AIDIC

Associazione Termotecnica Italiana

Cicli webinar "fil rouge" 2021
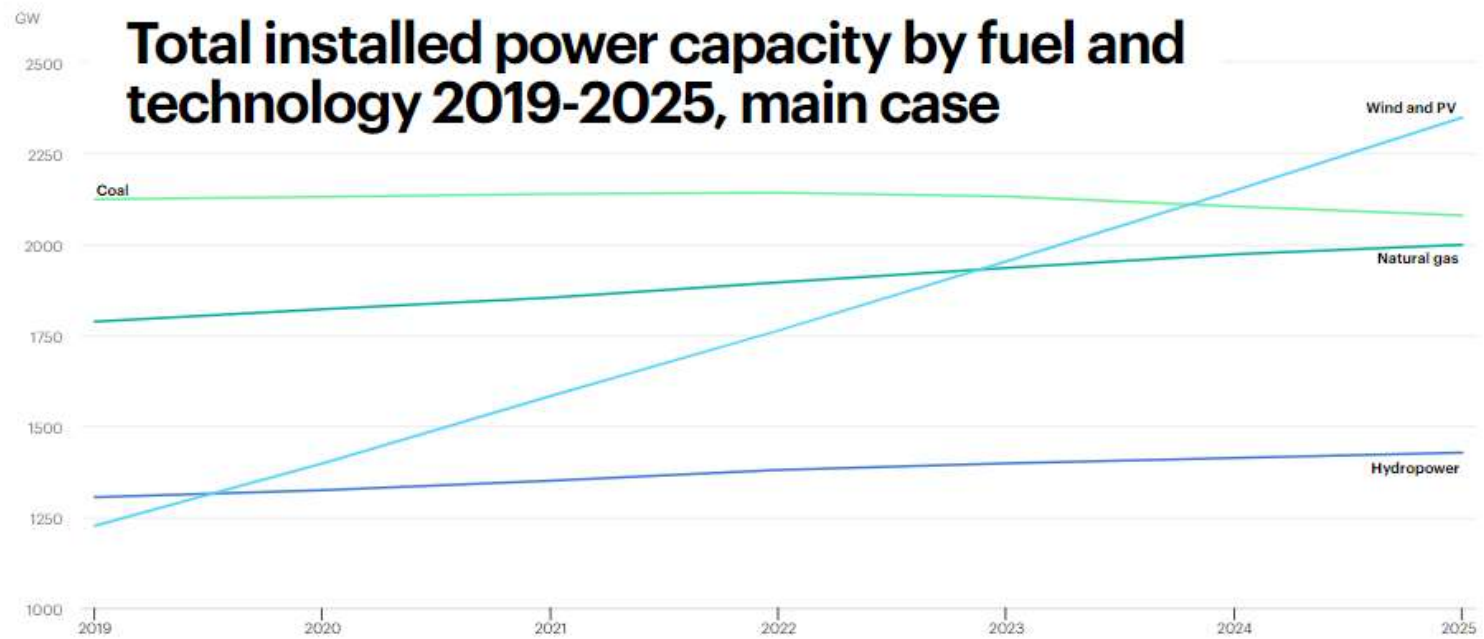
LA TRANSIZIONE ENERGETICA
3 GIUGNO

Prospettive dell'Elettrocatalisi nell'Industria Chimica

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NICL
Naples Industrial Chemistry Laboratory

www.nicl.it

Total installed power capacity by fuel and technology 2019-2025, main case

GW

- Wind and PV
- Coal
- Natural gas
- Hydropower

IEA, Total installed power capacity by fuel and technology 2019-2025, main case, IEA, Paris https://www.iea.org/data-and-statistics/charts/total-installed-power-capacity-by-fuel-and-technology-2019-2025-main-case

## PRODUZIONE LORDA DI ENERGIA ELETTRICA ITALIA

GWh; anni 1997-2019

	2018	2019*	Variazione (2018-2019)
Solidi	28'470	15'111	-46.92%
Gas naturale	128'538	143'198	11.41%
Prodotti petroliferi	3'289	3'369	2.43%
Altri	13'281	13'454	1.30%
Totale termoelettrico (A)	**173'578**	**175'132**	0.90%
Idroelettrico da pompaggi (B)	**1'716**	**1'723**	0.41%
Idroelettrico (da apporti naturali)	48'786	45'776	-6.17%
Eolico	17'716	20'245	14.28%
Fotovoltaico	22'654	23'689	4.57%
Geotermico	6'105	6'031	-1.21%
Biomassa e rifiuti	19'153	19'097	-0.29%
Totale rinnovabili (C)	**114'414**	**114'838**	0.37%
Totale (A+B+C)	**289'708**	**291'693**	0.69%

La voce "Prodotti petroliferi" comprende: olio combustibile, orimulsion, distillati leggeri, gasolio, coke di petrolio, bassi prodotti e altri residui della lavorazione del petrolio.
La voce "Altri" comprende: gas derivati, recuperi di calore ed espansione del gas compresso.
* Dati provvisori
Fonte: Elaborazioni Arera su dati GRTN/TERNA.

Rinnovabili flop. Deserta la gara Gse, assegnato solo il 12% degli incentivi

Il ministro Cingolani annuncia un nuovo decreto entro l'estate. Contratti diretti di fornitura di elettricità verde Axpo, Canadian, Solvay, Falck

di J.G.

27 maggio 2021

Il drammatico quinto bando

Di mese in mese, le aste per assegnare gli incentivi alle rinnovabili sono sempre più deserte. Il risultato del quinto bando ha visto svaporare l'88% delle offerte per incentivi alle rinnovabili, mentre il bando precedente aveva allocato un già modesto 25% di offerte di incentivi a solare, eolico e altre tecnologie rinnovabili.

Corrono i contratti diretti: Axpo, Canadian , Solvay, Falck

Anche il colosso chimico belga Solvay punta sull'energia rinnovabile e ha firmato un corporate power purchase agreement (Ppa) fisico con Falck Renewables della durata di 10 anni per lo sviluppo di un progetto solare in Puglia. Il 70% dell'elettricità prodotta dall'impianto solare andrà a beneficio di quattro dei sei stabilimenti italiani di Solvay: Bollate, Ospiate, Livorno e Rosignano, ottenendo una riduzione di emissioni annue di CO_2 di oltre 15mila tonnellate.

RENEWABLE POWER GENERATION INCREASINGLY OUT-COMPETES FOSSIL FUELS

Global weighted average LCOE and Auction/PPA prices for CSP, onshore and offshore wind, and solar PV, 2010 to 2023
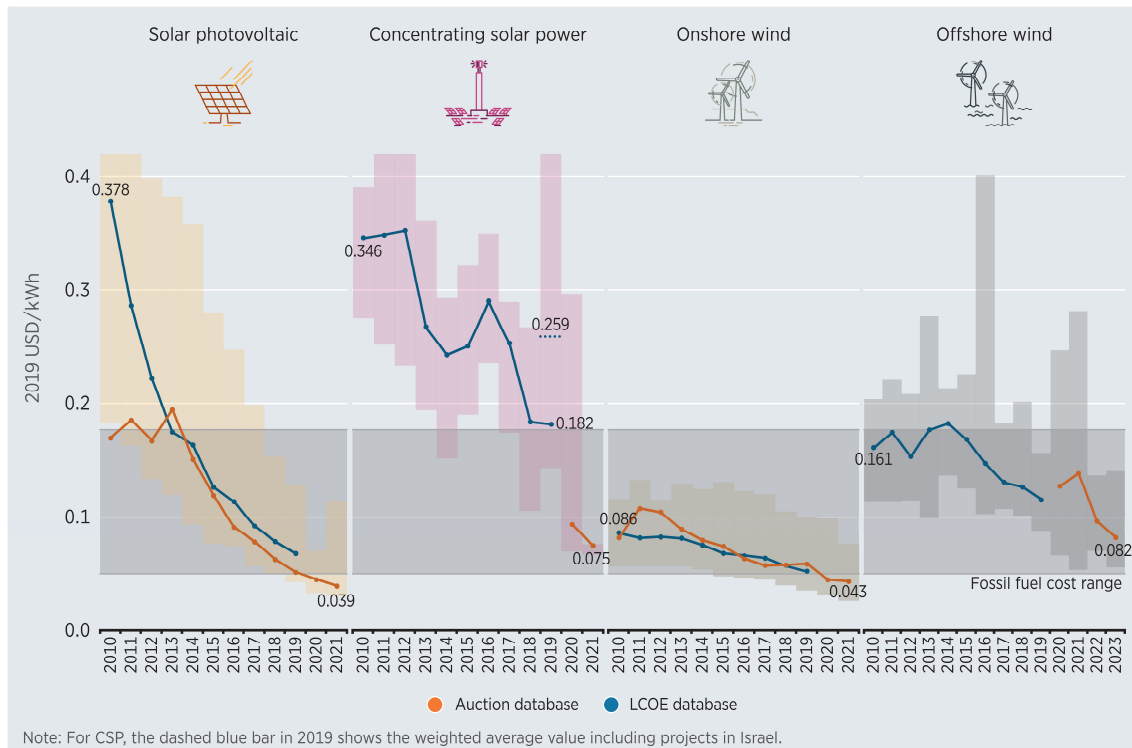
The thick lines are the global weighted average *LCOE, or auction values, by year. The grey bands that vary by year are cost/price range for the 5th and 95th percentiles of projects.. For the LCOE data, the real WACC** is 7.5% for OECD countries and China, and 10% for the rest of the world. The band that crosses the entire chart represents the fossil fuel-fired power generation cost range.
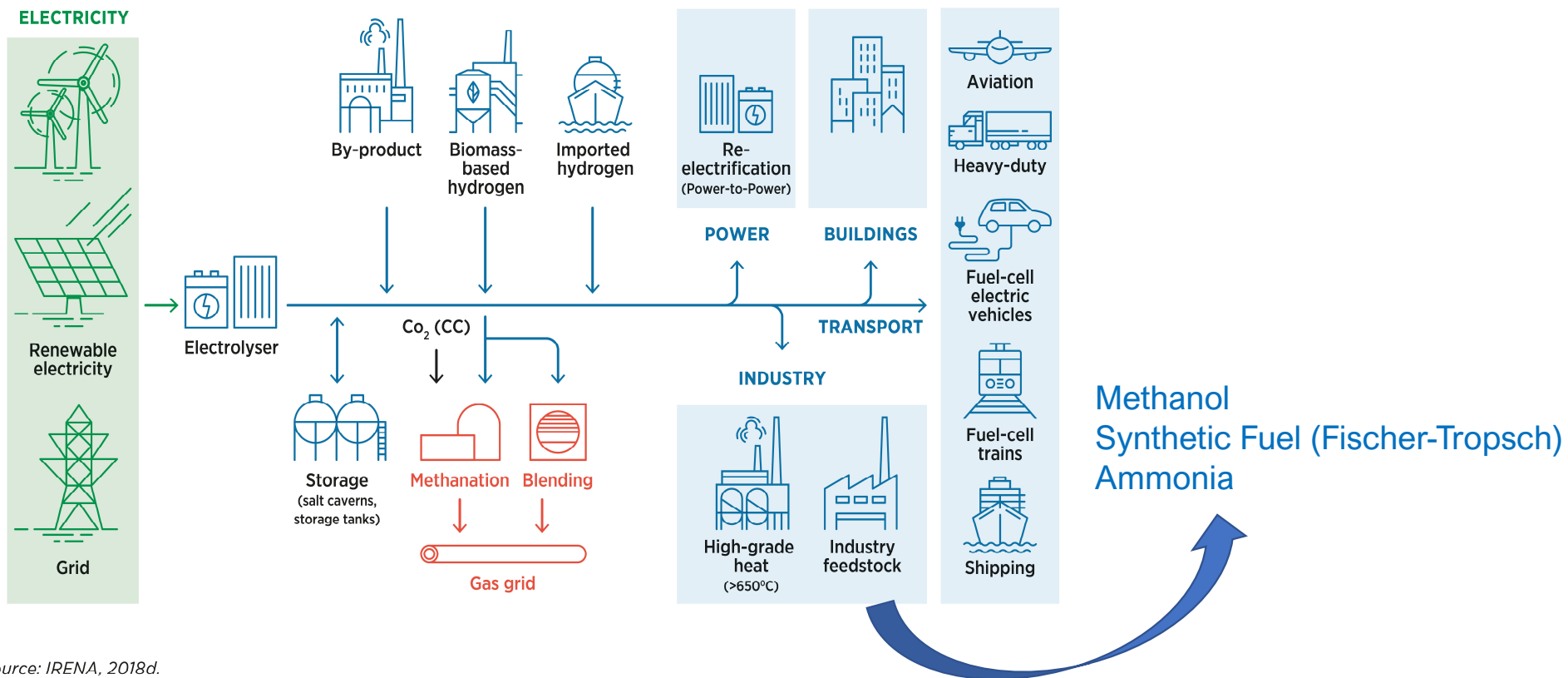
RENEWABLE POWER GENERATION COSTS 2019, International Renewable Energy Agency (IRENA)

*Global Data on Levelized Cost Of Electricity Generation (LCOE)
**Weighted average cost of capital (WACC)
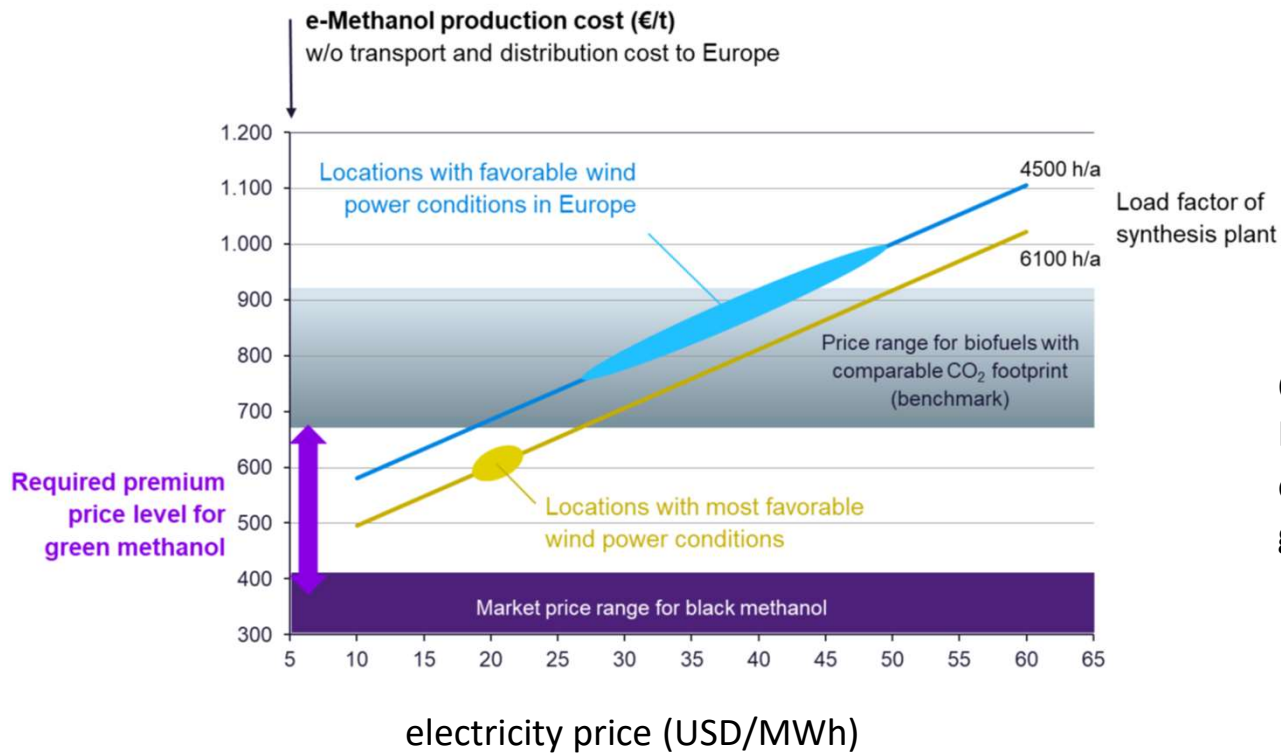
*Innovation landscape for a renewable-powered future:

Solution XI: Power to X

Integration of variable renewable energy (VRE) into end-uses by means of hydrogen

ELECTRICITY

Renewable electricity

Grid

Electrolyser

By-product

Biomass-based hydrogen

Imported hydrogen

Re-electrification (Power-to-Power)

POWER

BUILDINGS

CO_2 (CC)

Storage (salt caverns, storage tanks)

Methanation

Blending

Gas grid

INDUSTRY

High-grade heat (>650°C)

Industry feedstock

TRANSPORT

Aviation

Heavy-duty

Fuel-cell electric vehicles

Fuel-cell trains

Shipping

Methanol
Synthetic Fuel (Fischer-Tropsch)
Ammonia

Source: IRENA, 2018d.

*https://www.irena.org/publications/2019/Feb/Innovation-landscape-for-a-renewable-powered-future

e-Methanol production cost (€/t)
w/o transport and distribution cost to Europe

Locations with favorable wind power conditions in Europe

4500 h/a

Load factor of synthesis plant

6100 h/a

Price range for biofuels with comparable CO_2 footprint (benchmark)

Required premium price level for green methanol

Locations with most favorable wind power conditions

Market price range for black methanol

electricity price (USD/MWh)

Only one small commercial plant (4 kt/yr) in Iceland uses green Hydrogen from water electrolysis and CO_2 taken from local geological sources.

Withe paper "e-methanol". Siemens 2021

There are many regions worldwide benefiting from the generation of power from renewable sources
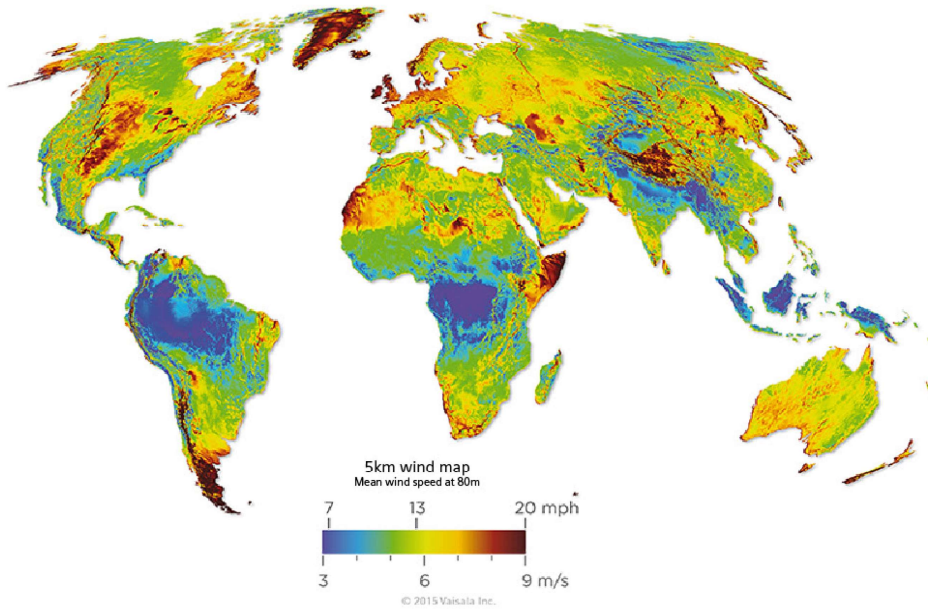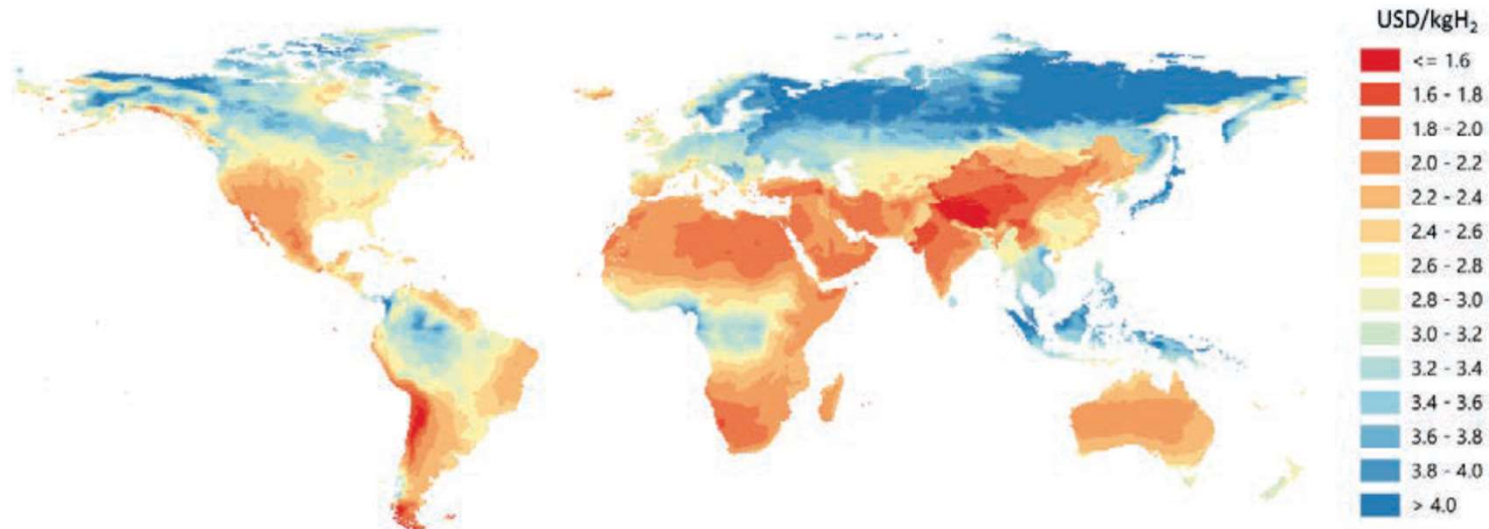

Global wind map
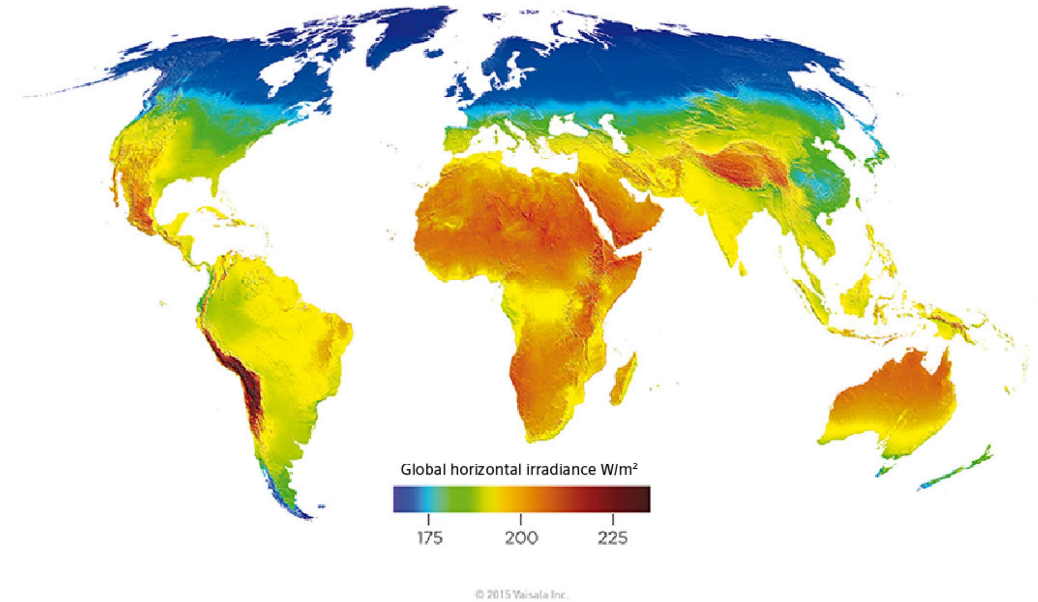
Global solar map

Hydrogen costs from hybrid solar PV and onshore wind systems in the long term.

USD/kgH₂

Color	Range
	<= 1.6
	1.6 - 1.8
	1.8 - 2.0
	2.0 - 2.2
	2.2 - 2.4
	2.4 - 2.6
	2.6 - 2.8
	2.8 - 3.0
	3.0 - 3.2
	3.2 - 3.4
	3.4 - 3.6
	3.6 - 3.8
	3.8 - 4.0
	> 4.0

Notes: This map is without prejudice to the status of or sovereignty over any territory, to the delimitation of international frontiers and boundaries and to the name of any territory, city or area. Electrolyser CAPEX = USD 450/kWe, efficiency (LHV) = 74%; solar PV CAPEX and onshore wind CAPEX = between USD 400–1 000/kW and USD 900–2 500/kW depending on the region; discount rate = 8%.
Source: IEA analysis based on wind data from Rife et al. (2014), *NCAR Global Climate Four-Dimensional Data Assimilation (CFDDA) Hourly 40 km Reanalysis* and solar data from renewables.ninja (2019).

The Future of Hydrogen Report prepared by the IEA for the G20, Japan
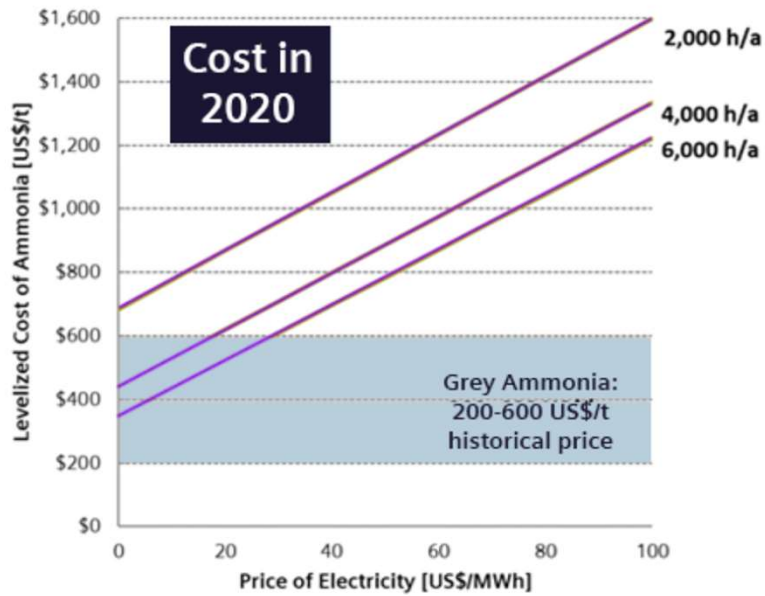Seizing today's opportunities., IEA June 2019

Hydrogen production costs using natural gas in different regions, 2018
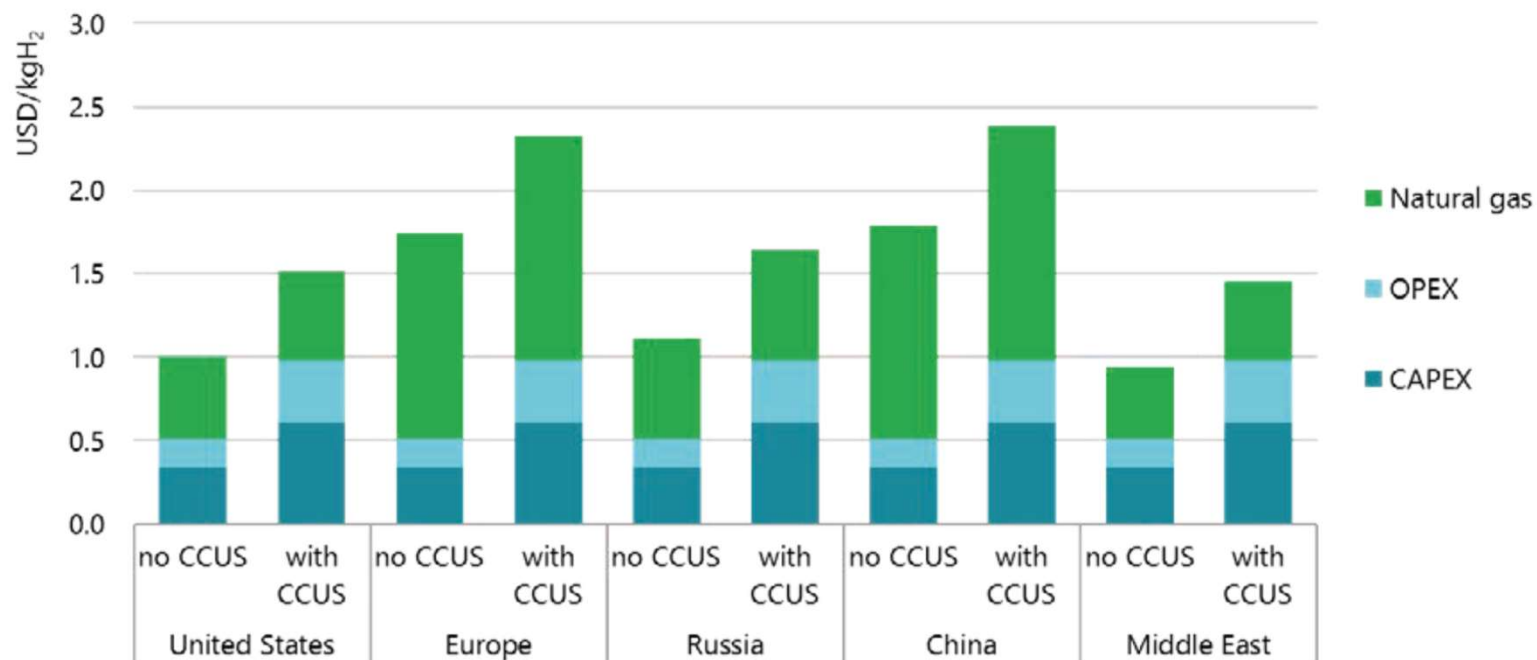
Notes: kgH2 = kilogram of hydrogen; OPEX = operational expenditure. CAPEX in 2018: SMR (steam methane reforming) without CCUS (carbon capture, utilisation and storage) = USD 500–900 per kilowatt hydrogen (kWH2), SMR with CCUS = USD 900–1 600/kWH2, with ranges due to regional differences. Gas price = USD 3–11 per million British thermal units (MBtu) depending on the region. More information on the underlying assumptions is available at www.iea.org/hydrogen2019.
Source: IEA 2019.

The Future of Hydrogen Report prepared by the IEA for the G20, Japan
Seizing today's opportunities., IEA June 2019

e-ammonia's positive business case: production cost is lower in geographies with favourable renewable electricity resources

Cost in 2020

Levelized Cost of Ammonia [US$/t]

2,000 h/a
4,000 h/a
6,000 h/a

Grey Ammonia: 200-600 US$/t historical price

Price of Electricity [US$/MWh]

Source: Siemens. Assumptions: 2020 Prices. WACC 8%, Aboveground hydrogen storage (2 days) based on high HB flexiblity.[4] HB / ASU CAPEX based on 600 MTPD.[3] No ammonia storage or transport considered.

Fossil fuel derived ammonia is subject to price fluctuations and fossil fuel price volatility.

Fossil Ammonia Price [US$/t]

USA
Black Sea
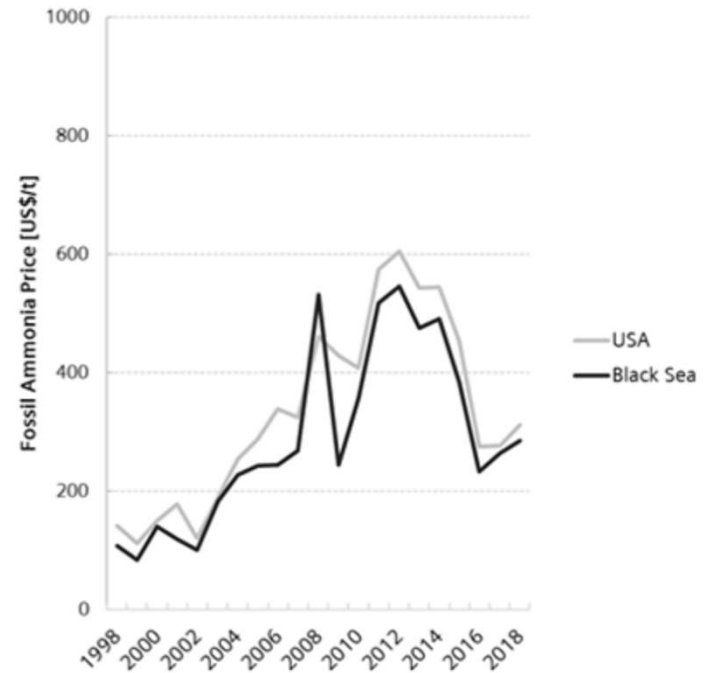
Source: Nutrien Factbook 2019

White paper l Power-to-X: A closer look at e-Ammonia. Simens 2021

Indicative production costs of electricity-based pathways in the near and long term
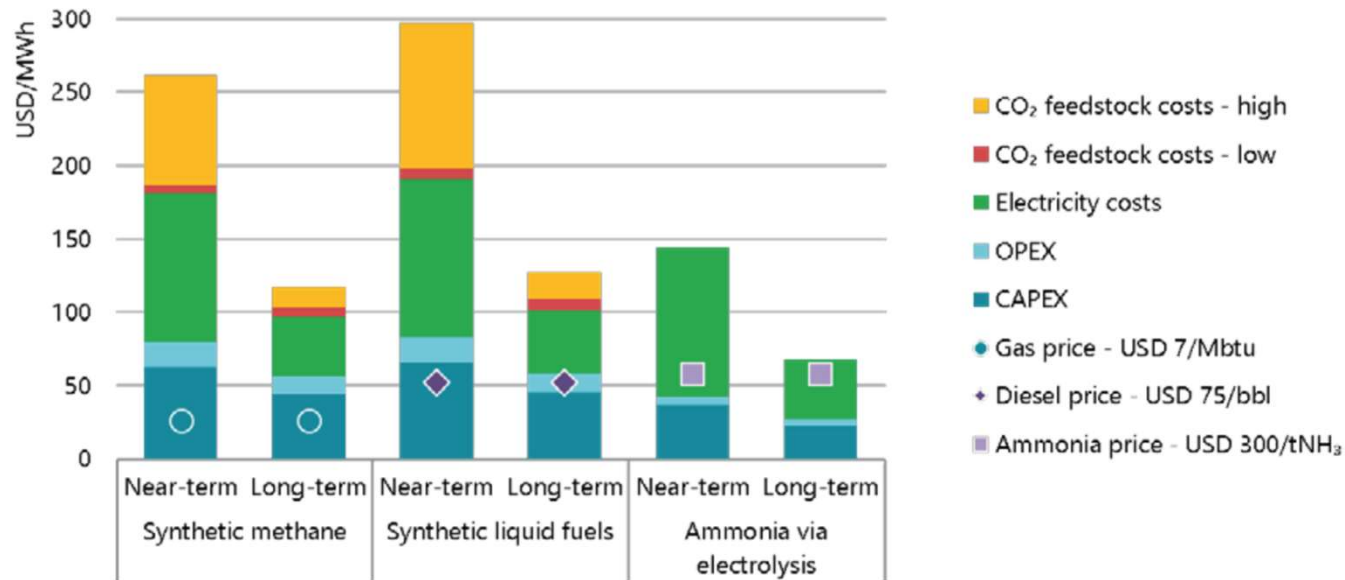
Notes: NH3 = ammonia.; renewable electricity price = USD 50/MWh at 3 000 full load hours in near term and USD 25/MWh in long term; CO2 feedstock costs lower range based on CO2 from bioethanol production at USD 30/tCO2 in the near and long term; CO2 feedstock costs upper range based on DAC = USD 400/tCO2 in the near term and USD 100/tCO2 in the long term; discount rate = 8%.
Source: IEA 2019.

Estimated ammonia production costs from solar and wind in China, 2020
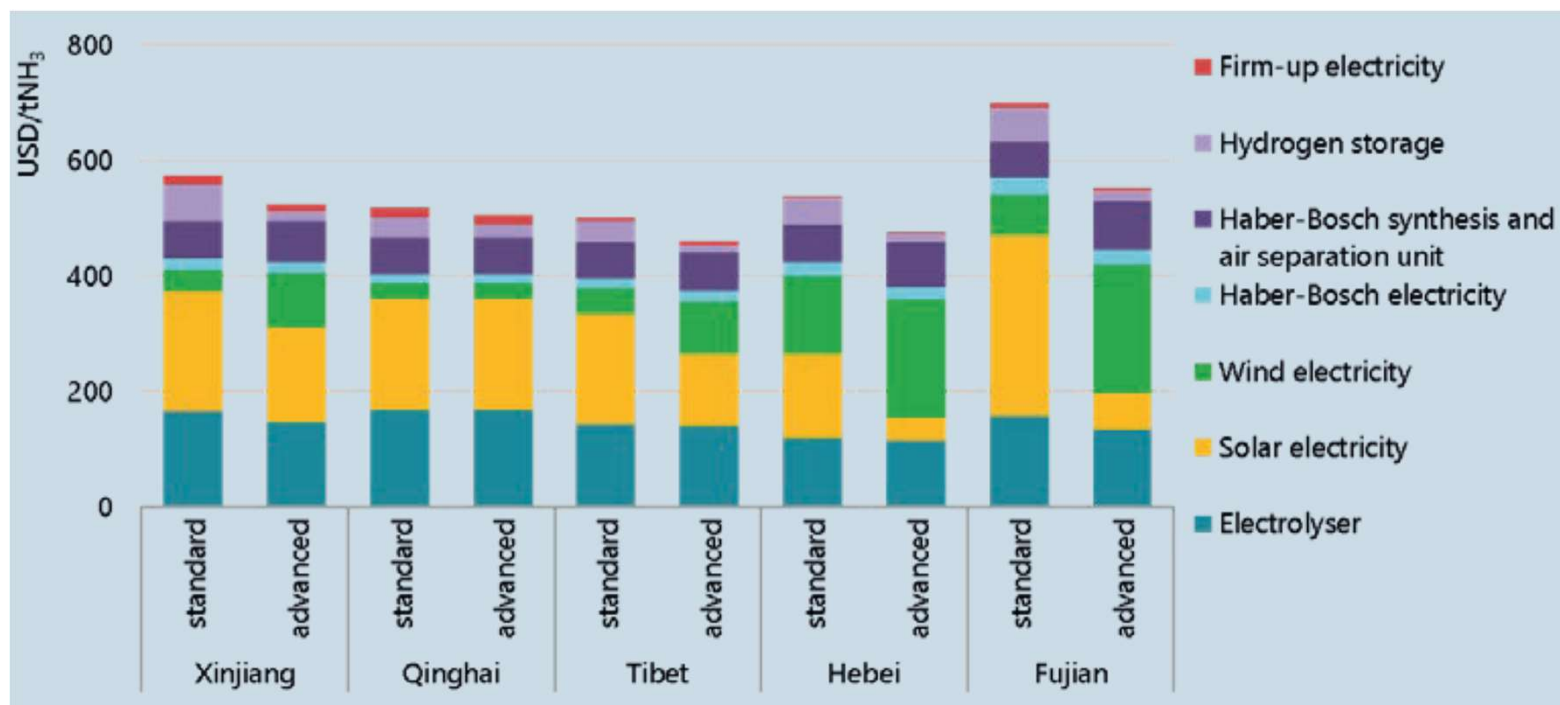
Notes: tNH3 = tonne of ammonia. Left-hand bars correspond to "standard" flexibility of the Haber-Bosch operations with a 40% downward flexibility of the Haber-Bosch synthesis; right-hand bars correspond to the "advanced" flexibility case, allowing 80% downward flexibility and the possibility of shutting down the synthesis process completely. From bottom to top, the bars show the following costs: electrolyser, electricity from solar and wind for hydrogen production, renewable electricity for running the Haber- Bosch synthesis, Haber-Bosch synthesis and air separation unit for nitrogen production, hydrogen buffer storage and firm-up electricity to run the Haber-Bosch process when there is not enough wind at night.
Source: IEA 2019..

A combination of cost reductions in electricity and electrolysers, combined with increased efficiency and operating lifetime, can deliver 80% reduction in hydrogen cost.
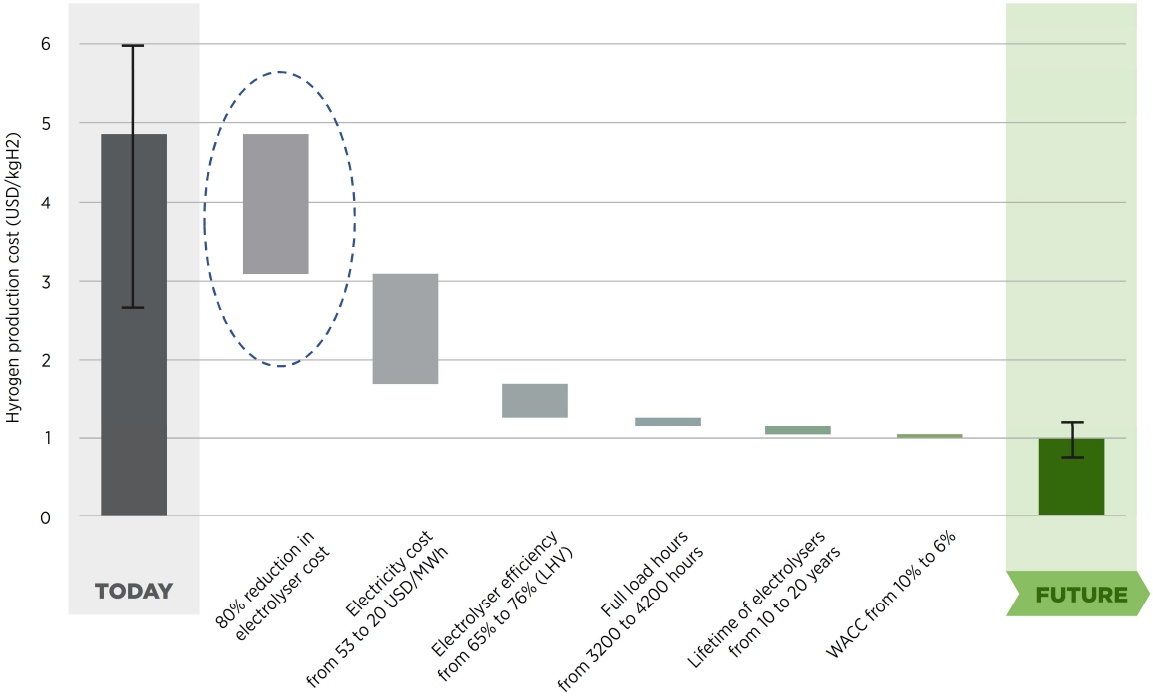
Note: 'Today' captures best and average conditions. 'Average' signifies an investment of USD 770/kilowatt (kW), efficiency of 65% (lower heating value – LHV), an electricity price of USD 53/MWh, full load hours of 3200 (onshore wind), and a weighted average cost of capital (WACC) of 10% (relatively high risk). 'Best' signifies investment of USD 130/kW, efficiency of 76% (LHV), electricity price of USD 20/MWh, full load hours of 4200 (onshore wind), and a WACC of 6% (similar to renewable electricity today).
Based on IRENA analysis (2020)

Different types of commercially available electrolysis technologies.
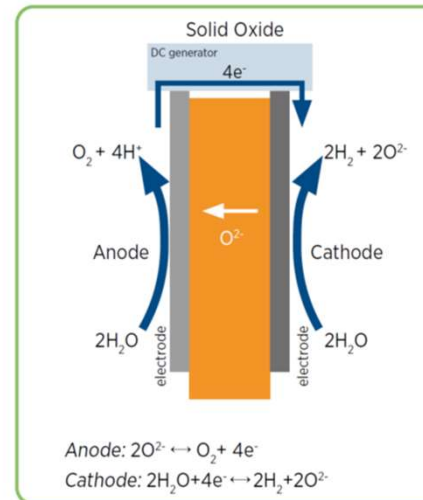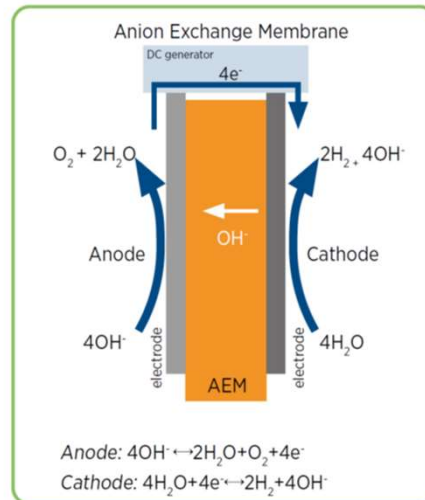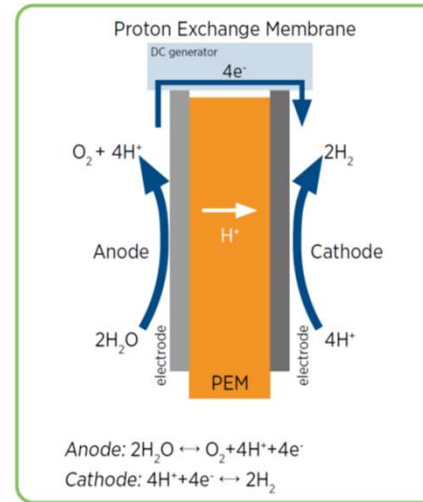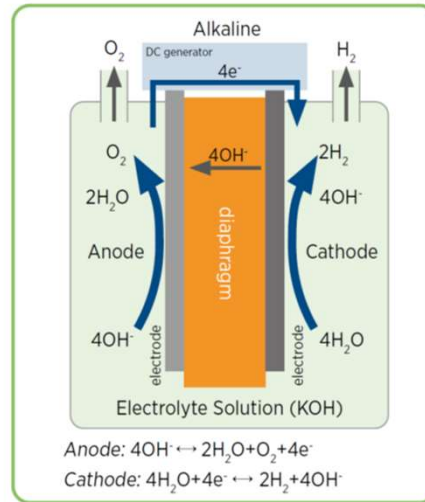
Based on IRENA analysis.

Characterisation of the four types of water electrolysers.

	Alkaline	PEM	AEM	Solid Oxide
Operating temperature	70-90 °C	50-80 °C	40-60 °C	700-850 °C
Operating pressure	1-30 bar	< 70 bar	< 35 bar	1 bar
Electrolyte	Potassium hydroxide (KOH) 5-7 molL^{-1}	PFSA membranes	DVB polymer support with KOH or NaHCO3 1molL^{-1}	Yttria-stabilized Zirconia (YSZ)
Separator	ZrO$_2$ stabilized with PPS mesh	Solid electrolyte (above)	Solid electrolyte (above)	Solid electrolyte (above)
Electrode / catalyst (oxygen side)	Nickel coated perforated stainless steel	Iridium oxide	High surface area Nickel or NiFeCo alloys	Perovskite-type (e.g. LSCF, LSM)
Electrode / catalyst (hydrogen side)	Nickel coated perforated stainless steel	Platinum nanoparticles on carbon black	High surface area nickel	Ni/YSZ
Porous transport layer anode	Nickel mesh (not always present)	Platinum coated sintered porous titanium	Nickel foam	Coarse Nickel-mesh or foam
Porous transport layer cathode	Nickel mesh	Sintered porous titanium or carbon cloth	Nickel foam or carbon Cloth	None
Bipolar plate anode	Nickel-coated stainless steel	Platinum-coated titanium	Nickel-coated stainless steel	None
Bipolar plate cathode	Nickel-coated stainless steel	Gold-coated titanium	Nickel-coated Stainless steel	Cobalt-coated stainless steel
Frames and sealing	PSU, PTFE, EPDM	PTFE, PSU, ETFE	PTFE, Silicon	Ceramic glass

Note: Coloured cells represent conditions or components with significant variation among different companies. PFSA = Perfluoroacidsulfonic; PTFE = Polytetrafluoroethylene; ETFE = Ethylene Tetrafluorethylene; PSF = poly (bisphenol-A sulfone); PSU = Polysulfone; YSZ = yttriastabilized zirconia; DVB = divinylbenzene; PPS = Polyphenylene sulphide; LSCF = La$_{0.58}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$; LSM = (La$_{1-x}$Sr$_x$)$_{1-y}$MnO$_3$; § = Crofer22APU with co-containing protective coating.

Based on IRENA analysis.

Key performance indicators for four electrolyser technologies today and in 2050.

	2020				2050			
	Alkaline	PEM	AEM	SOEC	Alkaline	PEM	AEM	SOEC
Cell pressure [bara]	< 30	< 70	< 35	< 10	> 70	> 70	> 70	> 20
Efficiency (system) [kWh/KgH$_2$]	50-78	50-83	57-69	45-55	< 45	< 45	< 45	< 40
Lifetime [thousand hours]	60	50-80	> 5	< 20	100	100-120	100	80
Capital costs estimate for large stacks (stack-only, > 1 MW) [USD/kW$_{el}$]	270	400	-	> 2 000	< 100	< 100	< 100	< 200
Capital cost range estimate for the entire system, >10 MW [USD/kW$_{el}$]	500-1000	700-1400	-	-	< 200	< 200	< 200	< 300

Note: PEM = Polymer Electrolyte Membrane (commercial technology); AEM = Anion Exchange Membrane (lab-scale today);
SOEC = Solid Oxide Electrolysers (lab-scale today).
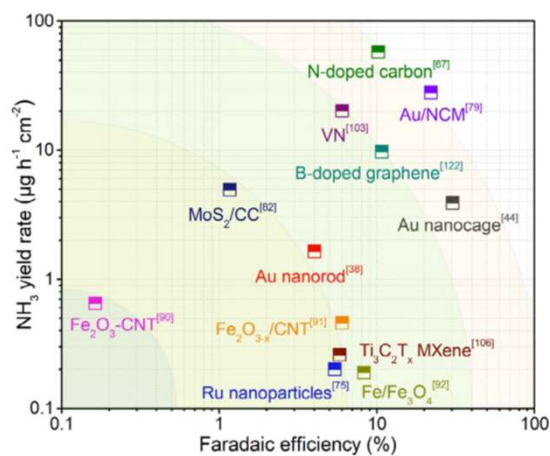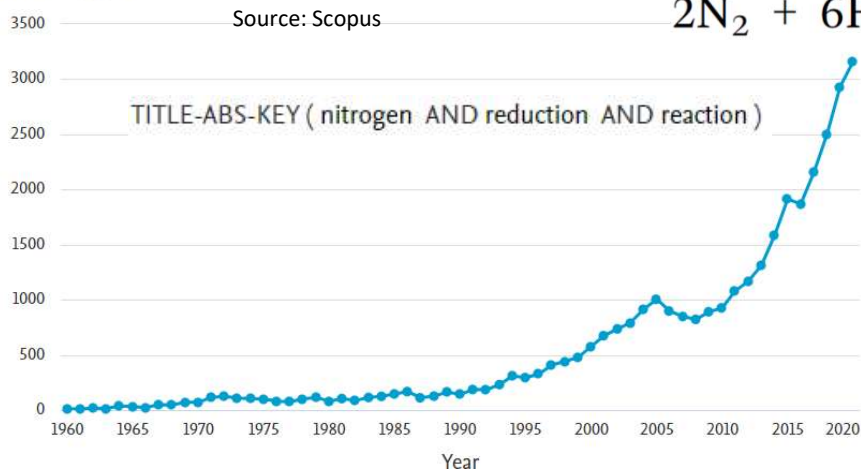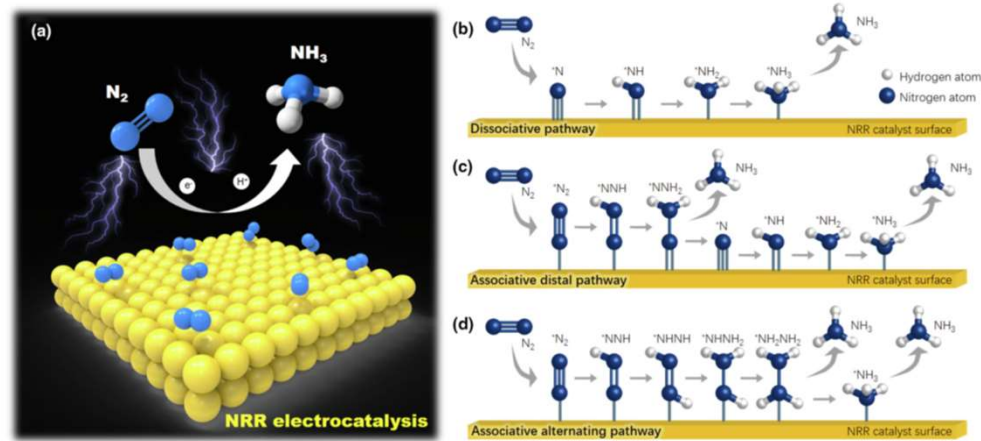Based on IRENA analysis.

Nitrogen Reduction Reaction (NRR)

$$2N_2 + 6H_2O \rightarrow 4NH_3 + 3O_2$$
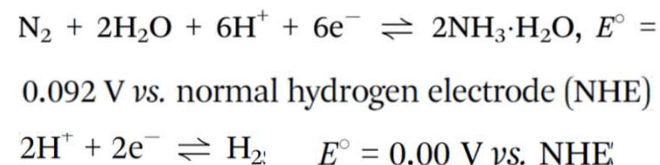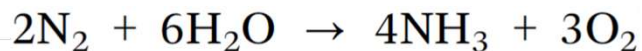
Documents by year

Source: Scopus

TITLE-ABS-KEY (nitrogen AND reduction AND reaction)

$$N_2 + 2H_2O + 6H^+ + 6e^- \rightleftharpoons 2NH_3 \cdot H_2O, \; E^\circ =$$

0.092 V vs. normal hydrogen electrode (NHE)

$$2H^+ + 2e^- \rightleftharpoons H_2, \quad E^\circ = 0.00 \text{ V vs. NHE}$$

Schematic illustrations of (a) the nitrogen reduction reaction (NRR) electrocatalysis and its possible mechanisms, including (b) dissociative pathway, (c) associative distal pathway, and (d) associative alternating pathway

An NRR performance map of different catalysts in terms of the NH$_3$ yield rate and the Faradaic efficiency. (NCM: nitrogen-doped nanoporous carbonmembranes; CC: carbon cloth; CNT: carbon nanotube; Fe$_2$O$_{3-x}$: Fe$_2$O$_3$-containing oxygen vacancies)

For electrochemical NH$_3$ synthesis to be competitive with the current H–B process, it would need to achieve at least a similar level of energy efficiency and NH$_3$ yield rate to the H–B process, i.e. **~ 70% and ~ 30 µmol h^{-1} mg$_{cat}$ $^{-1}$**, respectively.
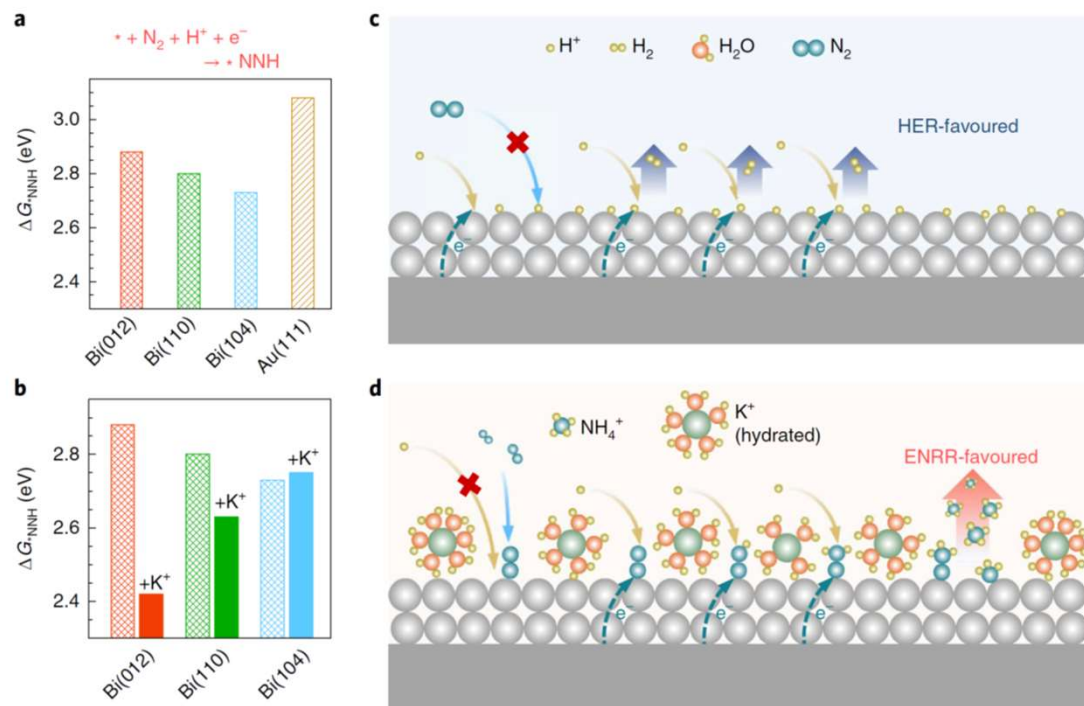
Faradaic efficiency of 66% and ammonia yield of 200 µmol mg$_{cat}$$^{-1}$ h^{-1}

Hao, YC., Guo, Y., Chen, LW. *et al.* Promoting nitrogen electroreduction to ammonia with bismuth nanocrystals and potassium cations in water. *Nat Catal* **2, 448–456 (2019).** https://doi.org/10.1038/s41929-019-0241-7

Promoting the NRR with bismuth catalysts and potassium cations.
a, The free-energy change (ΔG*NNH) required to form *NNH (* + N$_2$+ H$^+$ + e$^-$→ *NNH) on Bi (012), (110), (104) and Au (111) facets.
b, ΔG*NNH on Bi (012), (110) and (104) facets without (patterned bars) and with (filled bars) K$^+$ cations.
c,d, Mass transfer of protons and nitrogen molecules to the catalyst surface in electrolytes without (c) and with (d) K$^+$ cations. c, In acidic solutions without K$^+$ cations, protons can be transferred to the surface readily, and HER will dominate. d, K$^+$ hinders proton transfer to the catalyst surfaces. Nitrogen will be adsorbed preferentially, and the NRR is promoted.

# Carbon dioxide Reduction Reaction (CO$_2$RR)

Documents by year

Source: Scopus

TITLE-ABS-KEY (carbon AND dioxide AND reduction AND reaction)
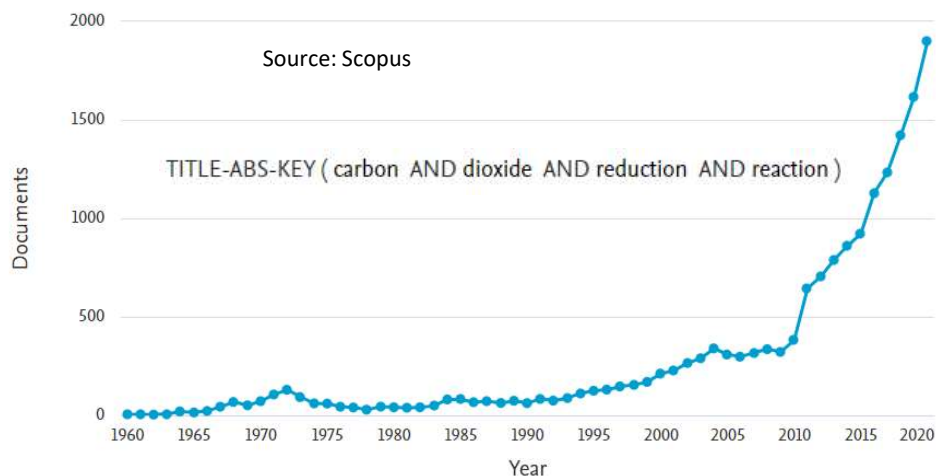
| Reaction	E^0/V (vs. SHE)
$CO_2 + e^- \rightarrow CO_2^{-\bullet}$	1.90
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.530
$CO_2 + 2H_2O + 2e^- \rightarrow CO + 2OH^-$	−1.347
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.610
$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$	−1.491
$CO_2 + 4H^+ + 4e \rightarrow HCHO + H_2O$	−0.480
$CO_2 + 3H_2O + 4e^- \rightarrow HCHO + 4OH^-$	−1.311
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.380
$CO_2 + 5H_2O + 6e^- \rightarrow CH_3OH + 6OH^-$	−1.225
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.240
$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^-$	−1.072
$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O$	−0.200
$CO_2 + 2H_2O + 4e^- \rightarrow C + 4OH^-$	−1.040
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	−0.340
$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-$	−1.177
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	−0.270
$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	−0.913
$2CO_2 + 2e^- \rightarrow C_2O_4^{2-}$	−1.003
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	−0.330
$2CO_2 + 9H_2O + 12e \rightarrow C_2H_5OH + 12OH$	−1.157
$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH + 5H_2O$	−0.320
$2H^+ + 2e^- \rightarrow H_2$	−0.420

Half reactions of CO2 reduction for possible processes along with the corresponding standard redox potential (25 1C, 1 atmosphere of gases and 1 M solutes in aqueous solution)
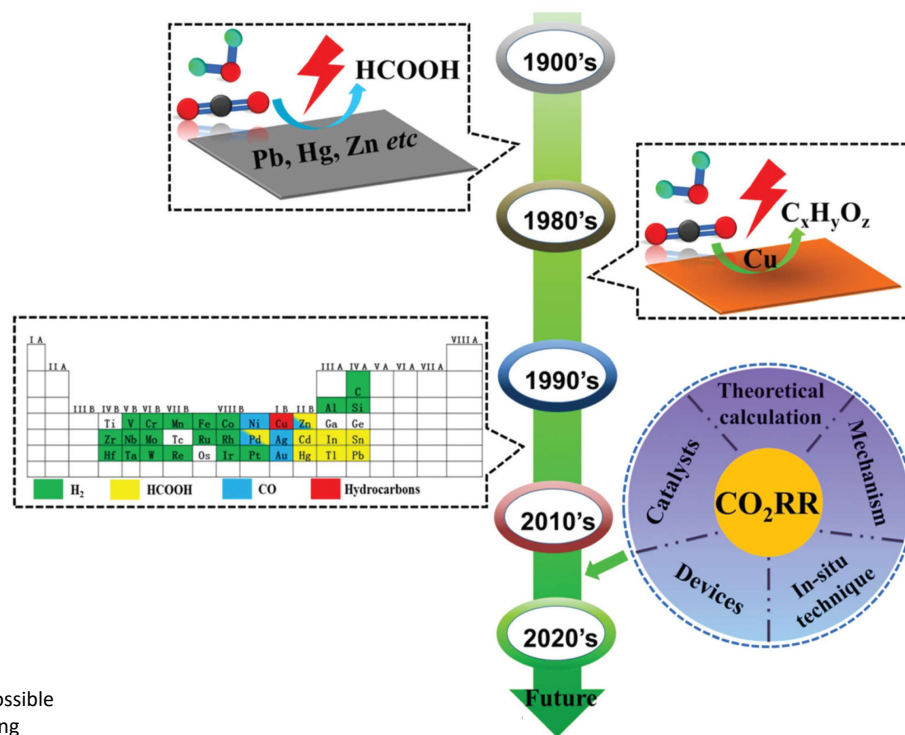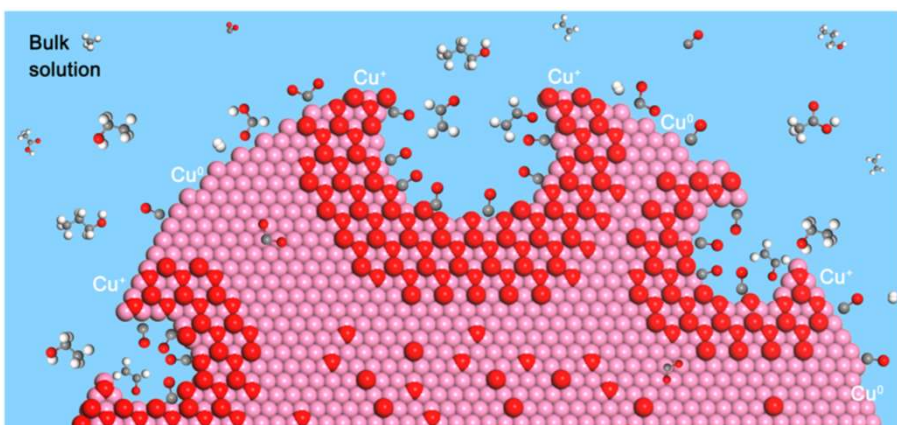
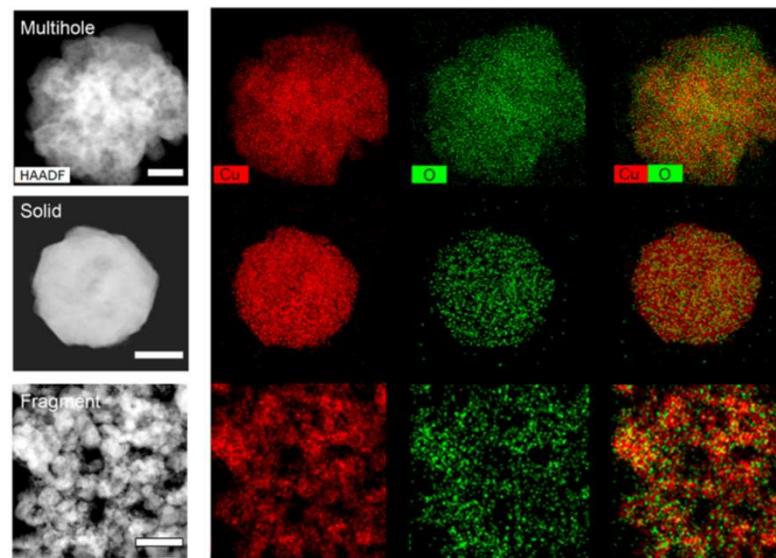# The possible reaction roadmap of CO$_2$
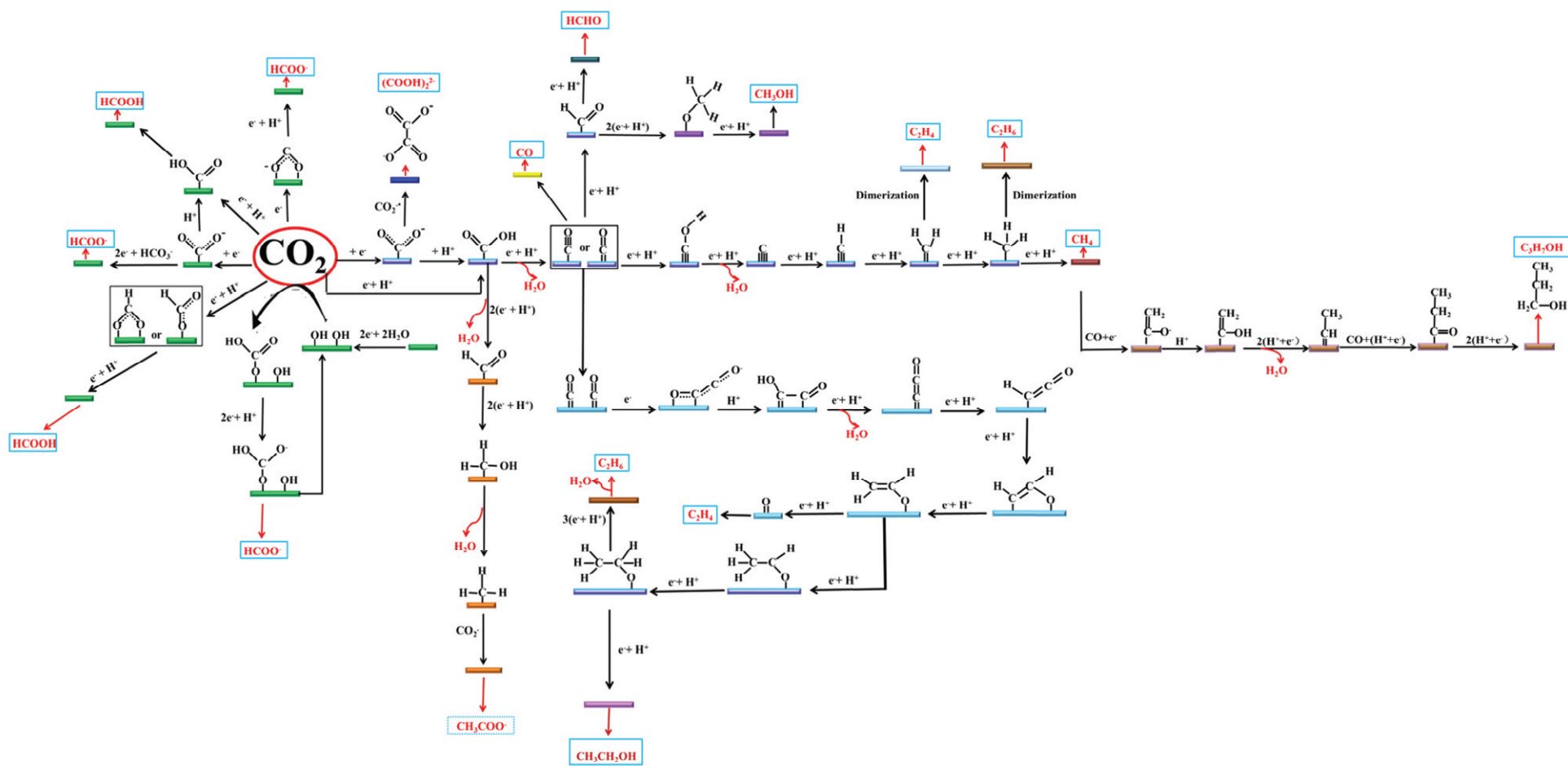
Continue improve in catalytic performances
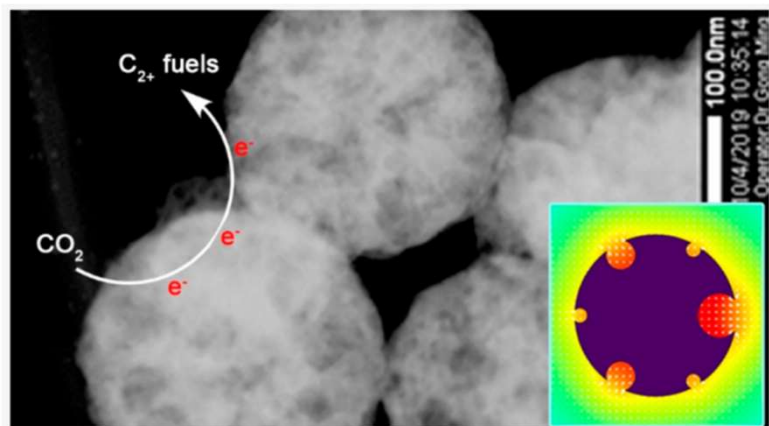
Copper in the +1 oxidation state has been thought to be active for catalyzing C_{2+} formation, whereas it is prone to being reduced to Cu^0 at cathodic potentials. Catalysts with nanocavities can confine carbon intermediates formed in situ, which in turn covers the local catalyst surface and thereby stabilizes Cu^+ species. Experimental measurements on multihollow cuprous oxide catalyst exhibit a C_{2+} **Faradaic efficiency of 75.2 ± 2.7%** at a C_{2+} **partial current density of 267 ± 13 mA cm^{-2}** and a large **C_{2+}-to-C_1 ratio of ~7.2.**

Scanning TEM-EDX elemental mapping of multihollow, solid, and fragment Cu_2O samples, showing the homogeneous distribution of Cu (red) and O (green).
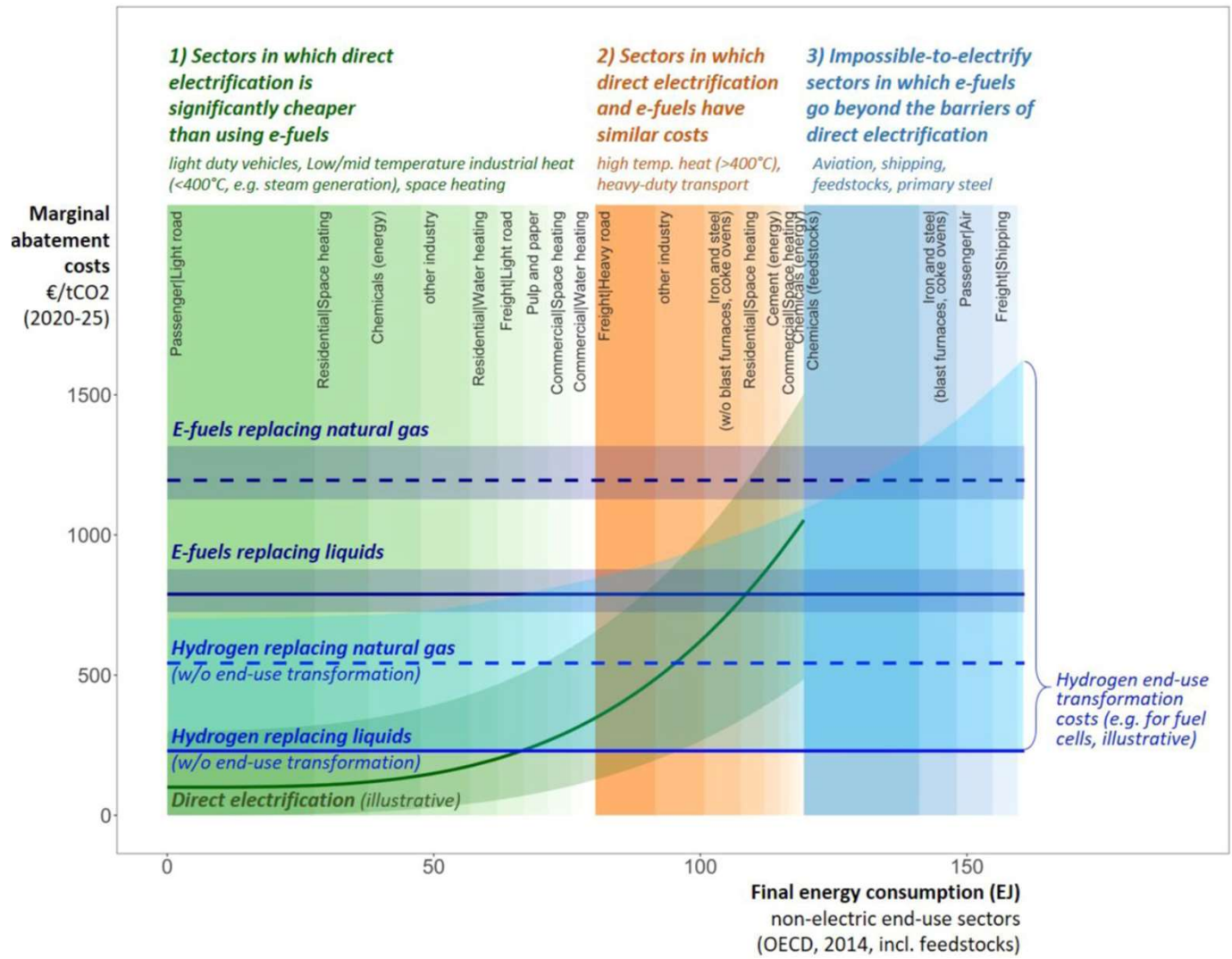

Schematic of carbon intermediates that are confined in the nanocavities, which locally protect copper oxidation state during CO2RR. White: hydrogen; gray: carbon; red: oxygen; violet: copper.
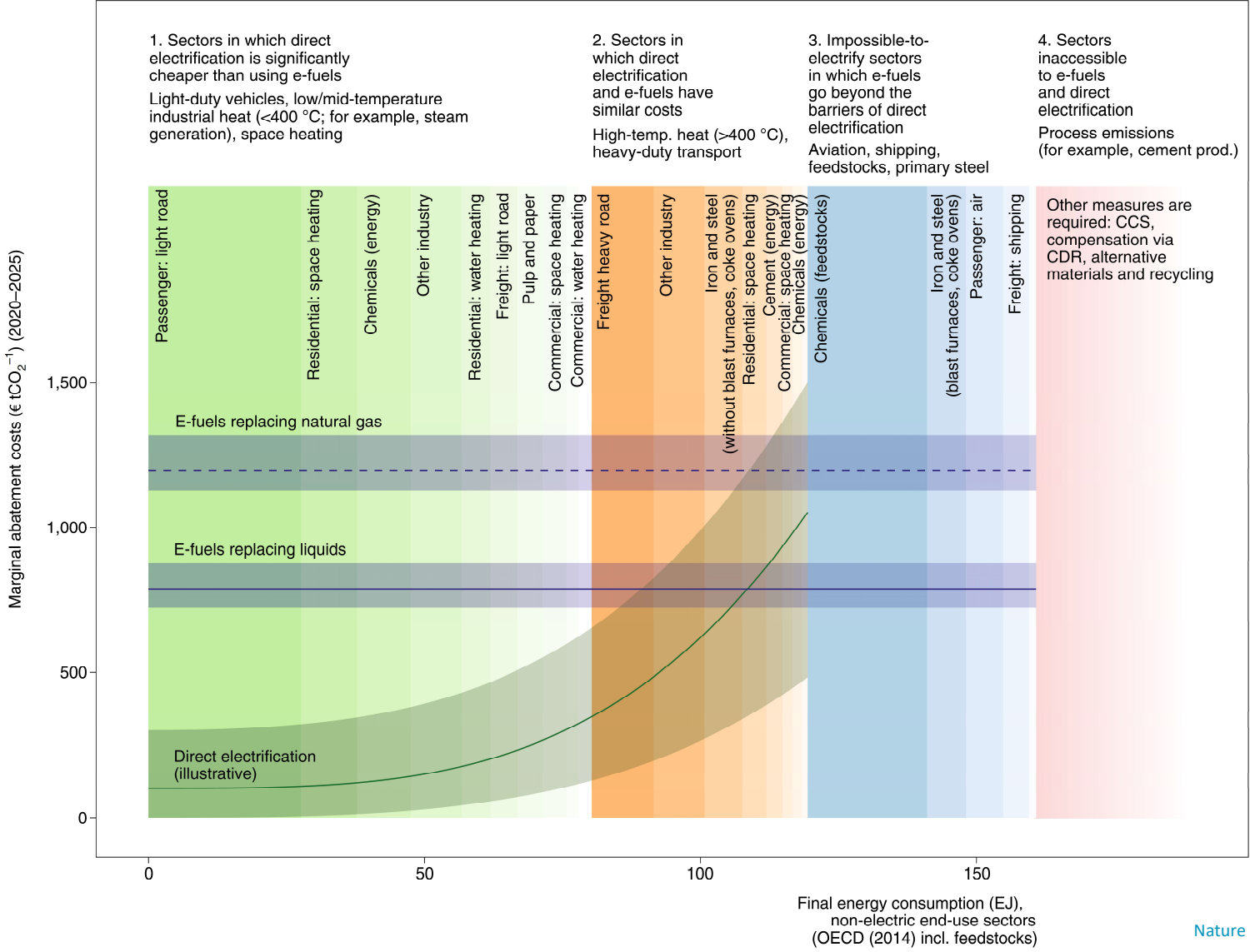
1) **Sectors in which direct electrification is significantly cheaper than using e-fuels**
light duty vehicles, Low/mid temperature industrial heat (<400°C, e.g. steam generation), space heating

2) **Sectors in which direct electrification and e-fuels have similar costs**
high temp. heat (>400°C), heavy-duty transport

3) **Impossible-to-electrify sectors in which e-fuels go beyond the barriers of direct electrification**
Aviation, shipping, feedstocks, primary steel

Marginal abatement costs €/tCO2 (2020-25)

Final energy consumption (EJ)
non-electric end-use sectors
(OECD, 2014, incl. feedstocks)

Marginal abatement cost curves including hydrogen (that is, fuel-switching CO_2 prices). In 2020–25 for e-methane (replacing natural gas), liquid e-fuels (replacing fossil liquids) and hydrogen (replacing liquids or gases) from the cost calculations as well as direct electrification alternatives (green, illustrative curve) across non-electric energy and industrial sectors in the OECD (2014 energy end-use data from IEA ETP 2017). The additional end-use transformation costs of using hydrogen are illustrative only. Shaded areas represent uncertainty ranges. The three categories of energy end uses are sorted according to the costs of directly electrifying the respective applications (horizontal sorting from low to high costs of direct electrification). Within each of the four categories, the sectors are sorted according to their size.

Marginal abatement cost curves (that is, fuel-switching CO_2 prices). Data in 2020–2025 for e-methane (replacing natural gas) and liquid e-fuels (replacing fossil liquids) from the cost calculations, and direct electrification alternatives (green, illustrative curve) across non-electric energy and industrial sectors in the OECD (2014 energy end-use data from IEA ETP 2017). The four categories of energy end uses are sorted according to the costs of directly electrifying the respective applications (horizontal sorting from low to high costs of direct electrification). Within each of the four categories, the sectors are sorted according to their size.
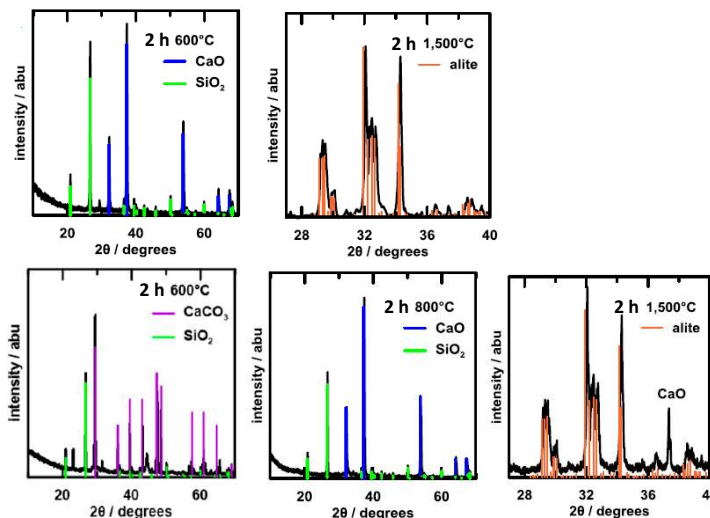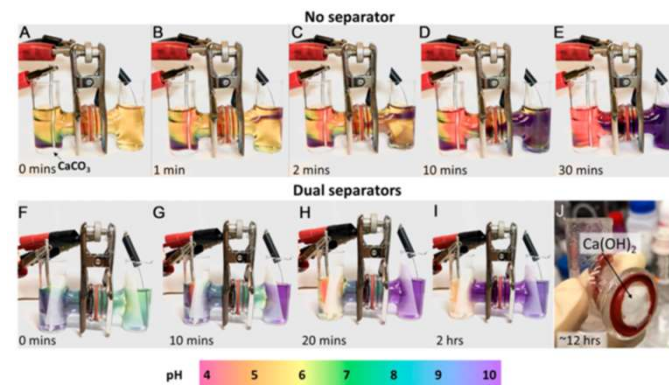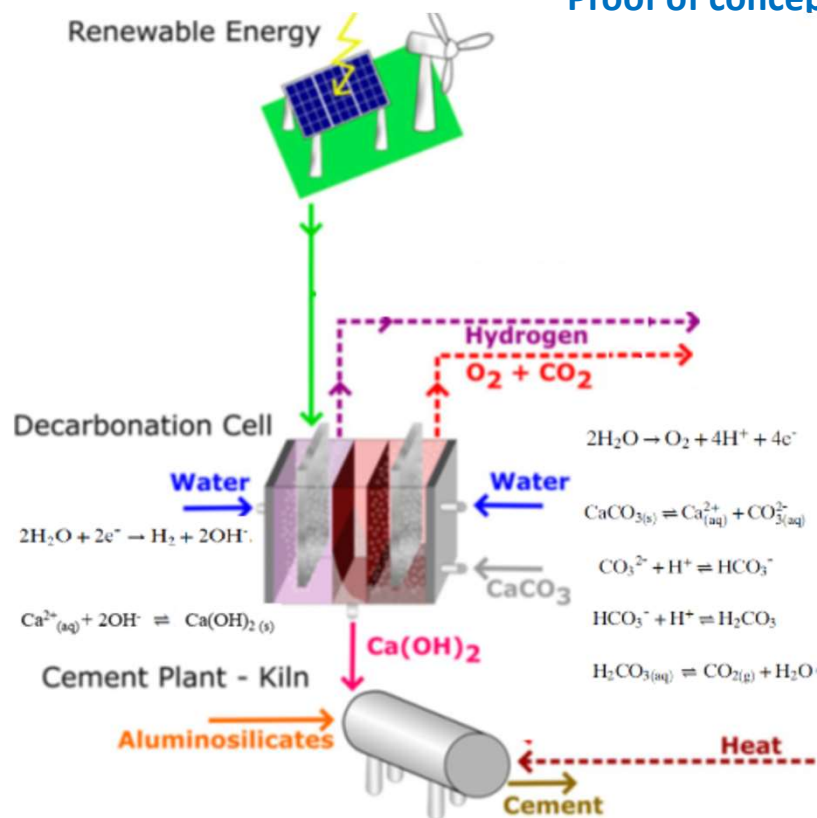
PERSPECTIVE

Electrochemical synthesis of cement

Cement production is currently the largest single industrial emitter of CO_2, accounting for ~8% (2.8 Gtons/y) of global CO_2 emissions. Deep decarbonization of cement manufacturing will require remediation of both the CO_2 emissions due to the decomposition of $CaCO_3$ to CaO and that due to combustion of fossil fuels (primarily coal) in calcining (~900 °C) and sintering (~1,450 °C).

Proof of concept

Renewable Energy

Decarbonation Cell

Water → ← Water

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

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

$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$

$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$

$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$

$H_2CO_{3(aq)} \rightleftharpoons CO_{2(g)} + H_2O$

$Ca^{2+}_{(aq)} + 2OH^- \rightleftharpoons Ca(OH)_{2(s)}$

Hydrogen
$O_2 + CO_2$
$CaCO_3$
$Ca(OH)_2$

Cement Plant - Kiln

Aluminosilicates

Heat

Cement

Conclusioni

- Le Tecnologie **Power to Chemicals** (ammoniaca e metanolo) sono vicine all'utilizzo con una forte driving force legata alla diminuzione dei costi dell'energia rinnovabile e dei costi di investimento degli elettrolizzatori.

- Nel settore dei carburanti l'approccio **e-fuel** non risulta competitivo rispetto all'utilizzo diretto dell'energia elettrica. Resta sicuramente da perseguire in questo settore l'utilizzo delle tecnologie waste to fuel.

- Le vie di sintesi **NRR** e **CO$_2$RR** sono arrivate in laboratorio a efficienze e produttività significative ma richiedono ancora forti investimenti in ricerca industriale.