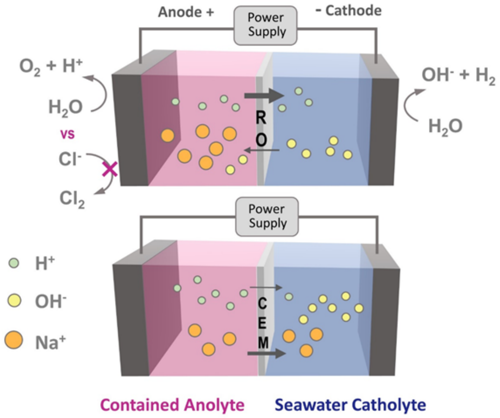
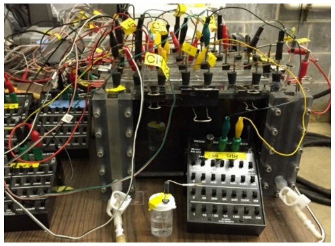
A new approach using reverse osmosis membranes for green hydrogen gas production with seawater in water electrolyzers

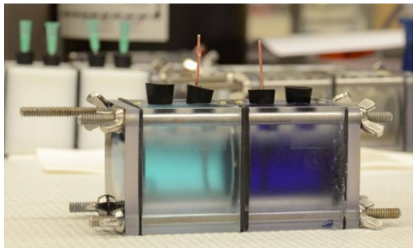
Seminar at UCLA
November 10, 2020

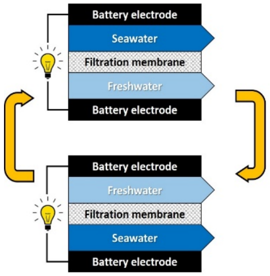
Bruce E. Logan
Civil & Environmental Engineering
Penn State University

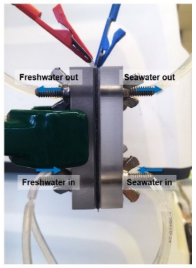


Research in the Logan Lab





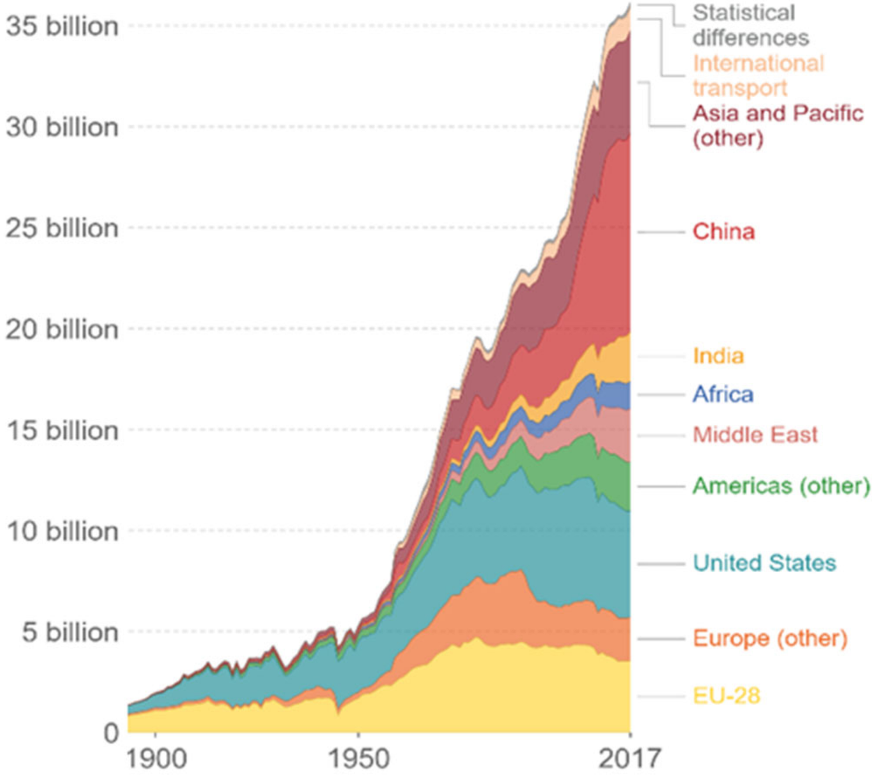


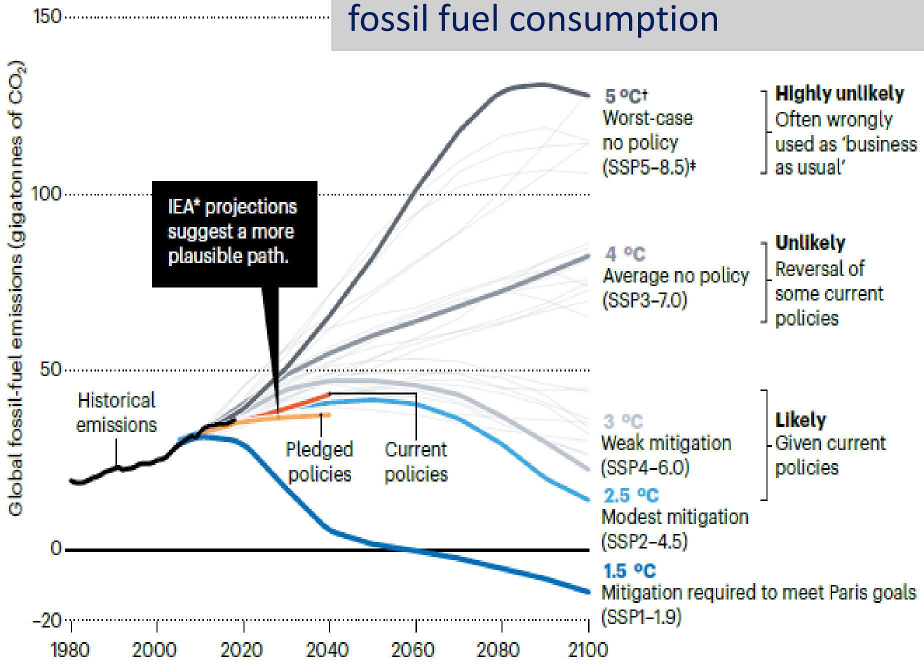


- Microbial Electrochemical Technologies
  - **Microbial fuel cells (MFCs):** Conversion of waste biomass into electricity
  - **Microbial electrolysis cells (MECs):** Conversion of waste biomass into H_2 gas
- Electricity generation and storage
  - Salinity gradient energy: Electricity extracted from seawater- river water
  - Thermal (flow) batteries: Electricity production using waste heat
- Desalination
  - Brackish water desalination using **Battery Electrode Deionization**; RO membrane fouling; ammonia recovery
- **Water electrolysis to make H_2**
  - **Why Hydrogen?**
  - **Why RO membranes?**

Climate change is not on the way… it is here!

Need to have a plan to reduce fossil fuel consumption





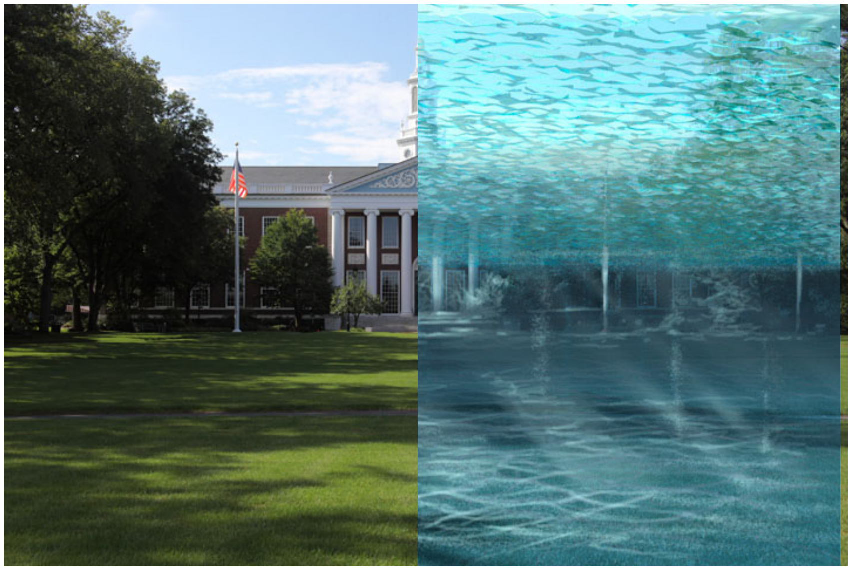
*The International Energy Agency (IEA) maps out different energy-policy and investment choices. Estimated emissions are shown for its Current Policies Scenario and for its Stated Policies Scenario (includes countries' current policy pledges and targets). To be comparable with scenarios for the Shared Socioeconomic Pathways (SSPs), IEA scenarios were modified to include constant non-fossil-fuel emissions from industry in 2018.

†Approximate global mean temperature rise by 2100 relative to pre-industrial levels.

‡SSP5–8.5 replaces Representative Concentration Pathway (RCP) 8.5.

Challenge: Avoid climate change 2100 scenario

Sea level rise: Could be as much as 6 – 13 ft

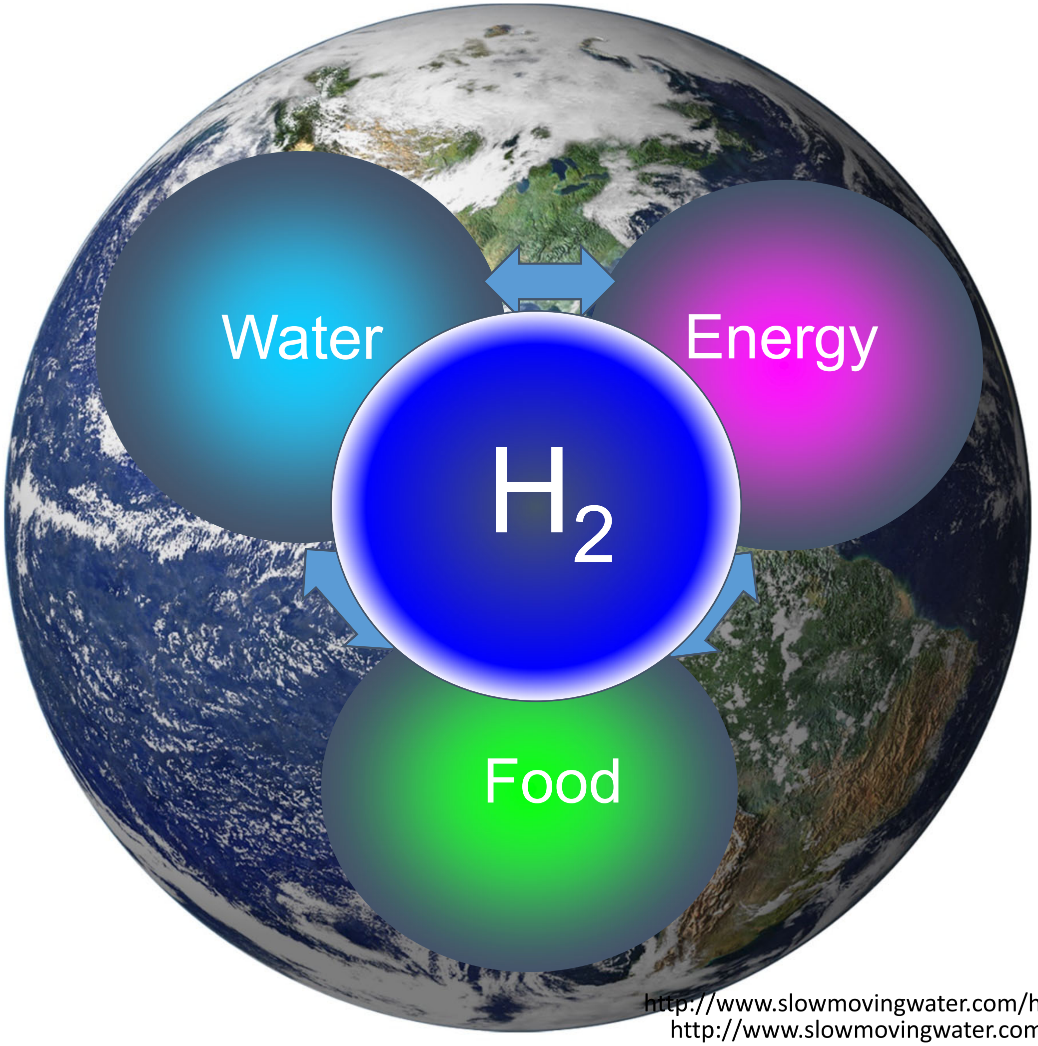


Harvard University, Cambridge, Massachusetts

- Recent estimates suggest that global mean sea level rise could exceed 2 m by 2100. (Oppenheimer and Alley, Science, Vol. 349, Issue 6244)
- These projections are higher than previous ones and based on improved understanding of the Antarctic Ice Sheet
- With consideration of meltwater, it could be as high as 13 ft (Rob DeConto, U. of MA, Amherst)
- 0.15 billion people live on land <3 ft above sea level

PennState

H_2: Energy-Food-Water Nexus for Solutions to Climate Change



Easy to see linkages between any 2 items

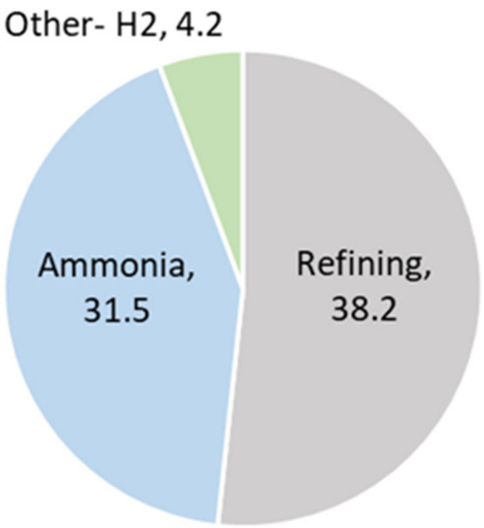
What things link all 3?

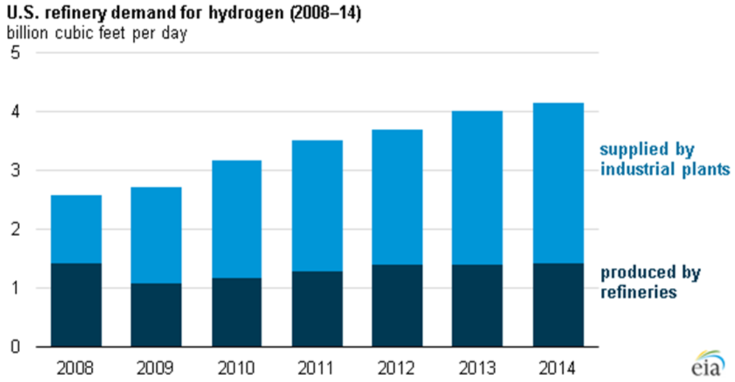
http://www.slowmovingwater.com/hydrogen-uses.htm

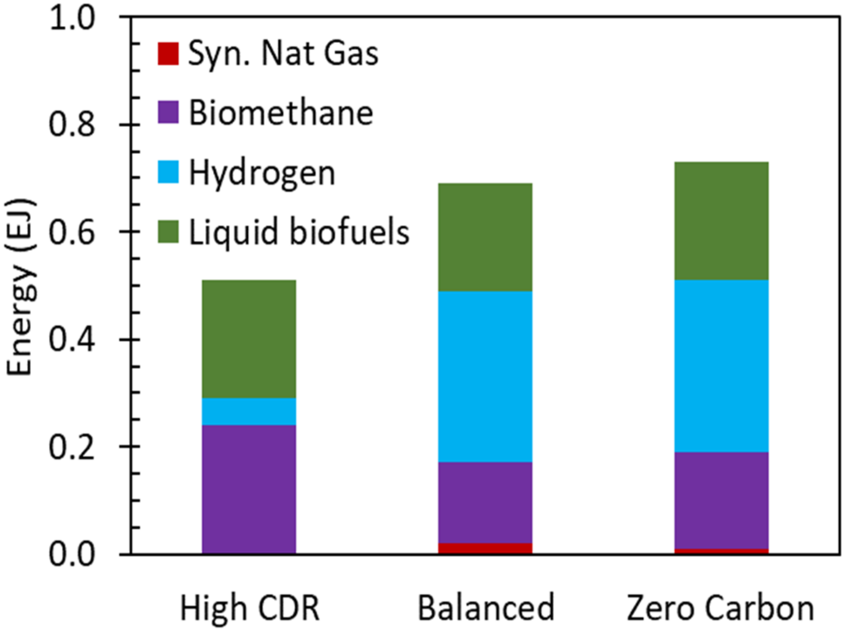
http://www.slowmovingwater.com/hydrogen-uses.htm

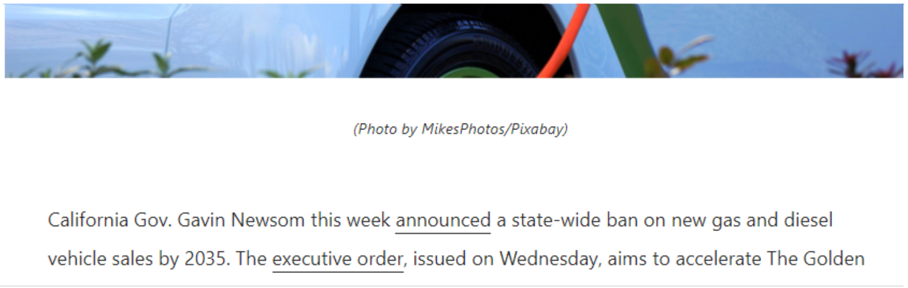
Why is H_2 important?

- 74 billion kg of H_2 used globally
- H_2 is mostly made using fossil fuels
    - 96% from fossil fuels, only 4% from water electrolysis
- ~1/2 used for oil refining (not fuel cells!)
- **~1/2 used to make Ammonia**



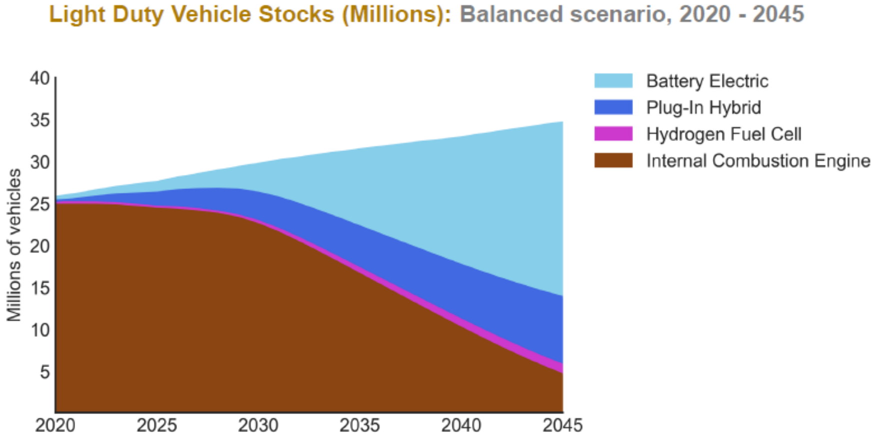




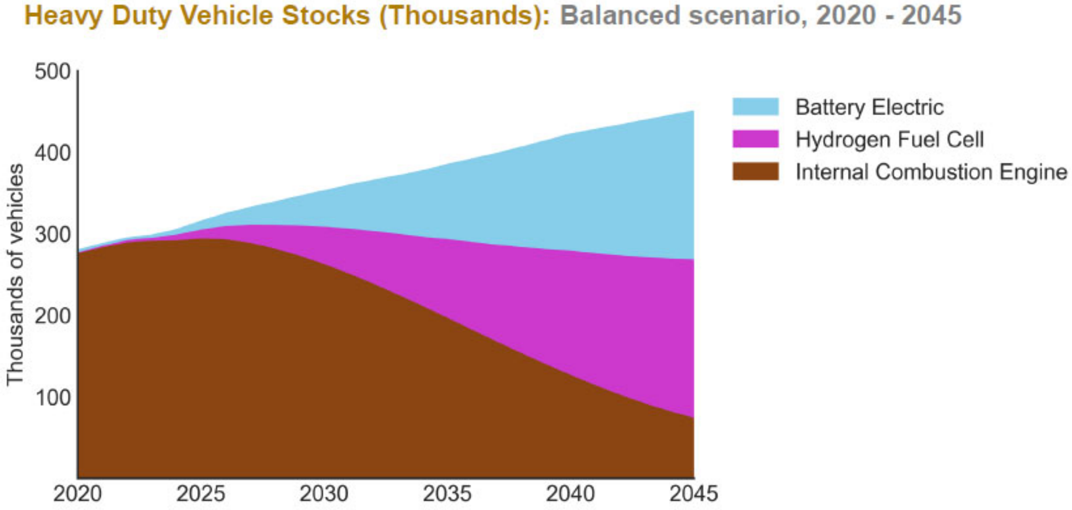


(Photo by MikesPhotos/Pixabay)

California Gov. Gavin Newsom this week announced a state-wide ban on new gas and diesel vehicle sales by 2035. The executive order, issued on Wednesday, aims to accelerate The Golden



Light Duty Vehicle Stocks (Millions): Balanced scenario, 2020 - 2045



Heavy Duty Vehicle Stocks (Thousands): Balanced scenario, 2020 - 2045

H_2 fueled airplanes

Business Concentrates

ENERGY

Ammonia en route to fuel ships and planes

Carbon-neutral ammonia could be a drop-in replacement for fossil fuels

Haldor Topsoe says ships such as this one can be adapted to run on green ammonia.

Green ammonia, made by reacting nitrogen with hydrogen generated by using renewable electricity to split water, is being touted as an environmentally friendly, low-emission fuel for ships and planes, backers say.

A new report by the Danish catalyst company Haldor Topsoe and partners concludes that replacing conventional fuel oil with green ammonia could be a cost-effective way of reducing greenhouse gas emissions from ships.

Because it is easier to store and can be burned in standard internal combustion engines, green ammonia would be a cheaper fuel for the shipping industry than hydrogen made from renewable energy. Nitrogen oxides—the only greenhouse gases emitted by the combustion of ammonia—could be eliminated by installing catalytic systems, according to Topsoe.

The firm's study forecasts that the cost of green ammonia from solar and wind energy will be $21.50–45.70 per GJ in 2025 and will drop to $13.50–15.00 in 2040. Fuel oil is currently priced at $12.50–15.00 per GJ. Ammonia can be mixed with fuel oil, enabling its use to rise steadily.

Conventionally made ammonia is already stored and handled in 120 ports worldwide, meaning it can easily be made available for shipping, the report concludes.

Green ammonia is also being lined up as a fuel for airplanes. The British aircraft-engine maker Reaction Engines says it is working on a fuel system in which ammonia is exposed to a lithium-calcium imide catalyst that splits it into nitrogen and hydrogen. Hydrogen and ammonia are then blended and burned in the engine.

Ammonia has an advantage over hydrogen in that it can be stored in an aircraft wing, as kerosene is today. Ammonia is less energy dense than kerosene, though, so initially its use would be limited to short-haul flights.

Reaction Engines is developing the technology with the UK's Science and Technology Facilities Council, which has secured funding for the project from the UK government.

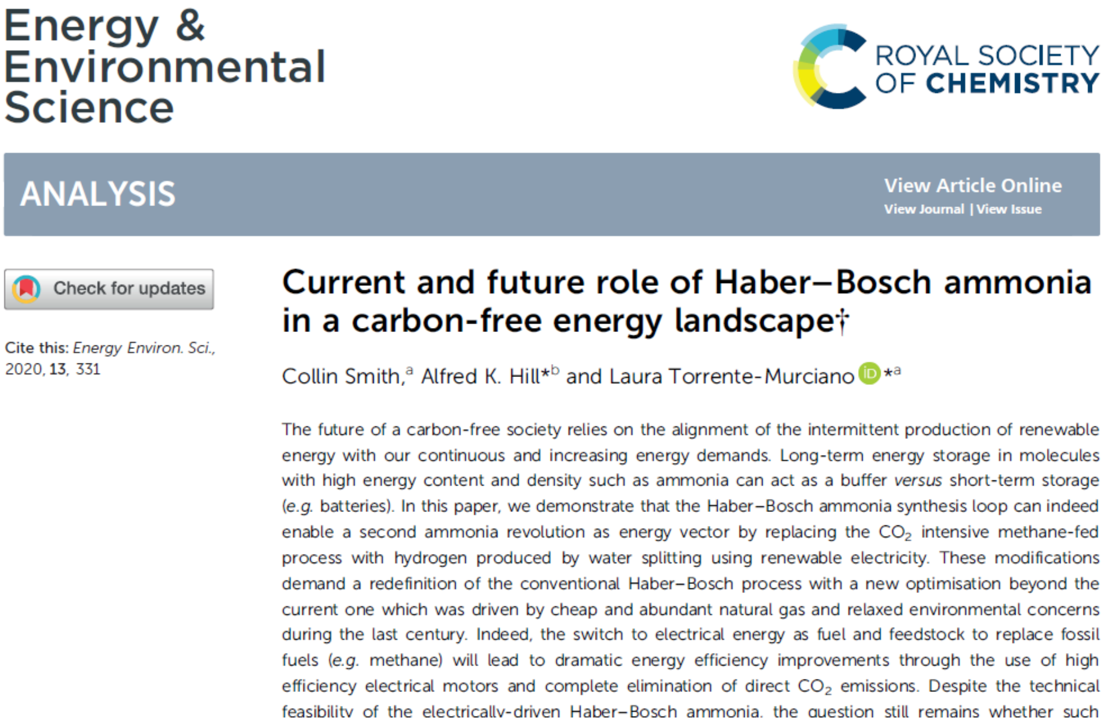
Ammonia is a major global commodity, with annual production of about 230 million metric tons, according to IHS Markit. The market research firm says green ammonia could "change the landscape" for the ammonia industry over the next 10–20 years.—ALEX SCOTT

NH_3 from H_2 for Fertilizers and food

- Energy used to make H_2 = food energy consumed by 80% of US population
- NH_3 production using Haber process drastically improved crop yields:
  - If yields remained at the 1900, four times more land would have been required in 2000
  - That would consume half of all ice-free land compared to ~15% used today

Ammonia Production: We need to re-think Haber Bosch

- Do not use a fossil fuel as the source of H_2
- Need a green ammonia technology
- Increase water electrolyzer efficiencies
- Pursue “a more holistic approach to the ammonia synthesis loop”
- “develop small-scale distributed and agile processes”



Energy & Environmental Science

ROYAL SOCIETY OF **CHEMISTRY**

ANALYSIS

Cite this: *Energy Environ. Sci.*, 2020, **13**, 331

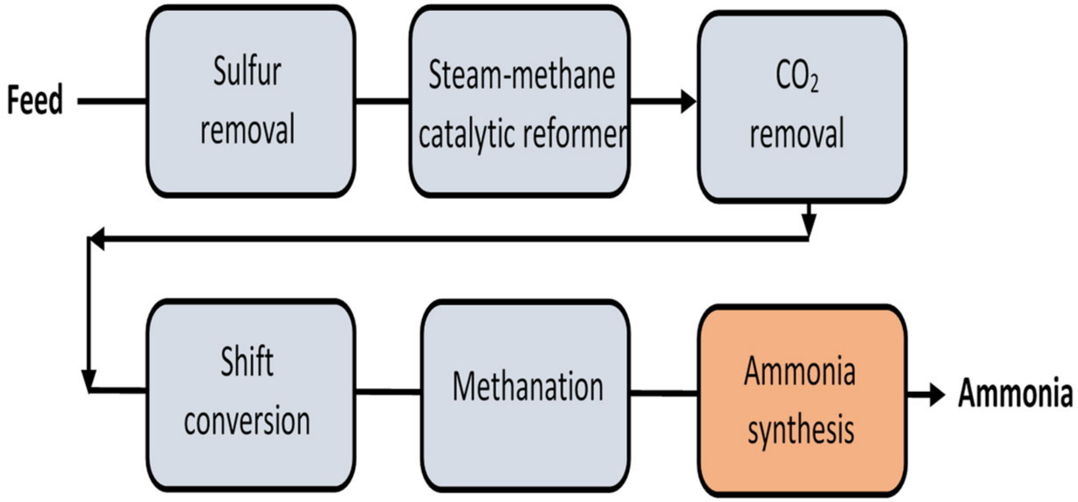
Current and future role of Haber–Bosch ammonia in a carbon-free energy landscape†

Collin Smith,[a] Alfred K. Hill*[b] and Laura Torrente-Murciano *[a]

The future of a carbon-free society relies on the alignment of the intermittent production of renewable energy with our continuous and increasing energy demands. Long-term energy storage in molecules with high energy content and density such as ammonia can act as a buffer *versus* short-term storage (*e.g.* batteries). In this paper, we demonstrate that the Haber–Bosch ammonia synthesis loop can indeed enable a second ammonia revolution as energy vector by replacing the CO_2 intensive methane-fed process with hydrogen produced by water splitting using renewable electricity. These modifications demand a redefinition of the conventional Haber–Bosch process with a new optimisation beyond the current one which was driven by cheap and abundant natural gas and relaxed environmental concerns during the last century. Indeed, the switch to electrical energy as fuel and feedstock to replace fossil fuels (*e.g.* methane) will lead to dramatic energy efficiency improvements through the use of high efficiency electrical motors and complete elimination of direct CO_2 emissions. Despite the technical feasibility of the electrically-driven Haber–Bosch ammonia, the question still remains whether such

Producing NH_3 from fossil fuels

- Steam reforming using CH_4 (49% of production)
- Sulfur in fuel is a problem
  - $H_2 + RSH \rightarrow H_2S + ZnO \rightarrow ZnS + H_2O$
- Cleaner/easier to start with just H_2, using Haber process
  - "Ammonia synthesis" would be the only step in this process
  - $3\ H_2 + N_2 \rightarrow 2\ NH_3$



Feed

Sulfur removal

Steam-methane catalytic reformer

CO_2 removal

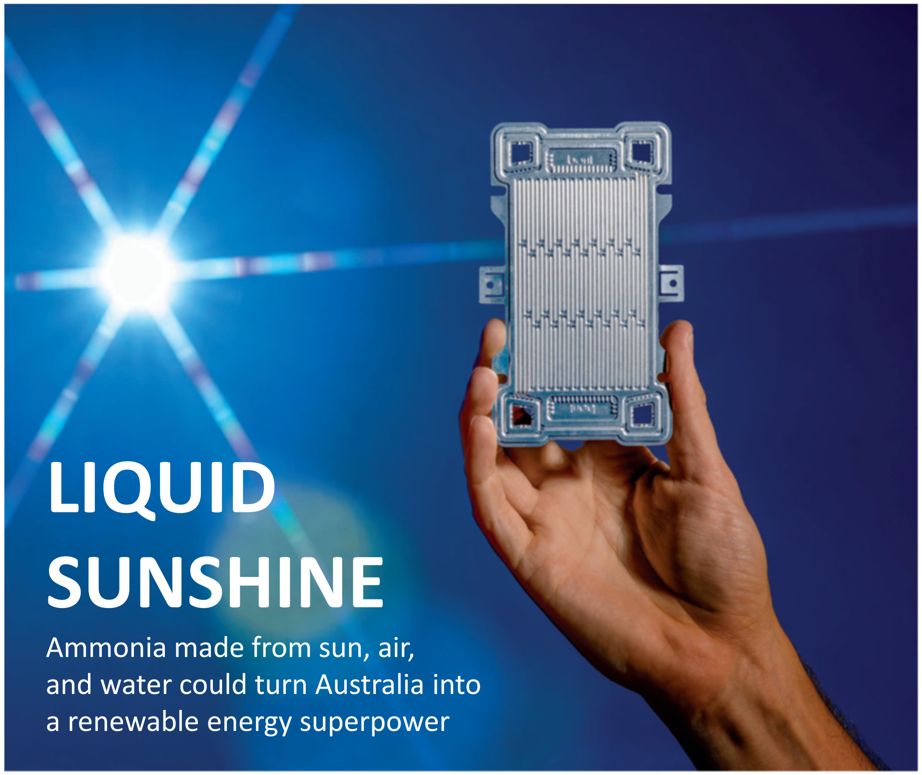
Shift conversion

Methanation

Ammonia synthesis

Ammonia

H_2 from renewable energy



LIQUID SUNSHINE

Ammonia made from sun, air, and water could turn Australia into a renewable energy superpower

Service, in *Science*, 13 JULY 2018 • VOL 361 ISSUE 6398

- Use solar energy for water splitting to produce H_2
- Solar and Wind electricity is cheaper than fossil fuel electricity
- Trials: 2.5 MW solar plant built by Yara, the world's biggest producer of ammonia, in Australia for $H_2 \rightarrow NH_3$

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

ENVIRONMENT

Spain

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 lyol
the project will als.
tovoltaic plant
to power electr of
into oxygen and out
combine the hy hem.
form ammonia. on
Fertiberia wi ses
erated oxygen a rget
acid, which it al e

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%.

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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 fertiliz
genera

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.

Germany

gas filtration
ENHAUSEN

HYDROGEN POWER

▶ Electrolyzer ready for German grid

An alkaline water electrolyzer from the engineering firm Thyssenkrupp has qua ified as a secondary power source for th 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.

says
ct
Volk-
of
lat-
g to
foam
on

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

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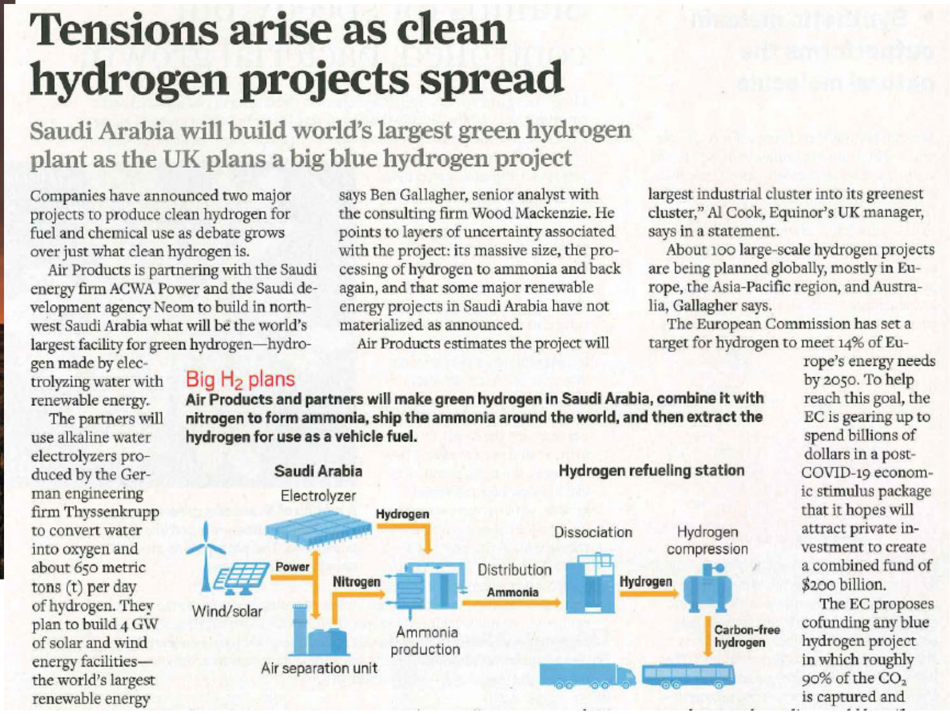


Tensions arise as clean hydrogen projects spread

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

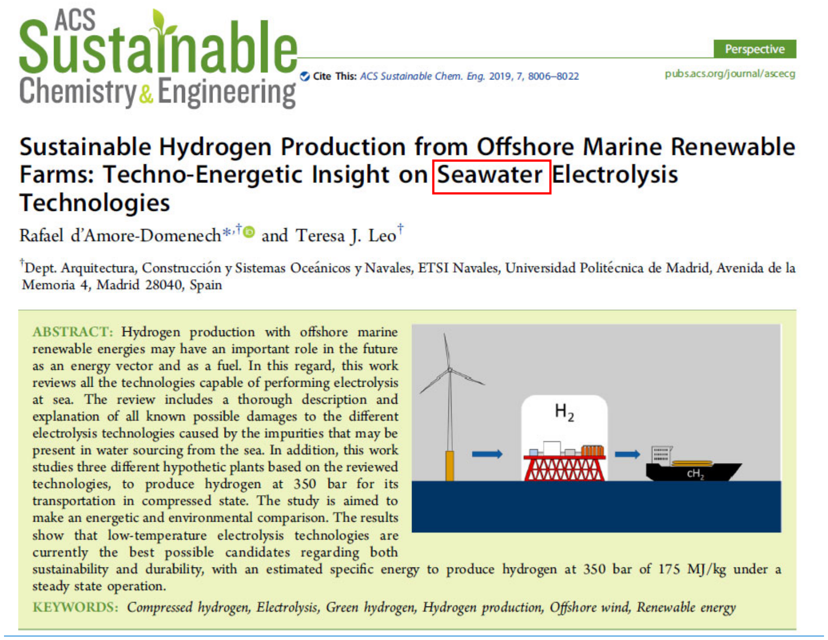
Big H_2 plans

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.

Challenges for Electrochemical H_2 production

- 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

- 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

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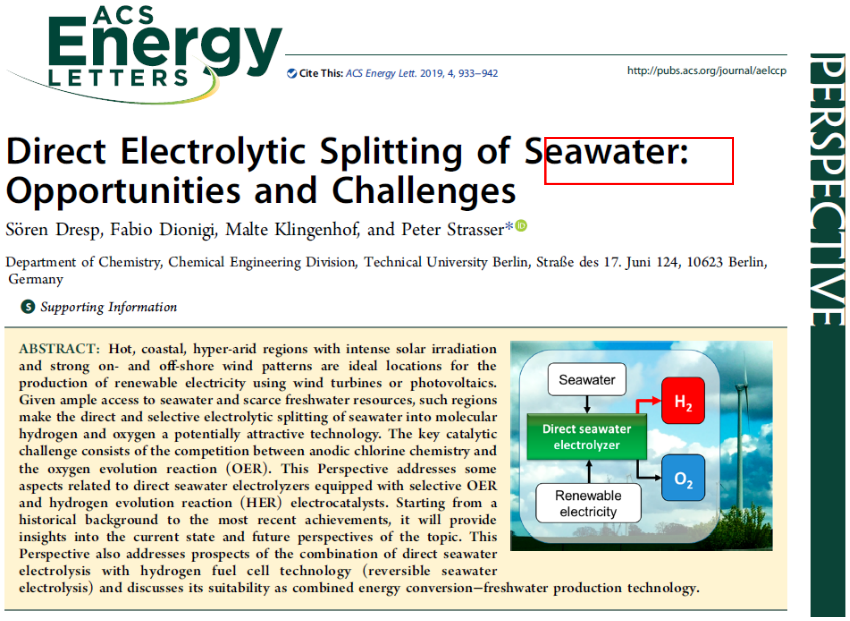
ABSTRACT: Hydrogen production with offshore marine renewable energies may have an important role in the future as an energy vector and as a fuel. In this regard, this work reviews all the technologies capable of performing electrolysis at sea. The review includes a thorough description and explanation 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

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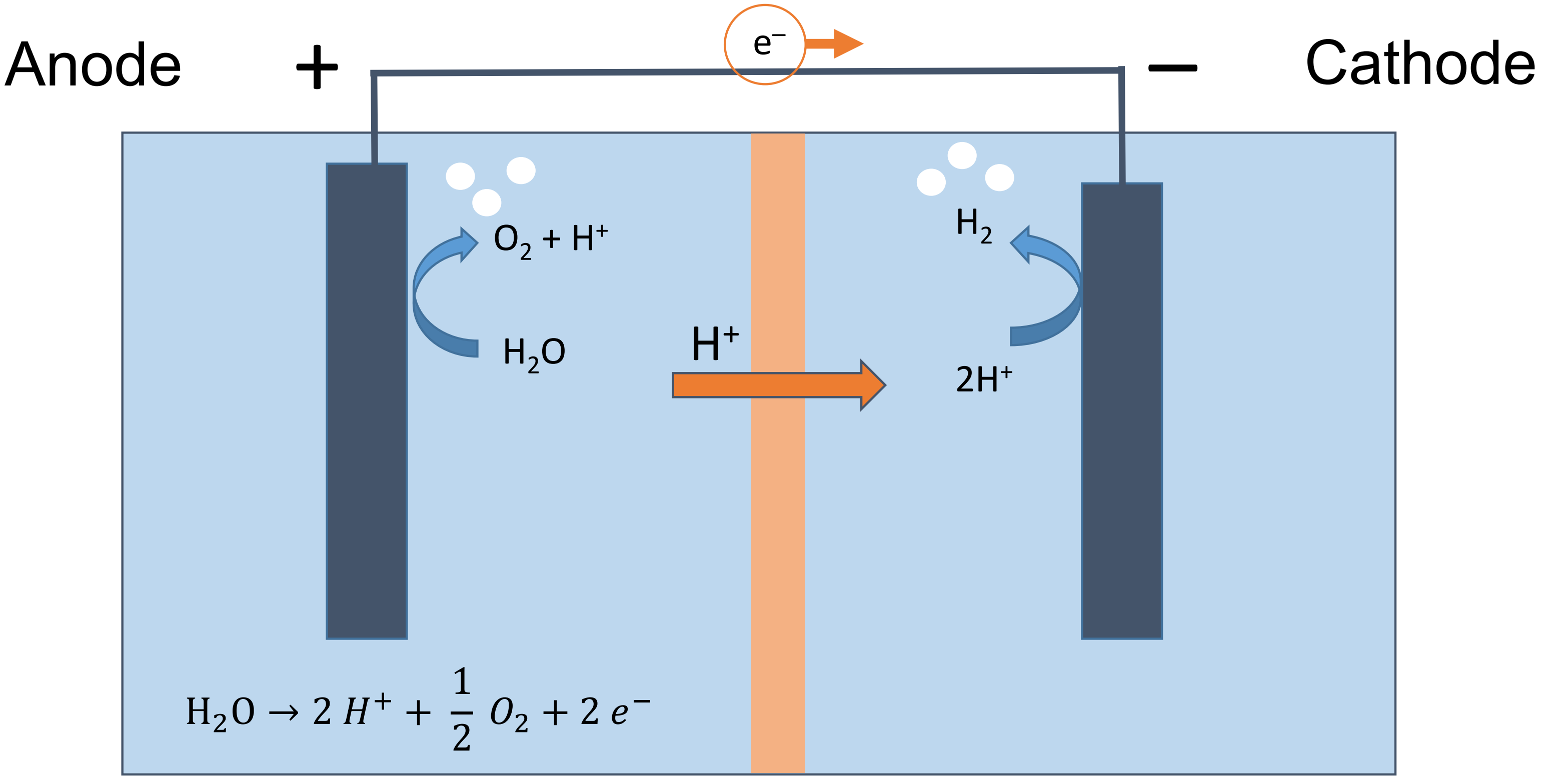
Department of Chemistry, Chemical Engineering Division, Technical University Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany

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.

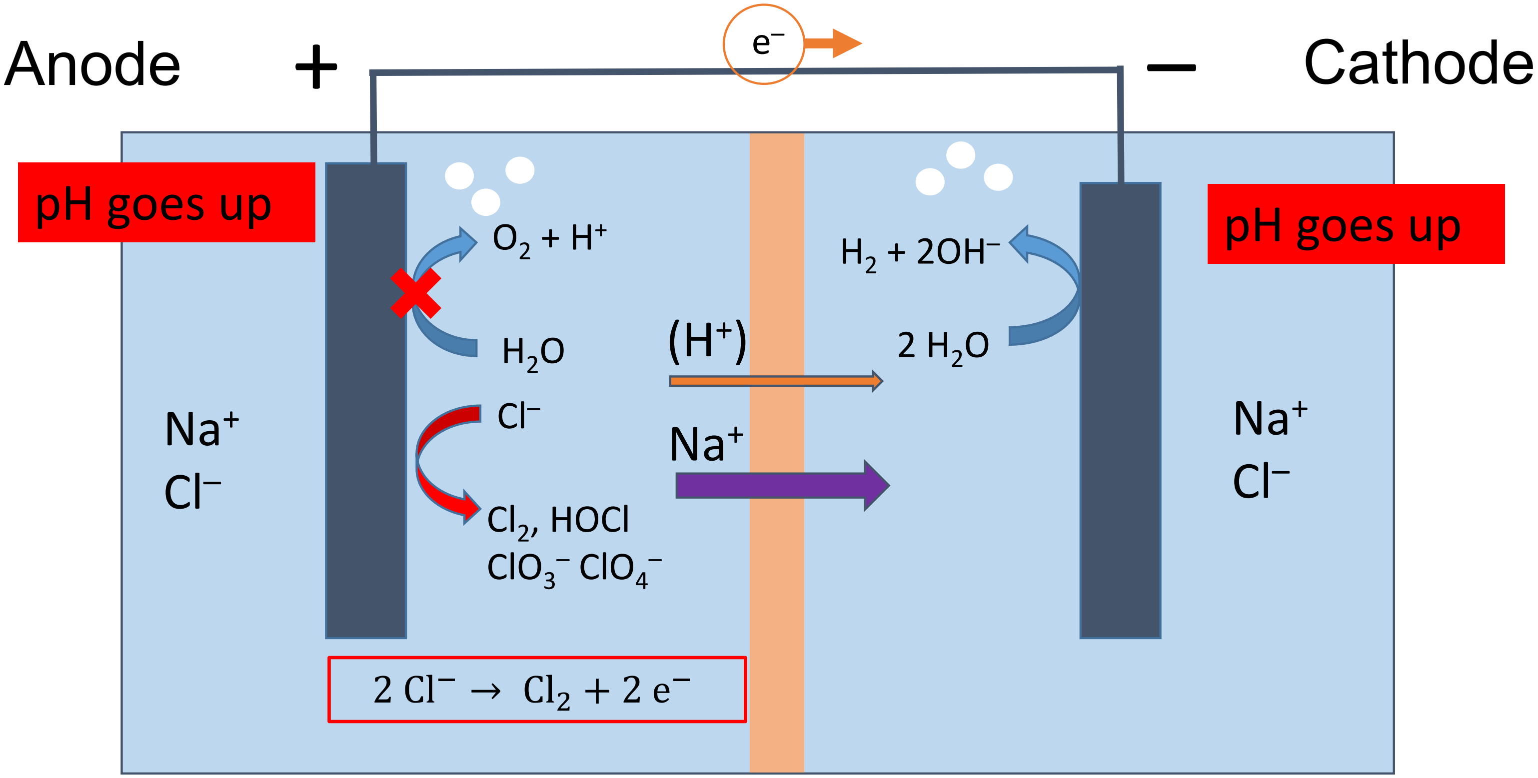
Water Electrolysis: PEM with acidic pH



$$\mathrm{H_2O} \rightarrow 2\,H^+ + \frac{1}{2}\,O_2 + 2\,e^-$$

H^+ permeable membrane:
Proton Exchange Membrane (PEM)
Cation Exchange Membrane (CEM)

Water Electrolysis: using NaCl?



Anode +

e^-

− Cathode

pH goes up

$O_2 + H^+$

H_2O

(H^+)

$H_2 + 2OH^-$

$2\ H_2O$

pH goes up

Na^+
Cl^-

Cl^-

Cl_2, $HOCl$
ClO_3^- ClO_4^-

Na^+

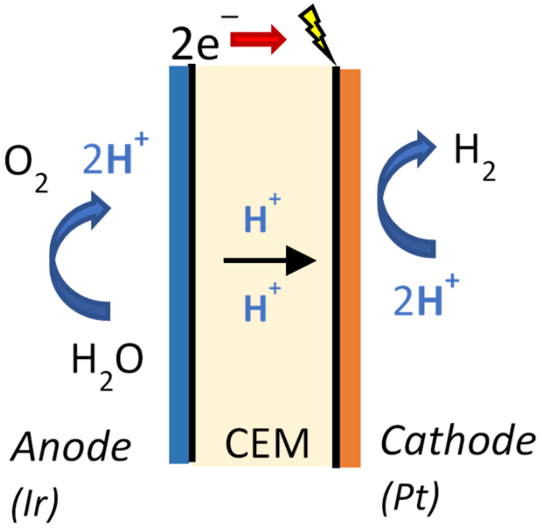
Na^+
Cl^-

$$2\,\mathrm{Cl}^- \rightarrow \mathrm{Cl}_2 + 2\,e^-$$

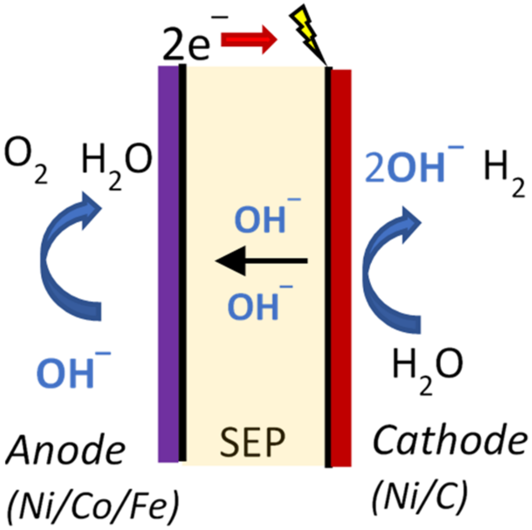
Proton Exchange Membrane (PEM)
Cation Exchange Membrane (CEM)

Water Electrolyzers: Two main approaches

PEM/Acidic

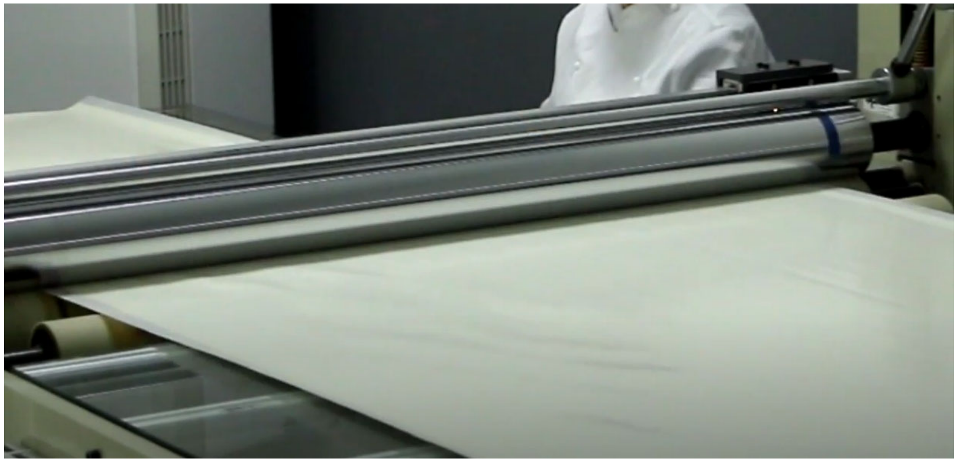


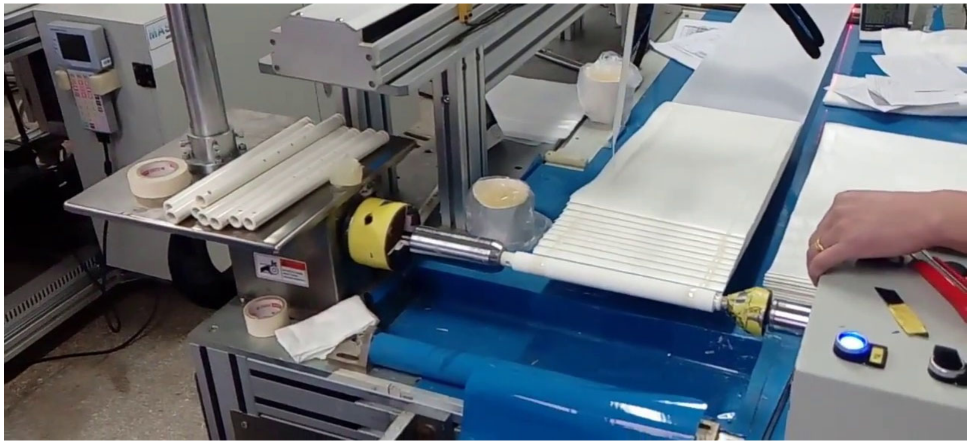
Alkaline



Reverse Osmosis membranes are “cheap”!

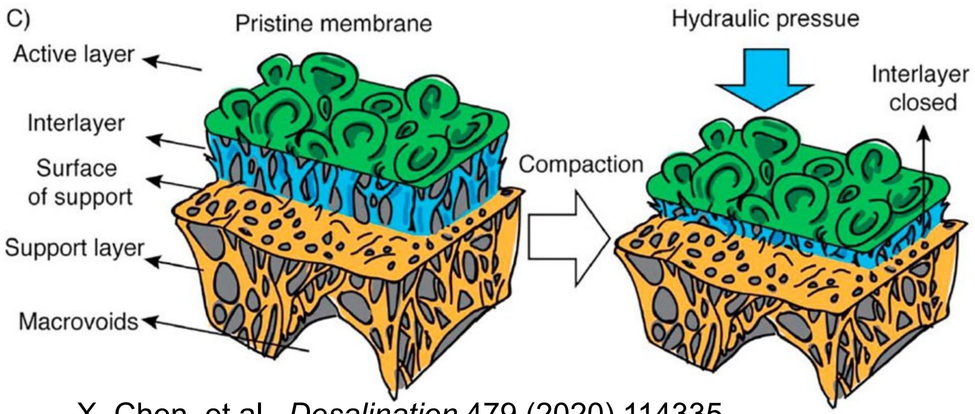
- Mass production has reduced RO membrane costs compared to many other types of membranes
- Ion Exchange (IX) membranes are expensive! ~\$100 – \$1000 /m^2
- RO: Size selective membranes are (relatively) inexpensive < \$10 /m^2
- Can we use RO membranes for WE?





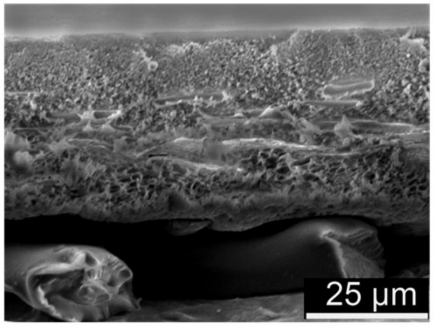
https://www.youtube.com/watch?v=BFjvOyjlU5k

RO membranes



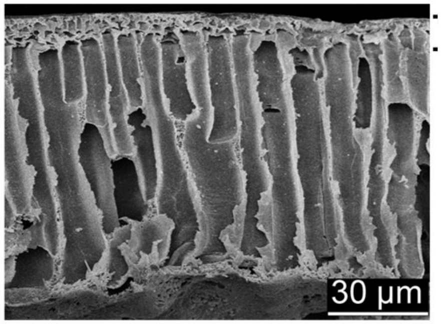
X. Chen, et al., *Desalination* 479 (2020) 114335

TFC-RO



S = 9583 µm

TFC-FO

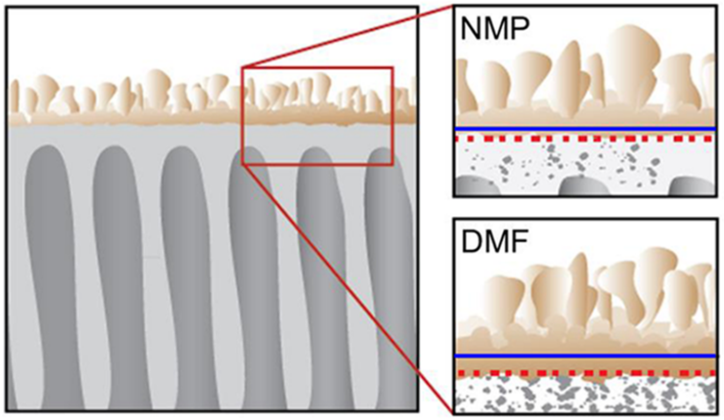


S =492 µm

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

Active layer of TFC RO membranes ~ 130-300 nm

NMP = 132 ± 28 nm

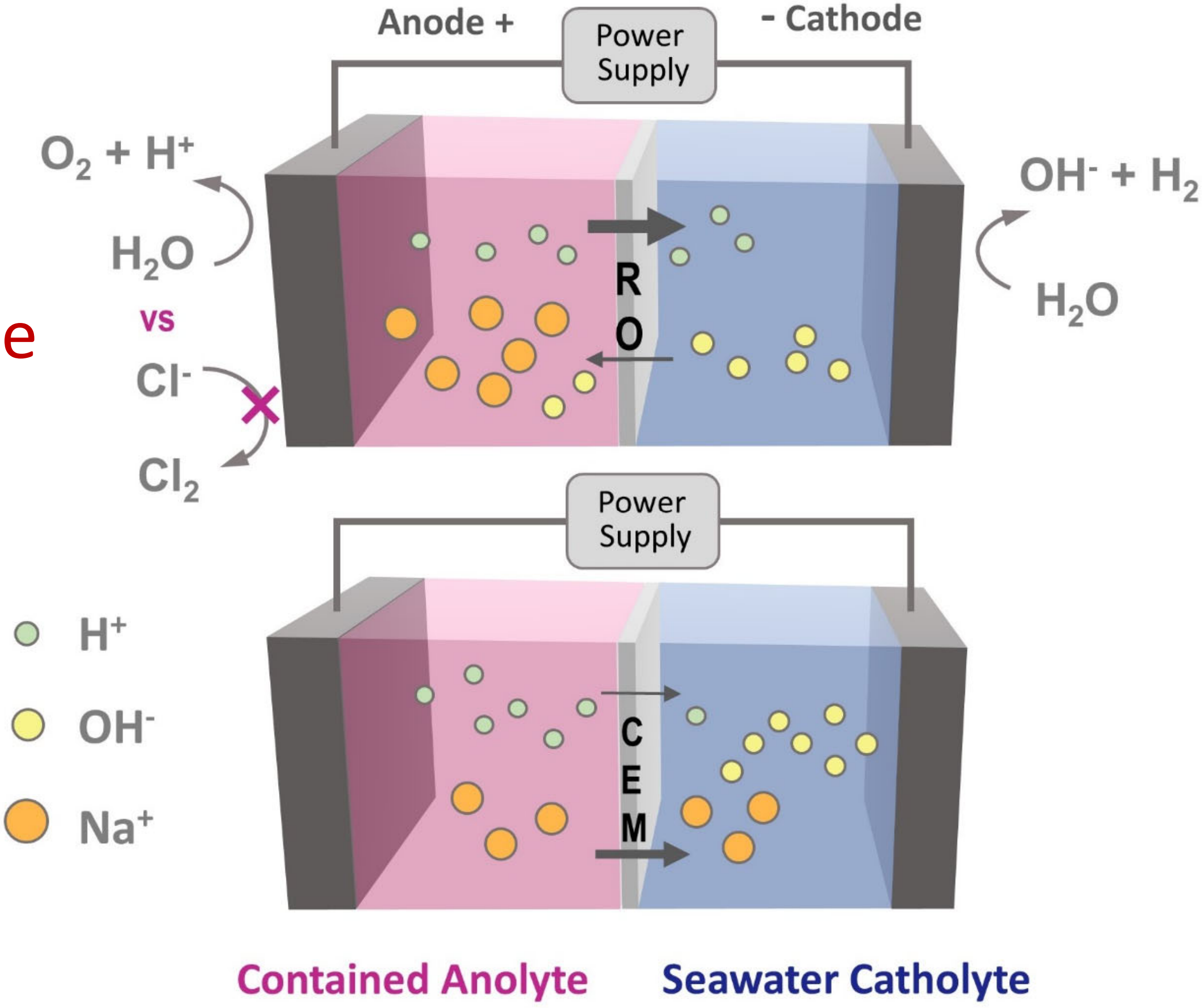


DMF= 171 ± 10 nm

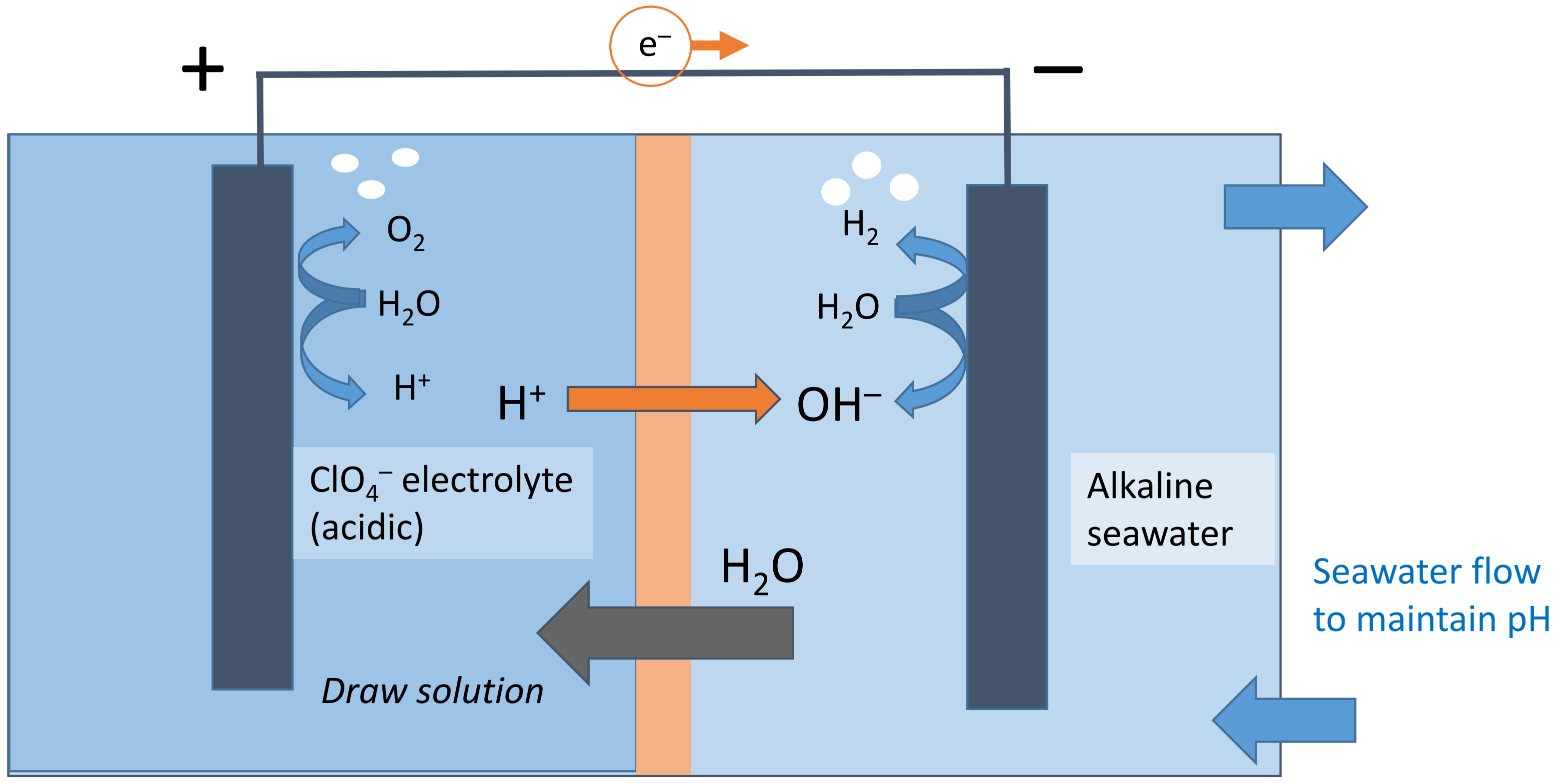
Xinglin Lu, Siamak Nejati, Youngwoo Choo, Chinedum O. Osuji, Jun Ma, Menachem Elimelech. 2015. Elements Provide a Clue: Nanoscale Characterization of Thin-Film Composite Polyamide Membranes. ACS Appl. Mater. Interfaces. 7, 16917–16922

RO
- Low pH anolyte
- Higher pH catholyte (seawater)

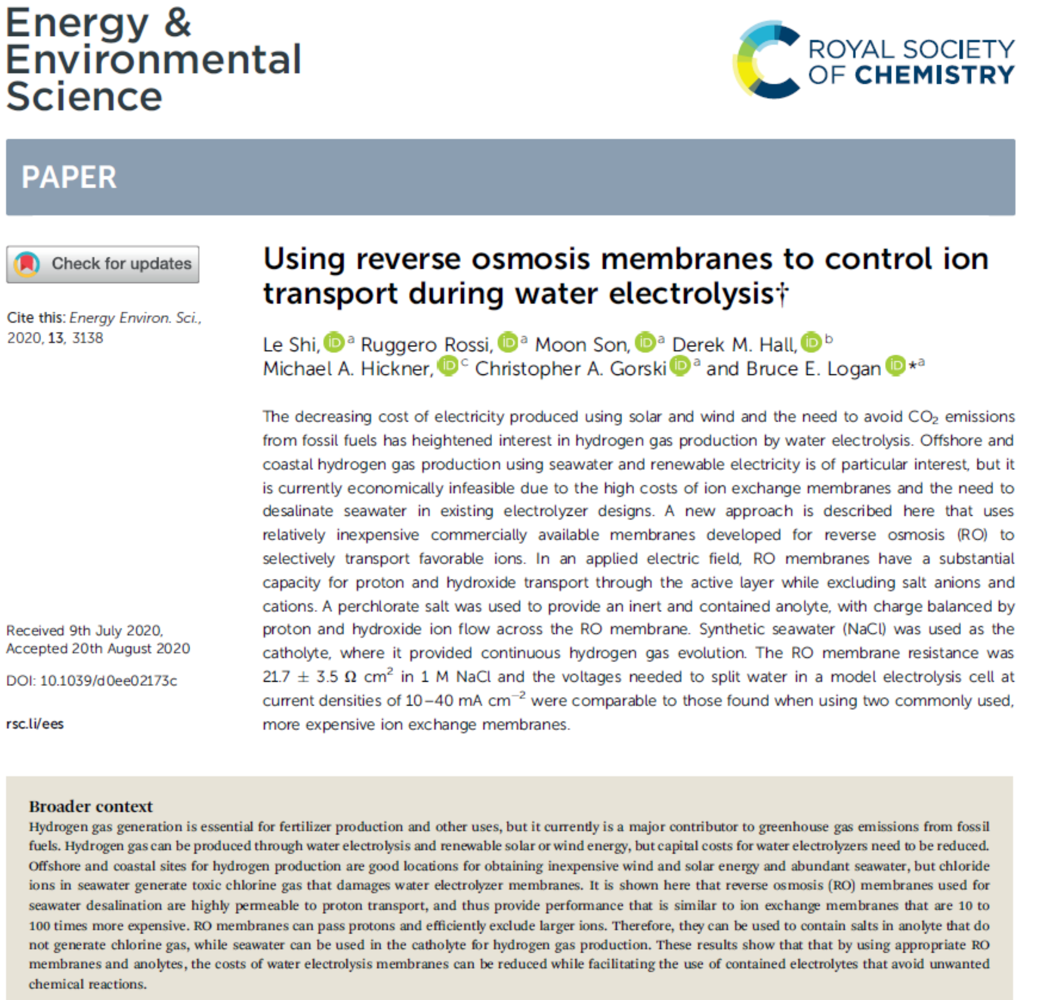
PEM/Acidic



Solution to Seawater Electrolysis



H^+ permeable RO membrane



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

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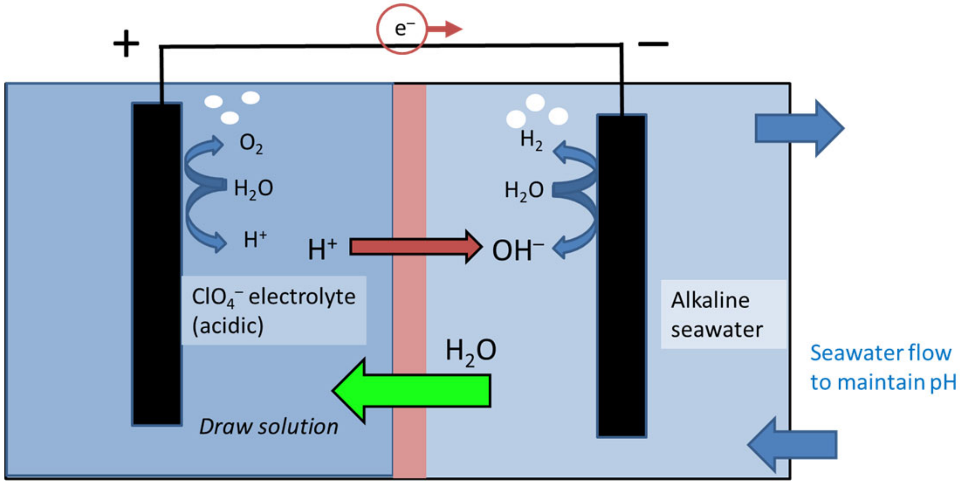
The decreasing cost of electricity produced using solar and wind and the need to avoid CO_2 emissions from fossil fuels has heightened interest in hydrogen gas production by water electrolysis. Offshore and coastal hydrogen gas production using seawater and renewable electricity is of particular interest, 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.

Broader context

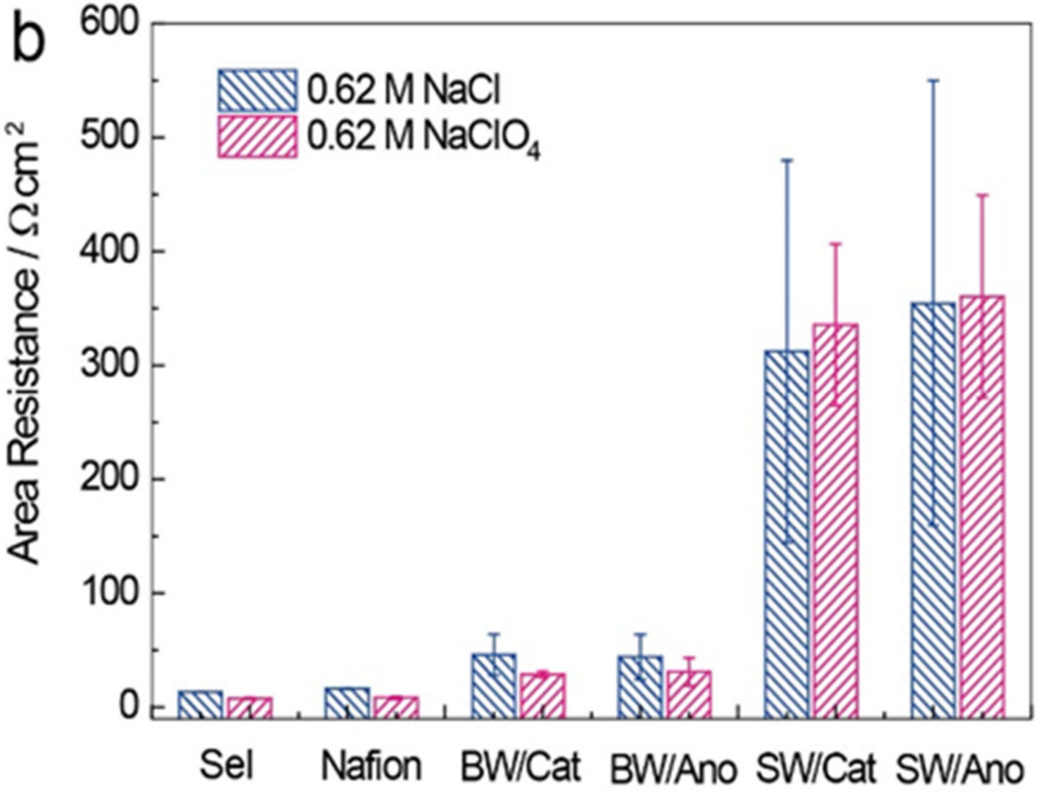
Hydrogen gas generation is essential for fertilizer production and other uses, but it currently is a major contributor to greenhouse gas emissions from fossil fuels. Hydrogen gas can be produced through water electrolysis and renewable solar or wind energy, but capital costs for water electrolyzers need to be reduced. Offshore and coastal sites for hydrogen production are good locations for obtaining inexpensive wind and solar energy and abundant seawater, but chloride ions in seawater generate toxic chlorine gas that damages water electrolyzer membranes. It is shown here that reverse osmosis (RO) membranes used for seawater desalination are highly permeable to proton transport, and thus provide performance that is similar to ion exchange membranes that are 10 to 100 times more expensive. RO membranes can pass protons and efficiently exclude larger ions. Therefore, they can be used to contain salts in anolyte that do not generate chlorine gas, while seawater can be used in the catholyte for hydrogen gas production. These results show that that by using appropriate RO membranes and anolytes, the costs of water electrolysis membranes can be reduced while facilitating the use of contained electrolytes that avoid unwanted chemical reactions.

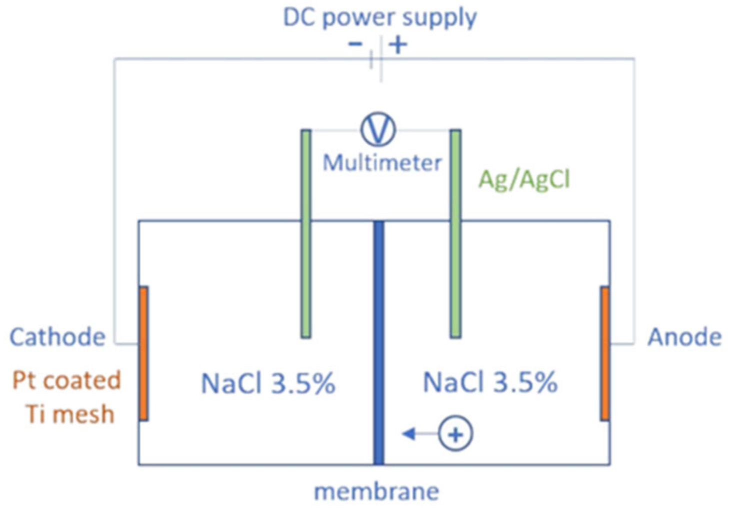
RO membrane must have a sufficient conductivity to sustain ionic current = Low resistance (Ω m^2)



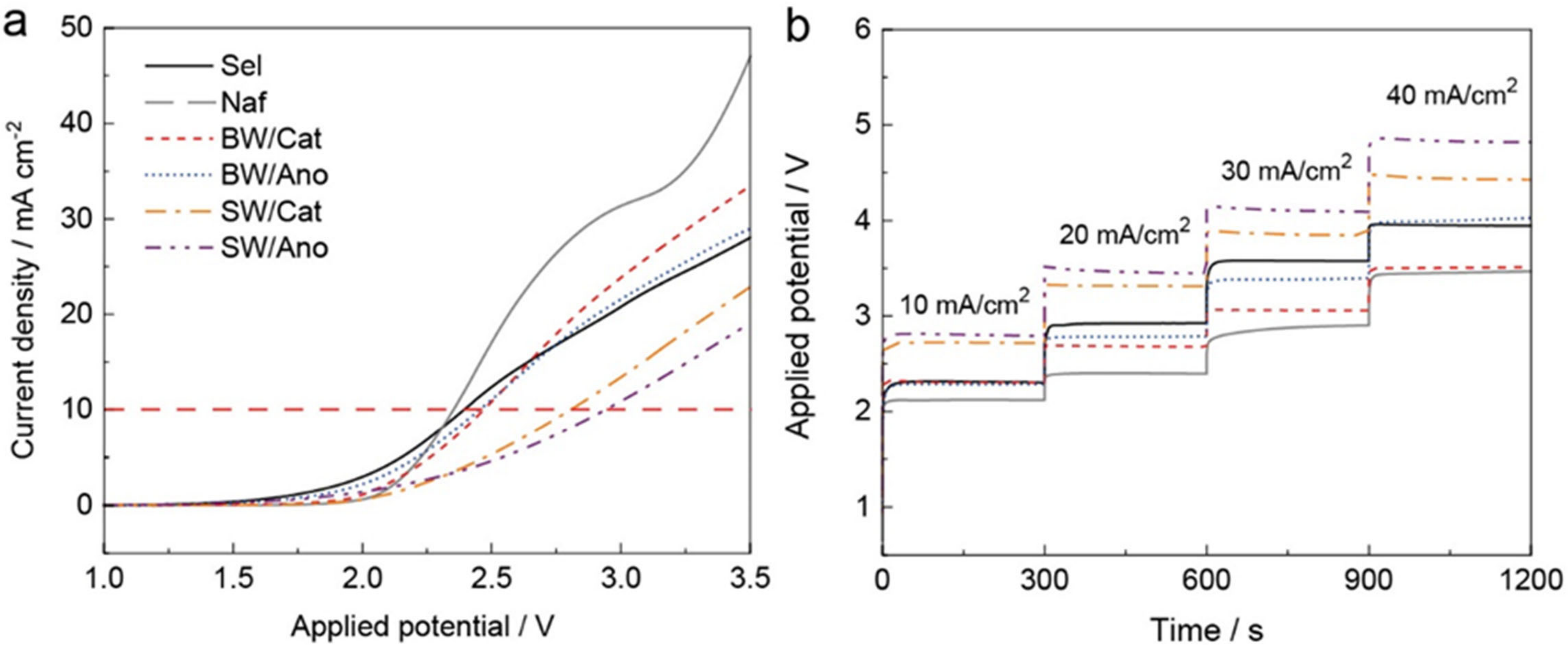
H^+ permeable RO membrane

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

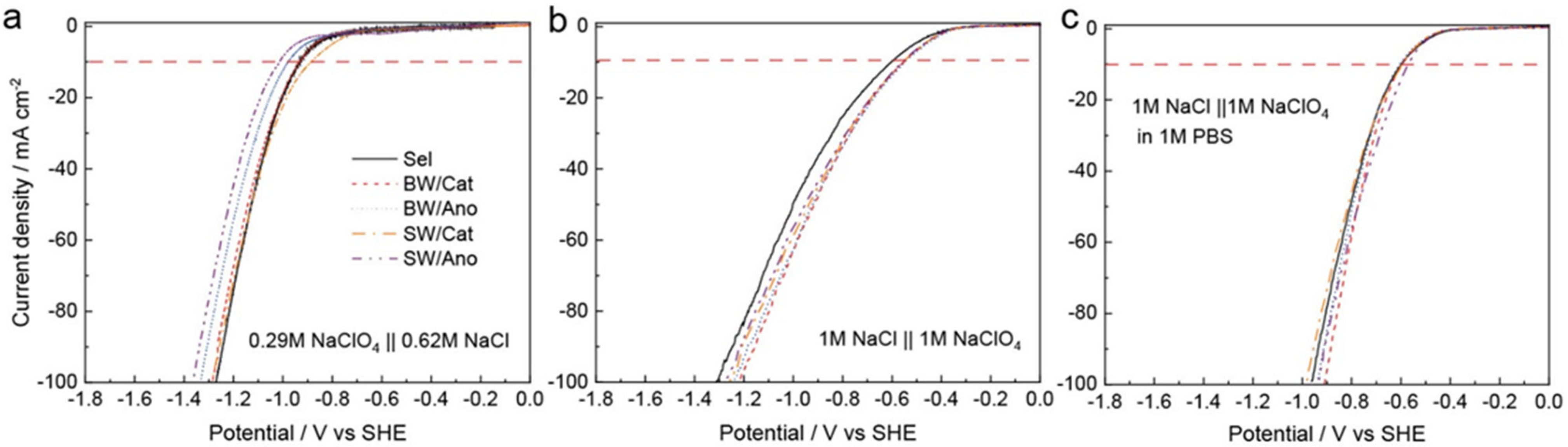




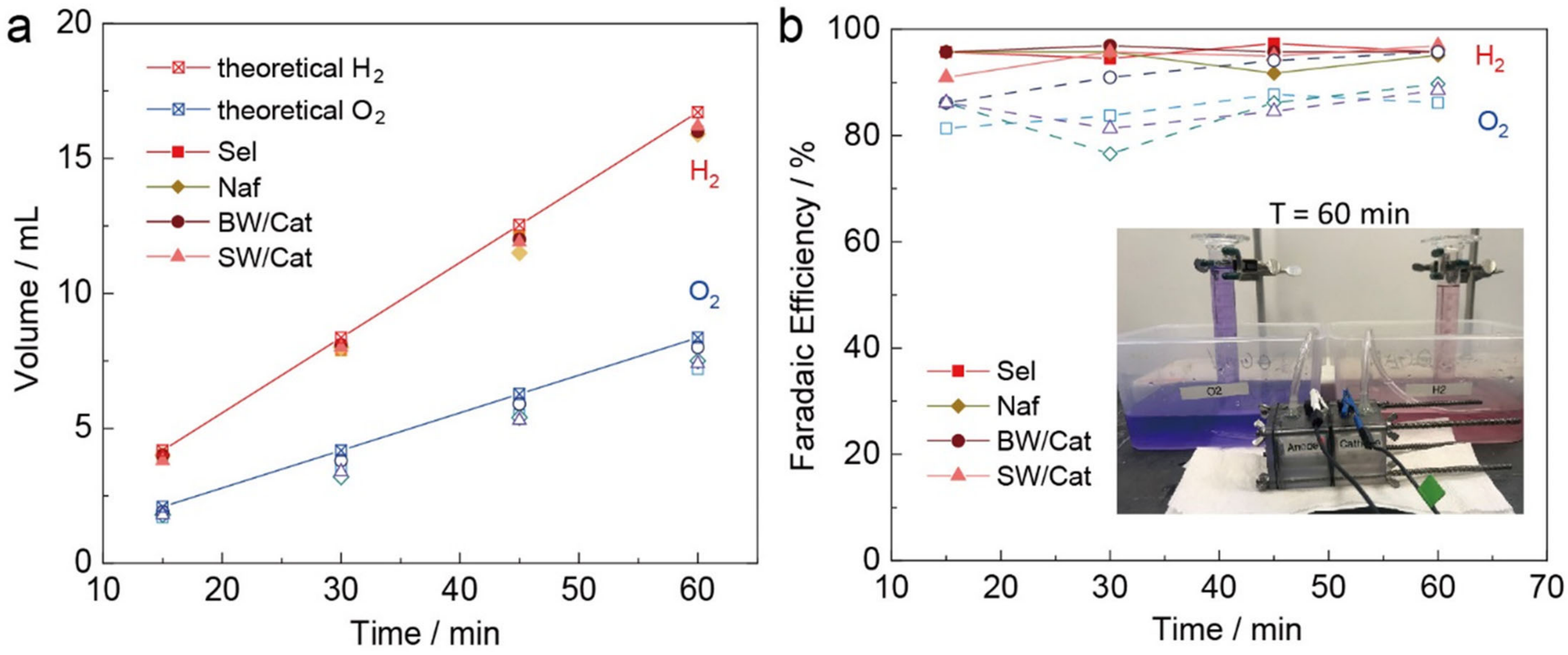
BW RO membrane can sustain current similar to Nafion (best CEM) for applied voltages



Current densities similar for membranes but solutions impacted overpotentials

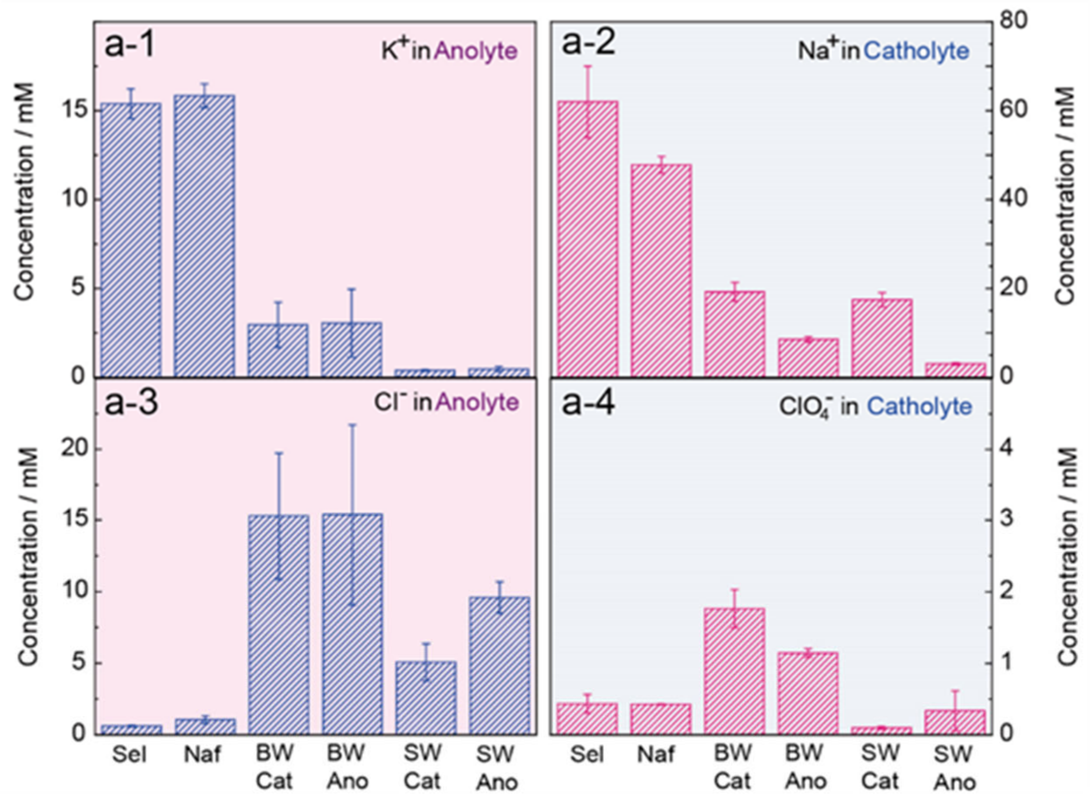


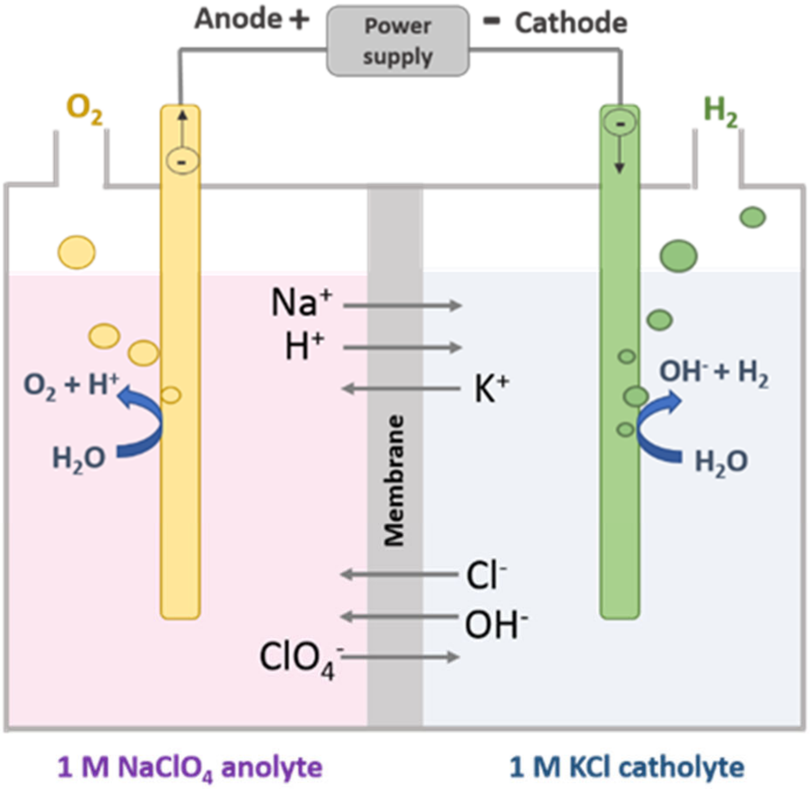
H_2 gas recovery (and O_2 evolution)



Using different counter ions to measure crossover

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

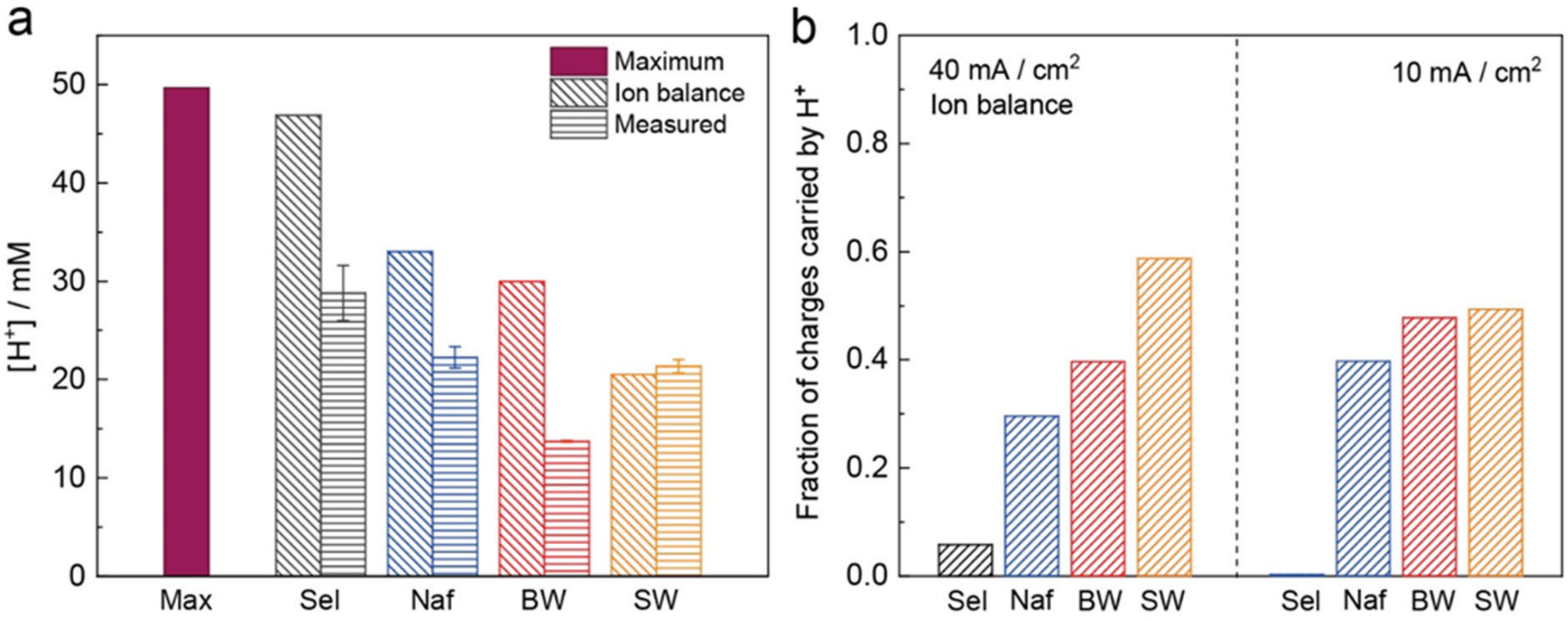




Comparison of proton transport through membranes to total ion transport

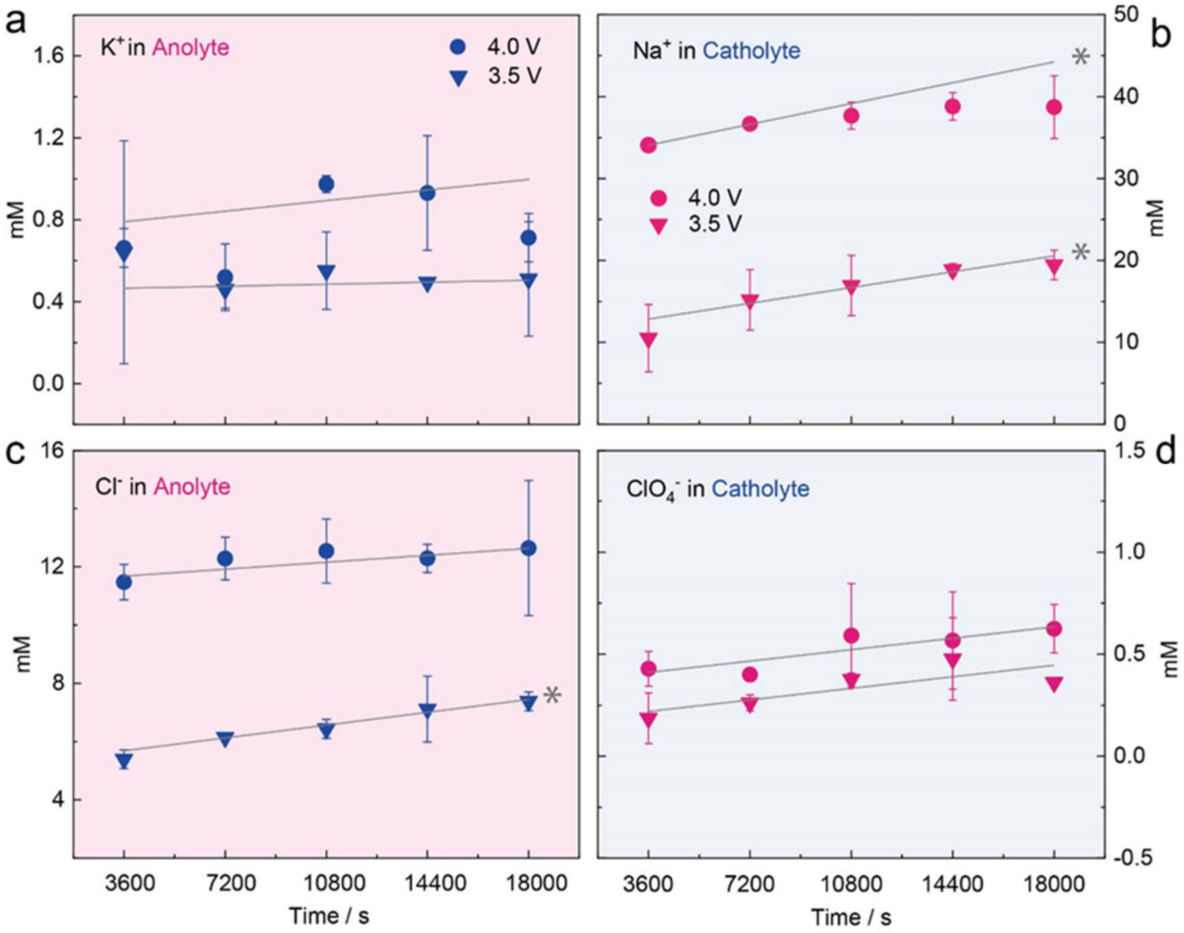
Method: Measure proton concentration (pH) to see how much H+ accumulated versus concentrations of salt ions.

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



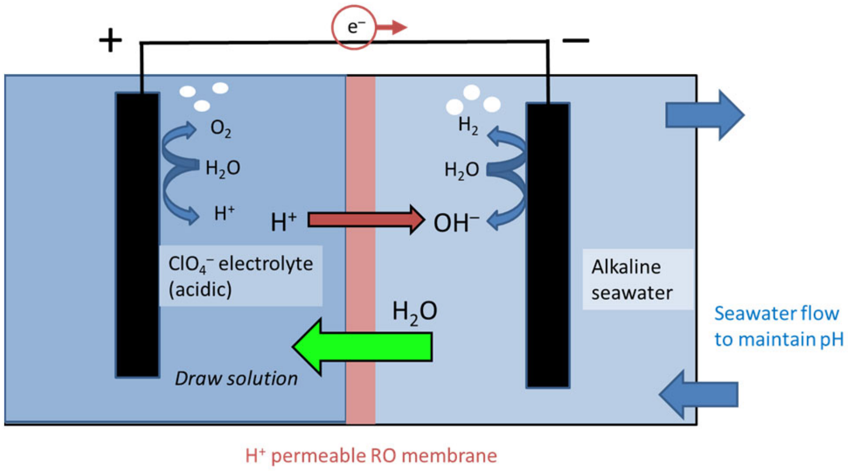
Analysis of whether ion transport changes over time

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



Other Considerations

- Explore inexpensive catalysts:
  - Replace Ir (An) & Pt (Cat) with BDD & Ni/C?
- 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)



What is the required water flux (LMH)?

- Assume we need 100 mA/m² for current
- Need 0.34 LMH of water (very low for RO)

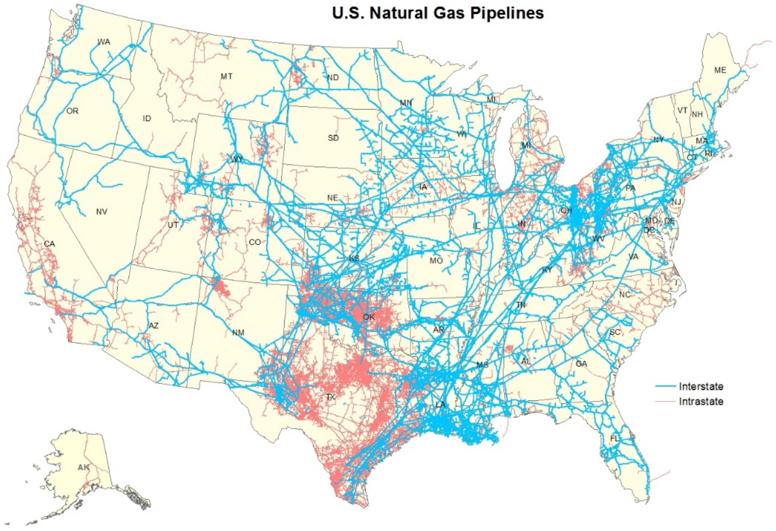
$$Q = 100\,\frac{\mathrm{mA}}{\mathrm{cm}^2}\,\frac{1\mathrm{A}}{10^3\ \mathrm{mA}}\,\frac{10^4\mathrm{cm}^2}{\mathrm{m}^2}\,\frac{1\ \mathrm{C}}{1\ \mathrm{A\ s}}\,\frac{3600\ \mathrm{s}}{\mathrm{h}}\,\frac{\mathrm{mol\ e^-}}{96{,}500\ \mathrm{C}}\,\frac{\mathrm{mole\ H_2}}{2\ \mathrm{e^-}}\,\frac{1\ \mathrm{mol\ H_20}}{1\ \mathrm{mol\ H_2}}\,\frac{1\ \mathrm{L}}{55.6\ \mathrm{mol}} = 0.34\ \mathrm{LMH}$$

Distribution of H_2

Energy grids = Electrical + Natural gas + H_2?

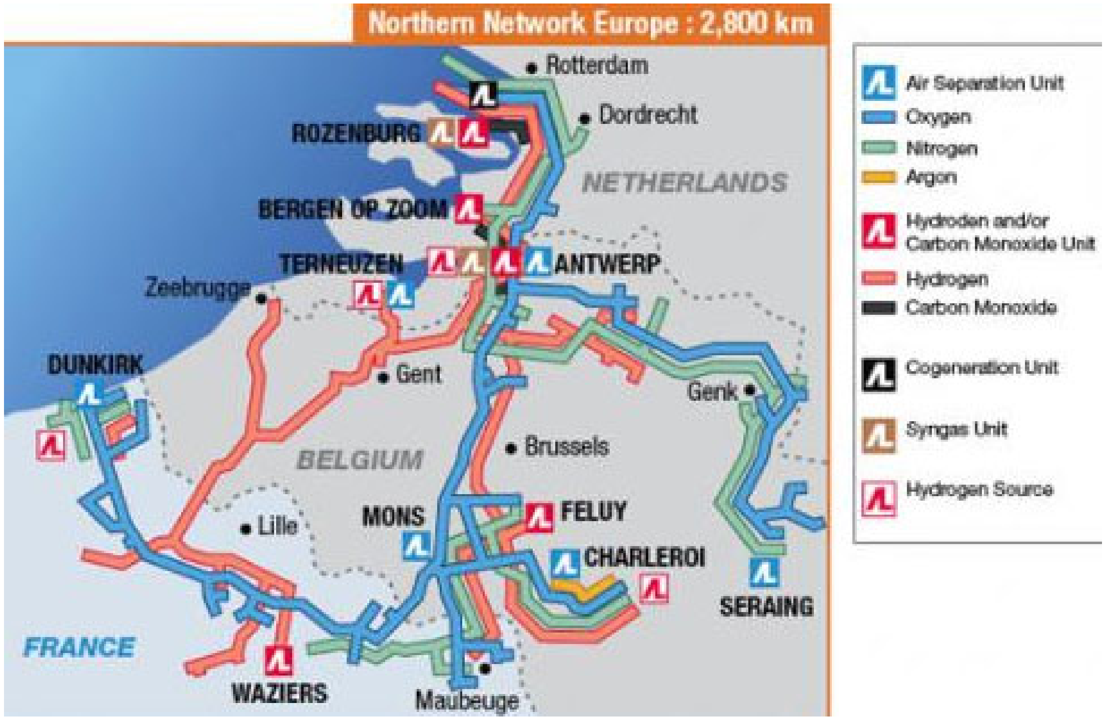
- Compression and transport in tanks?
- H_2 in pipelines
  - Can add it into natural gas pipelines (<5%)
  - Dedicated H_2 pipelines

Liquid hydrogen storage tank



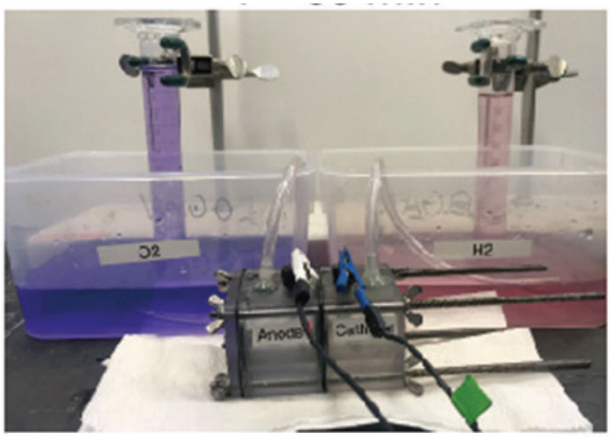
ource: American Energy Mapping (AEM) 2013

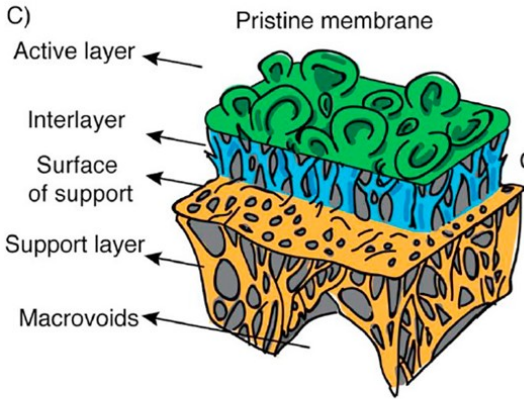
Hydrogen Pipelines: Europe & Gulf Coast USA



Conclusions

- **Some RO membranes** can be used to replace expensive ion exchange membranes in water electrolyzers
- The RO membranes allow H^+ and OH^- ions to move in the water to balance charge (not Na^+ or Cl^-)
- ClO_3^- ions are effectively kept separated in anode, but there is some leakage due to diffusion
- Use of RO membranes and less expensive catalysts could lower electrolyzer capital costs and enable H_2 production using seawater





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

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Energy & Mineral Eng.

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Questions / Comments