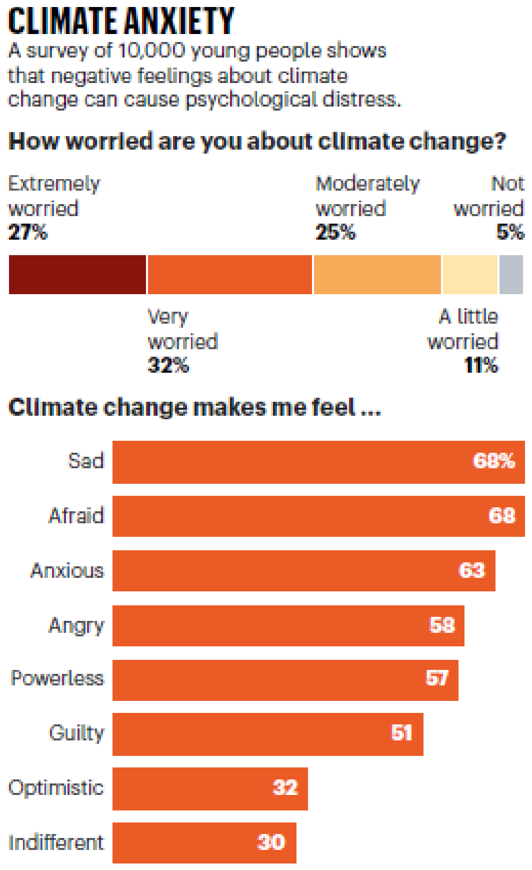
16-25 years old

YOUNG PEOPLE'S CLIMATE ANXIETY REVEALED IN LANDMARK SURVEY

Children worldwide worry about the future and feel let down by governments.

ost commonly chosen were 'sad', 'afraid', nxious', 'angry' and 'powerless' (see 'Climate nxiety'). Overall, 45% of participants said their elings about climate change affected their aily lives.

The countries with the highest proportion f respondents who felt 'very worried' or xtremely worried' by climate change were e Philippines (84%), India (68%) and Brazil 7%), nations that have been hit hard by imate change. Portugal – where wildfires re becoming increasingly severe – had the ghest level of very worried or extremely wor-ed respondents (65%) out of the high-income ountries surveyed, which included France, nland, Australia and the United States.



feelings about climate change had negatively affected their daily life.

Not just energy: Need to address **All Gases + LUC**

Land Use, Land-Use Change and Forestry (LULUCF): A greenhouse gas inventory sector that covers emissions and removals of greenhouse gases resulting from direct human induced land use, land use change and forestry activities.

Based on UN Report (highest #'s)

- CO_2 (FF) = **38 Gt/y**
- + Other gases (OG) = 52.4 Gt/y
- **+ OG + LUC = 59.1 Gt**

30 years…

- CO_2 = ~ 1000 Gt
- UN = 1770 Gt

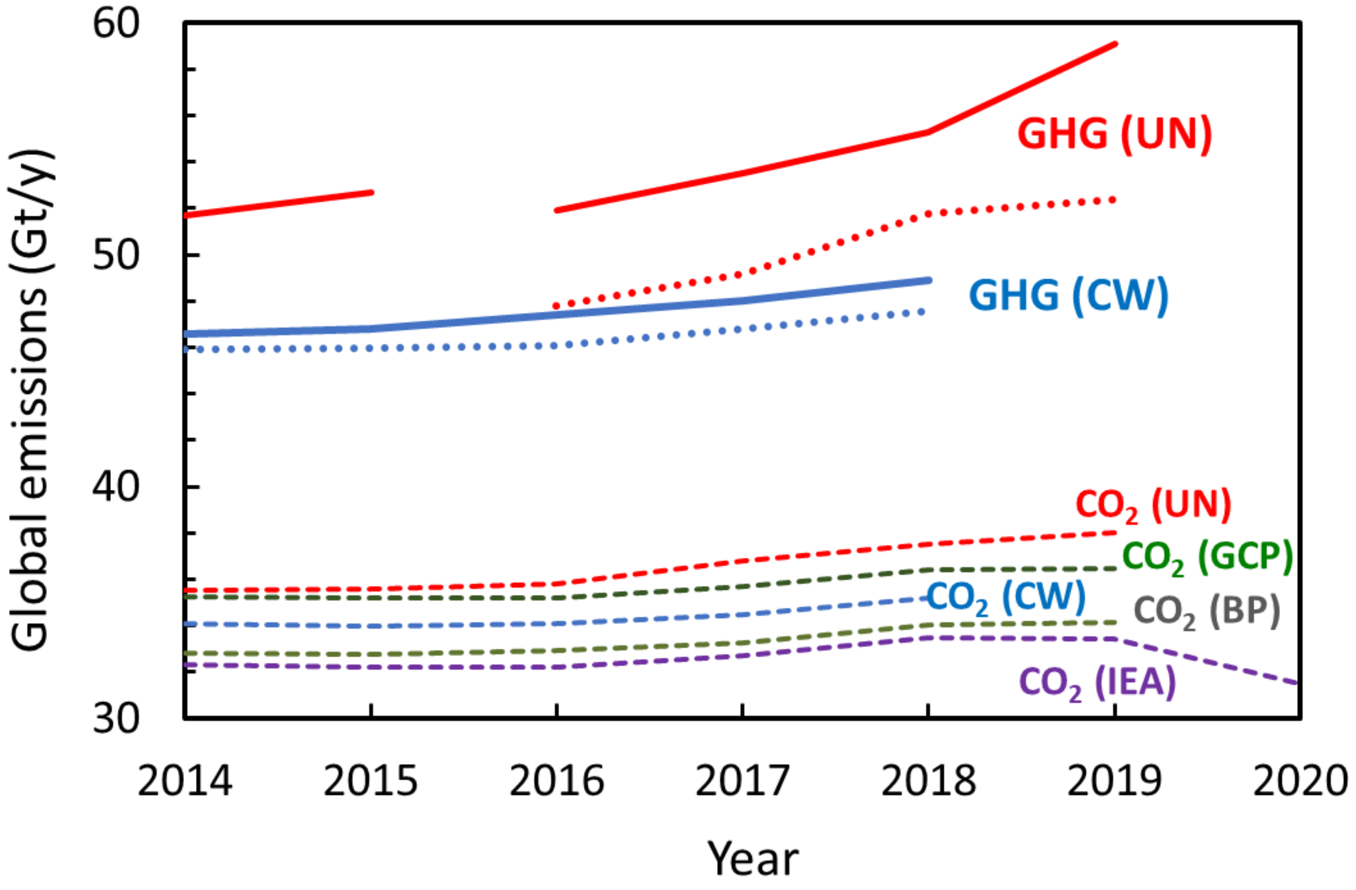


Fig. 14.10. Global GHG or CO_2 emissions reported by several different agencies: all GHG plus LUC, solid lines; all GHG with no LUC, dotted lines; and only CO_2 emissions, dashed lines. Sources of data: UN (*United Nations Environment Programme* 2020) and previous UN reports; CW (*Climate Watch* 2021), GCP, BP (*Dudley* 2019), IEA (*IEA* 2021). The break in the line for the UN data reflects a change in how it was reported.

Source: Logan (2022)

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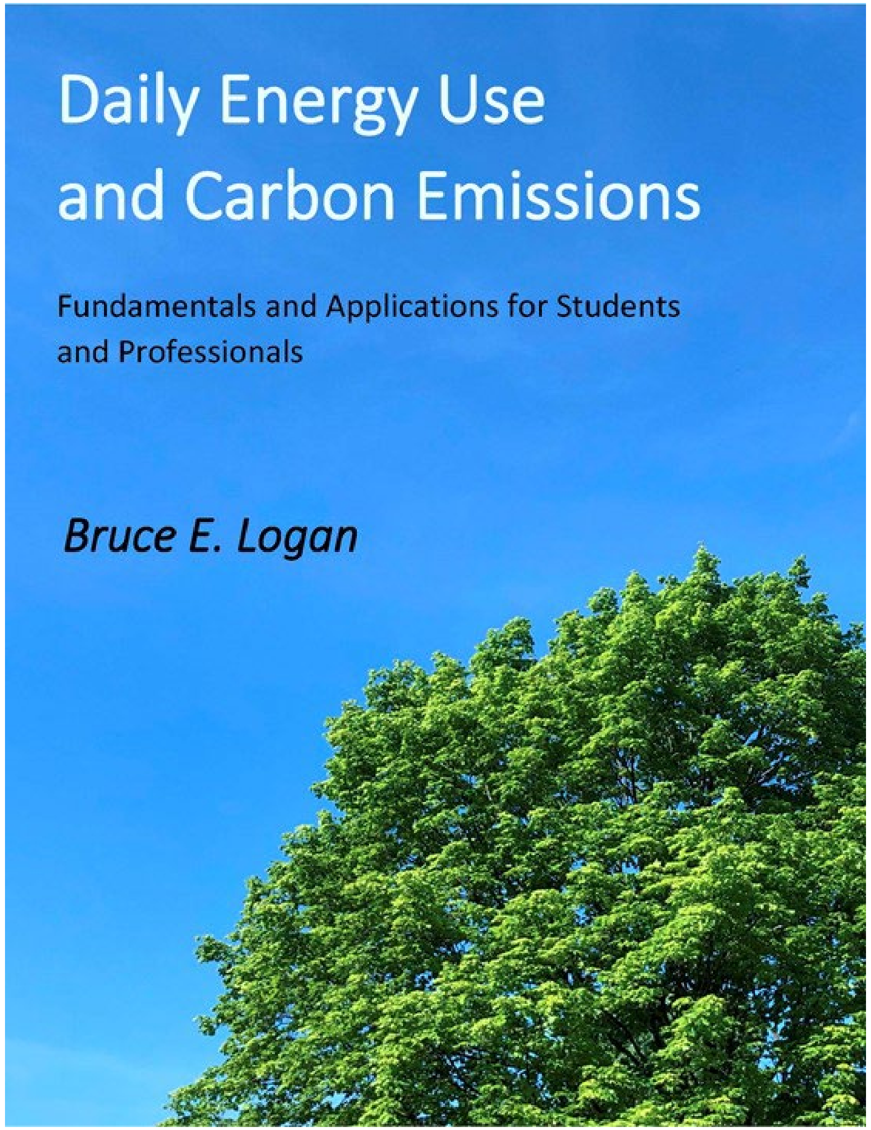
Why I wrote a book on Energy Use and Carbon Emissions?

To address the challenges of slowing climate change

- Learn about
  - Your personal energy use vs average American
  - How are CO_2 emissions tied to your energy use?
  - How to better understand the amounts of energy use and carbon emissions (based on “social math”: units of D, C and w).
  - Alternative carbon-neutral fuel options like H_2
- Apply knowledge to infrastructure design: Reduce fossil fuel energy use and CO_2 and GHG emissions
  - How do we build and modify our infrastructure to address climate change
  - Climate justice



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CONCLUSION: Green H_2 makes sense

Water electrolyzers

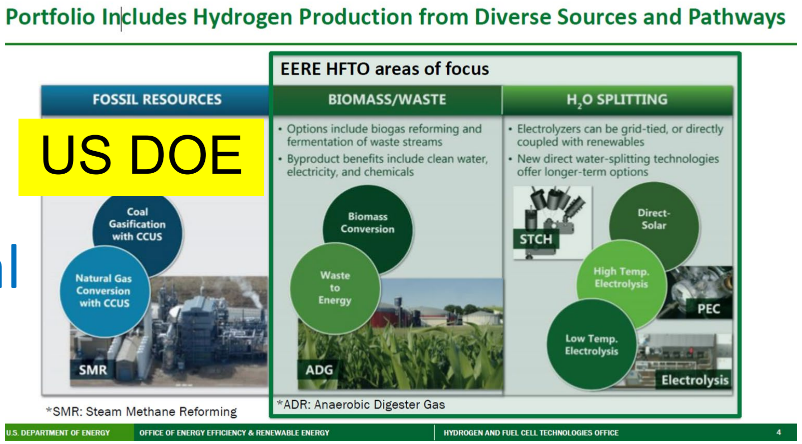
- RO membranes open a new research direction in water electrolyzer and other separation systems
- Negligible Cl_2 generation with RO membranes or vapor-fed anode configurations

MECs

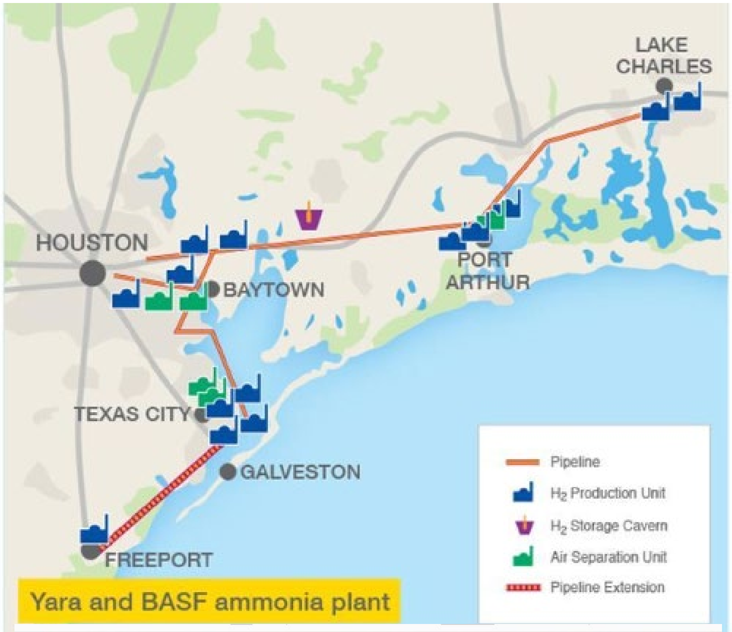
- Provide a bio + electrochemical route to green H_2

Netherlands

US DOE



Praxair Gulf Coast Hydrogen Pipeline System
~ 267 miles and proposed extension



Yara and BASF ammonia plant

Saudi Arabia will build a $5 Billion H_2 plant

Saudi green hydrogen project announced to be largest in world

https://www.hydrogenfuelnews.com/saudi-green-hydrogen-project-announced-to-be-largest-in-world/8540205/?MvBriefArticleId=18039

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