atee Club Pyrogazéification

atee Club Power to Gas

24 MAI 2022 - PARIS

DÉCARBONER LE MIX GAZIER:
COMMENT AMPLIFIER LE MOUVEMENT ?

Les Rencontres des Clubs Pyrogazéification et Power-to-gas

Réduction électrocatalytique du CO_2

Marc Robert

Université Paris Cité
cnrs
IUF institut universitaire de France

Catalytic recycling of CO_2 [*artificial photosynthesis*]
a few remarks …

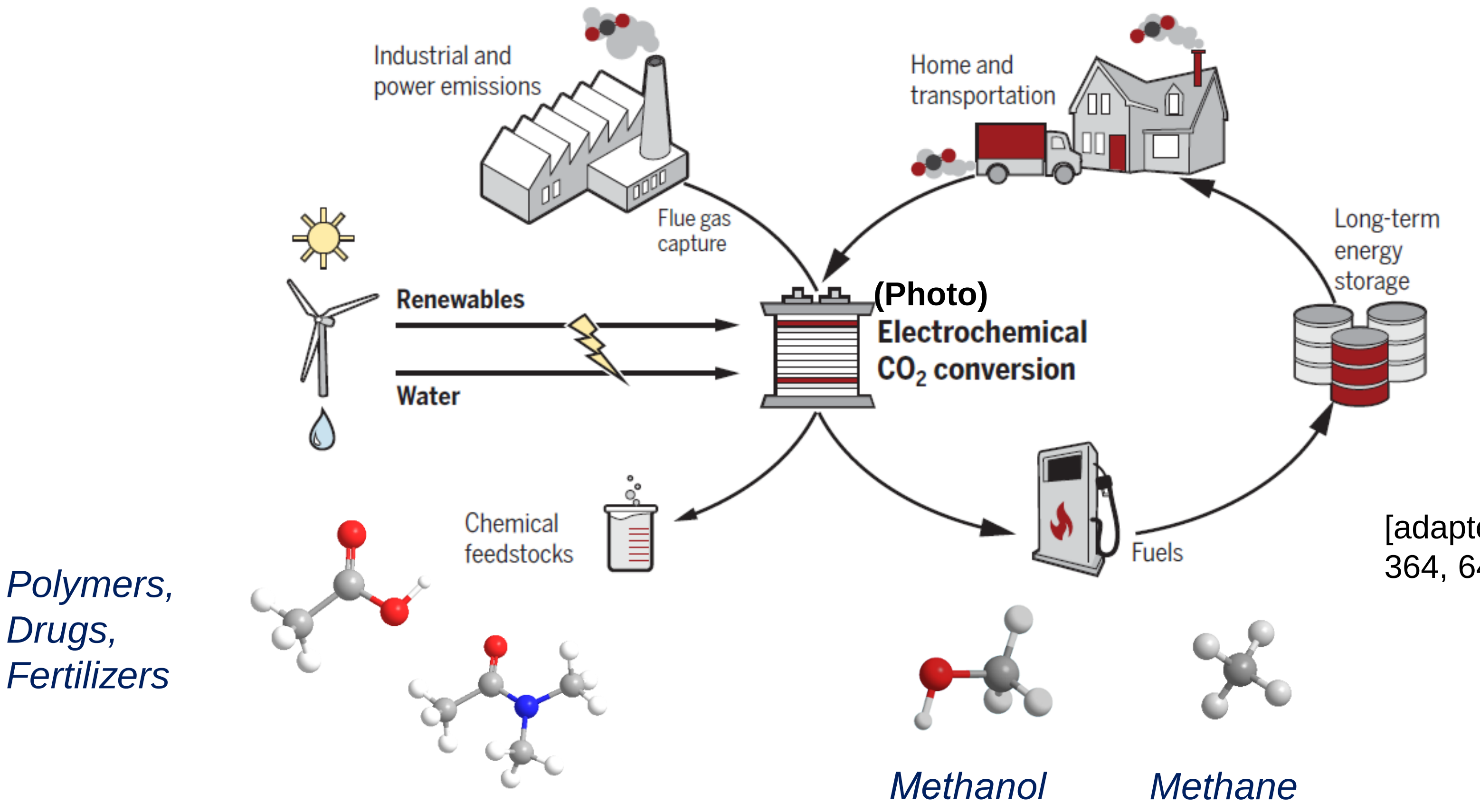
mitigation of CO_2 anthropogenic emissions ?
(***NO****, because of the order of magnitude and time scale* …)

storing renewable energies into chemical bonds for producing commodity chemicals, fuels, pharmaceuticals

electrifying our activities (industry, transportation, heating …)

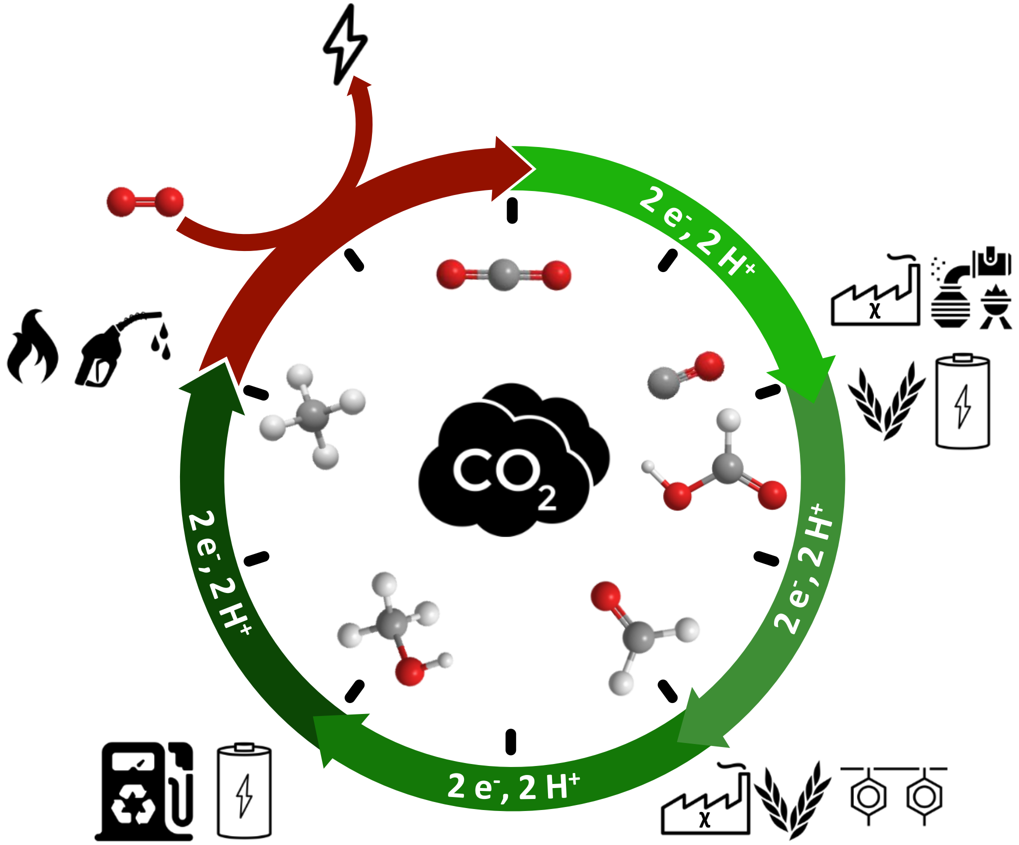
using CO_2 as a renewable feedstock for a circular economy

Renewably powered (photo)electrosynthesis will displace petrochemical processes : a Revolution, not an Evolution



[adapted from *Science* **2019**, 364, 6438, eaav3506]

The CO_2 clock



Catalysis is mandatory.

What operating constraints ?

- *earth abundant metals*
- *ambient T and P*
- *water as solvent*

ACS Energy Lett. **2016**, 1, 281

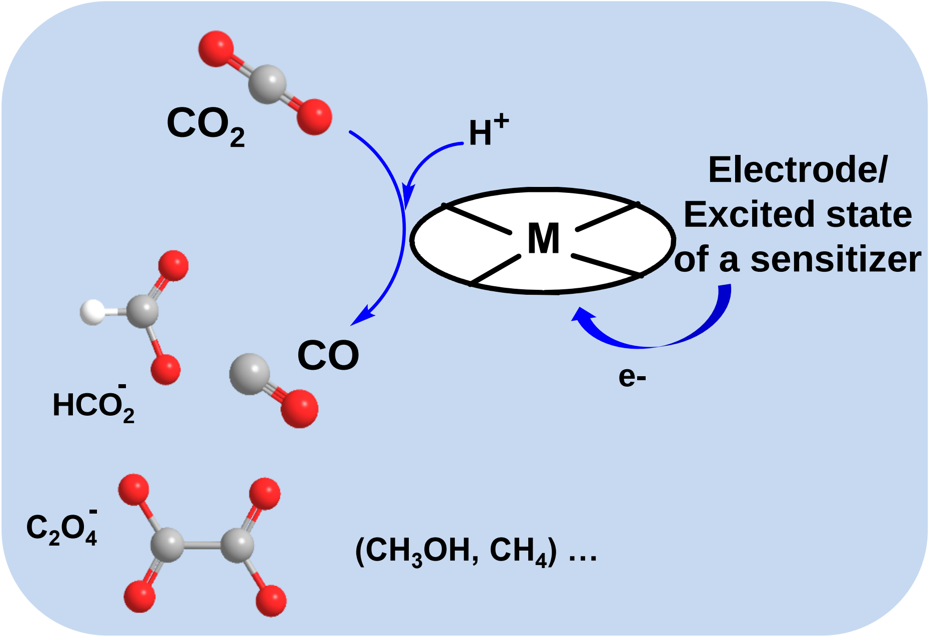
Molecular catalysis of the reduction of CO_2

Electrocatalysis
Noble metals (Au, Ag, Pd), Cu, Sn
as catalytic electrodes

Electrochemical
(or light driven electrochemical)
Molecular Catalysis

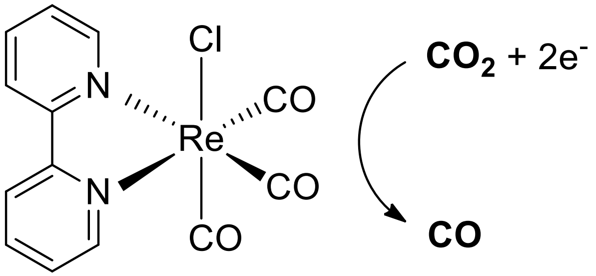
Low oxidation states of transition
metal complexes in solution

Hybrid systems combining
conductive (semi-conductive) materials
and molecular catalysts



Chem. Soc. Rev. **2013**, *42*, 2423
ACS Catalysis **2017**, 7, 70
Chem. Soc. Rev. **2020**, *49*, 5772

Catalysis of the electrochemical reduction of CO_2 to CO – *What metals* ?



Lehn and Meyer reported that **Re(bipy)$(CO)_3$Cl** catalyzed the reduction of **CO_2 to CO** with **98%** current efficiency in **DMF:H_2O 90:10** solutions @ **glassy carbon** electrode

- **Rhenium (Re)** : 3 000 €/kg , 53 t/yr
  (Chile, USA, Kazakhstan, Poland)
- **Ruthenium (Ru)** : 2 400 €/kg , 12 t/yr
  (South Africa, Russia)
- **Cobalt (Co)** : 28 €/kg , 55 10^3 t/yr
  (RDC, Zambia, Cameroun, Finland)
- **Tin (Sn)** : 24 €/kg , 0.37 Mt/yr
  (Indonesia, China, Peru)
- **Nickel (Ni)** : 16 €/kg , 1.3 Mt/yr
  (Russia, Australia, Canada, France)
- **Copper (Cu)** : 10 €/kg , 4.5 Mt/yr
  (Chile, Peru, China)
- **Manganese (Mn)** : 1.8 €/kg , 55 Mt/yr
  (China, South Africa, Australia)
- **Iron (Fe)** : 0.16 €/kg , 2400 Mt/yr
  (China, Australia, Brazil, India)

Towards the use of **cheap**, **non toxic**, and **abundant** transition metals

Lehn, et al. *J. Chem. Soc. Commun.* **1984**, 328
Meyer, et. al, *J. Chem. Soc. Commun.* **1985**, 1414

Molecular catalysis of the reduction of CO_2

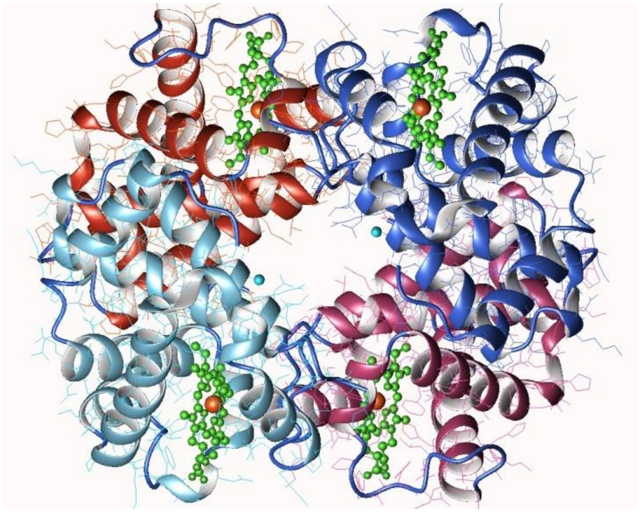
A few constraints

- use Earth ‘abundant’ metals [Fe, Co*]
- work in mild conditions (*T* and *P*)
- water is the solvent

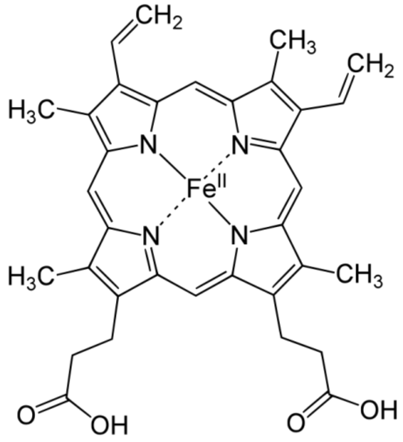
Ag, Au and other noble metals are **<u>not</u> abundant metals…*
Cu, Co, Ni, Mo, Zn, Sn, Bi are not either

Chem. Soc. Rev. **2013**, *42*, 2423
ACS Catalysis **2017**, 7, 70
Chem. Soc. Rev. **2020**, *49*, 5772

bio-inspired Fe porphyrins as CO_2 catalysts

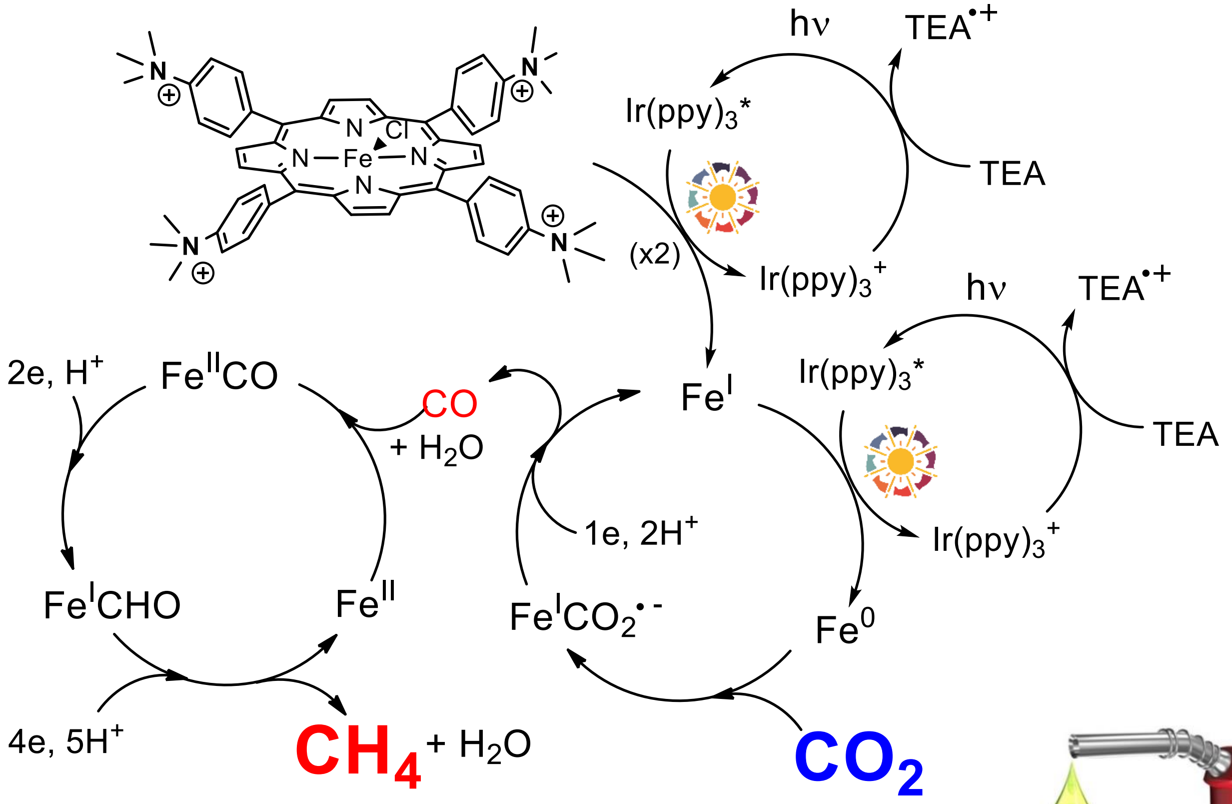


hemoglobin



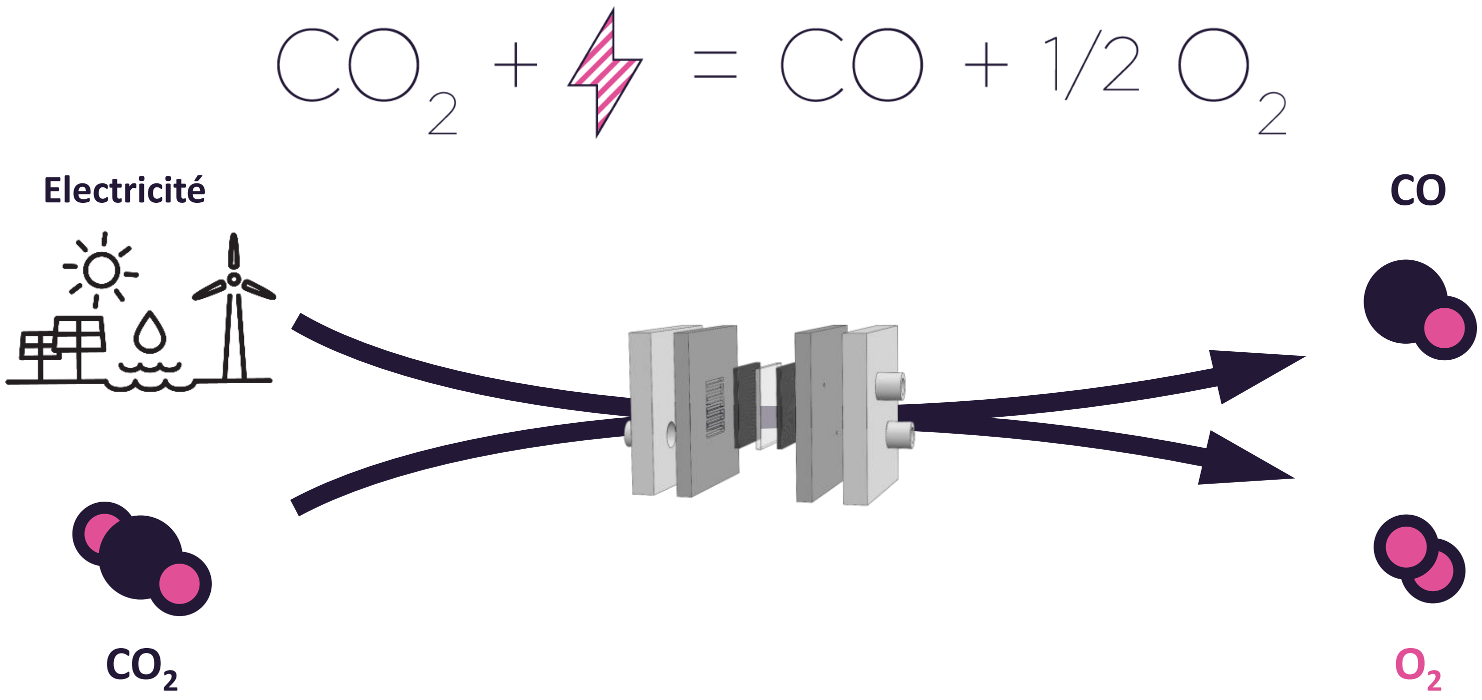
Transformation du CO_2 en méthane (CH_4) à l'aide de lumière solaire et d'une molécule à base de fer (métal le + abondant sur Terre)

Nature, Juillet 2017



Génération d'un « carburant solaire »

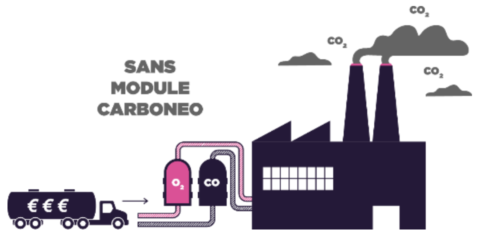
Les électrolyseurs à CO_2



carboneo
DÉCARBONER L'INDUSTRIE

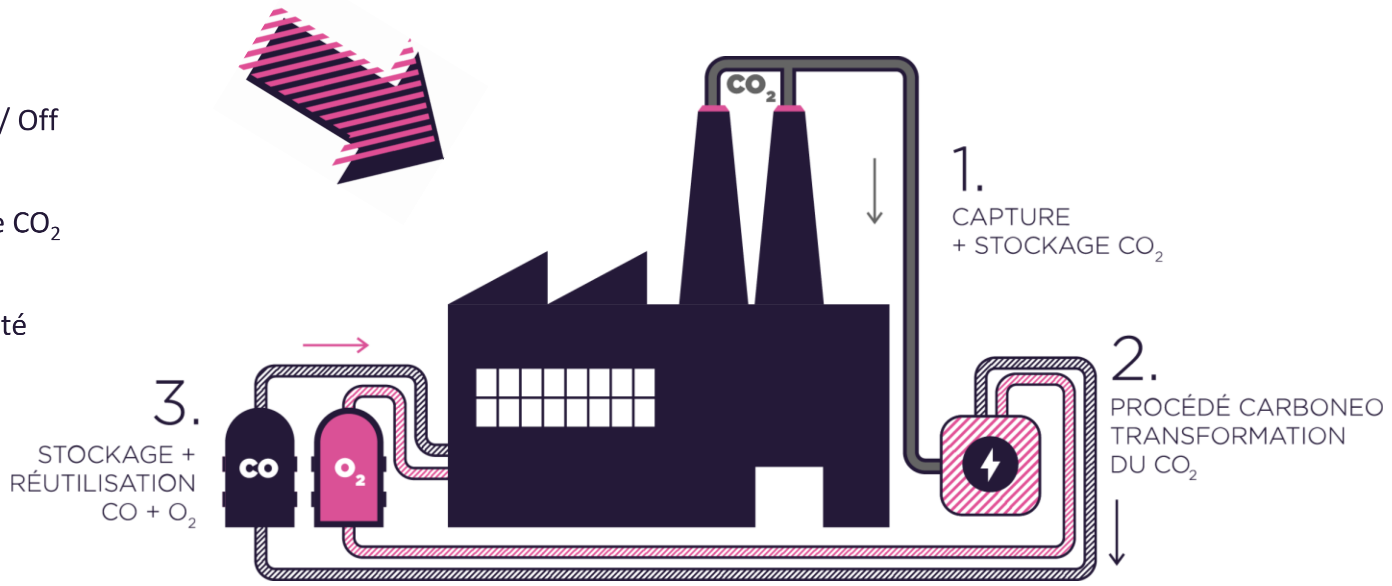
Etablir un cycle local du carbone

Une empreinte carbone fortement réduite



- Faible coût logistique
- Maintenance abordable
- Production abordable

- Procédé On / Off
- Recyclage de CO_2
- Grande pureté

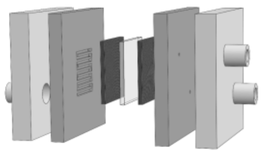
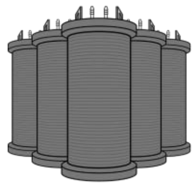


Quelques ordres de grandeur

Transformer 1 kg$_{CO2}$ avec une sélectivité de **90 %**
Demande **7 kWh** (1,4 kAh – 5 V)
Produisant **0.63 kg$_{CO}$** & **0.36 kg$_{O2}$**

Transformer 1 kg$_{CO2}$ avec une sélectivité de **90 %**
Demande **27 kWh** (5,4 kAh – 5 V)
Produisant **0.41 kg$_{CH4}$** & **0.72 kg$_{O2}$**

Gaz	Masse molaire g/mol	Densité kg/m^3
CO_2	44	1,808
CO	28	1,145
O_2	32	1,309
CH_4	18	0,65

1 cm²	Stack de 5 x 100 cm²	1 m²
		

CO_2 transformé

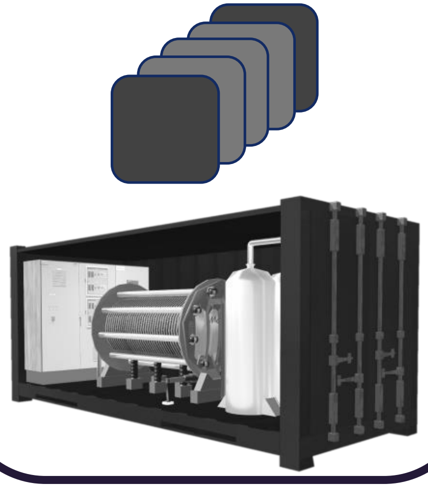
1 cm²	Stack de 5 x 100 cm²	1 m²
55 mL/h	**28 L/h**	**550 L/h**
1 mg/h	**0,5 g/h**	**1 kg/h**

C = 96 485 C/mol
2 e$^-$ par CO
8 e$^-$ par CH_4

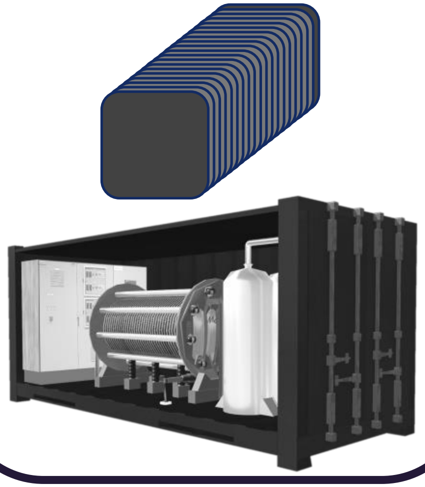
Quelques ordres de grandeur (suite)

6 t/an
1 électrode
1 m²

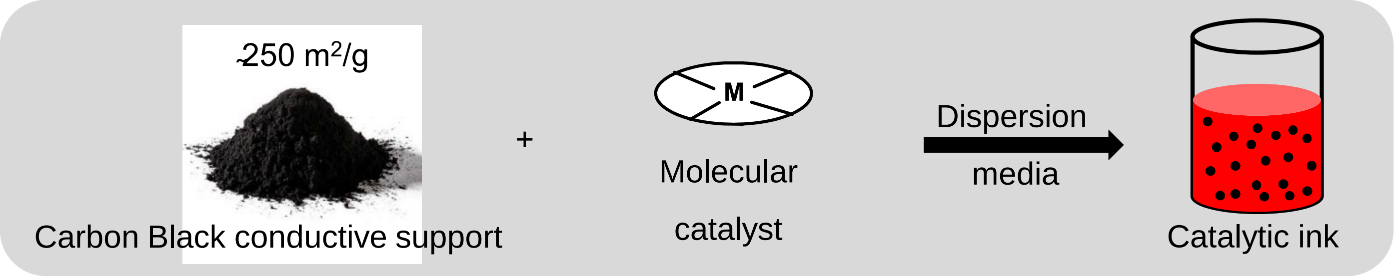
30 t/an
5 électrodes
1 m²

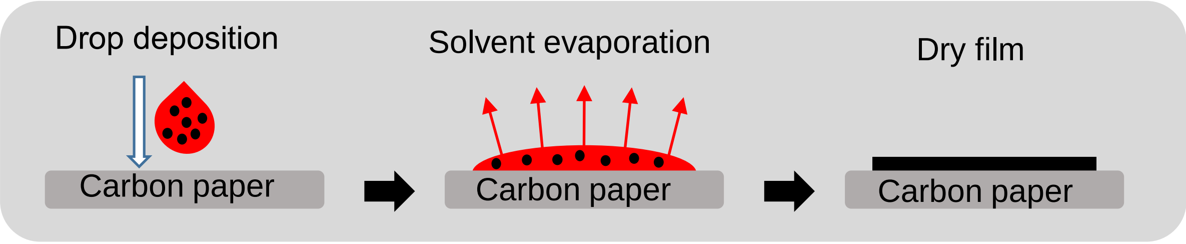


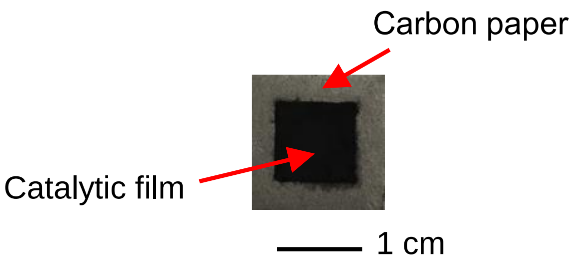
300 t/an
50 électrodes
1 m²

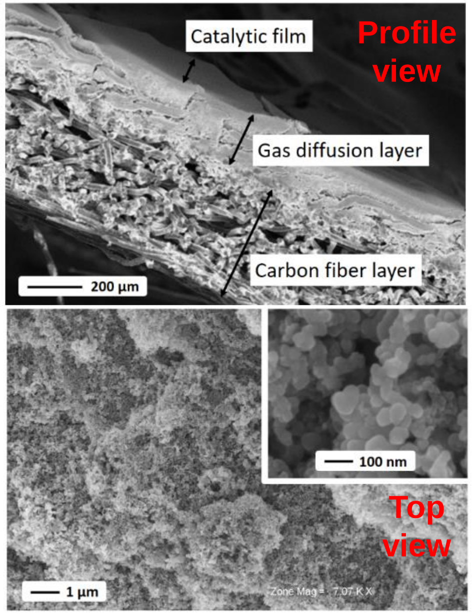


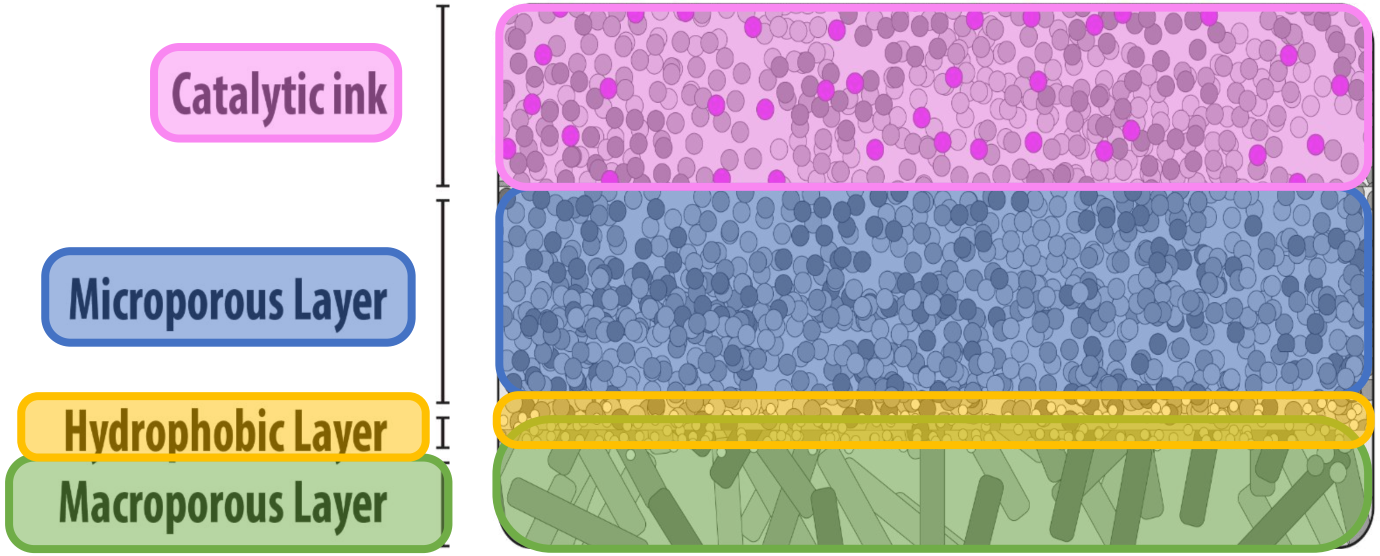
Molecular electrocatalysts can mediate fast, selective CO_2 reduction to CO in a flow cell



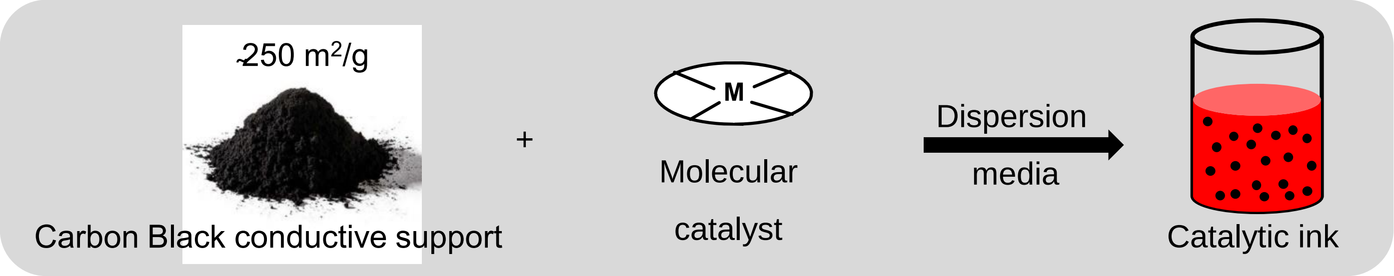


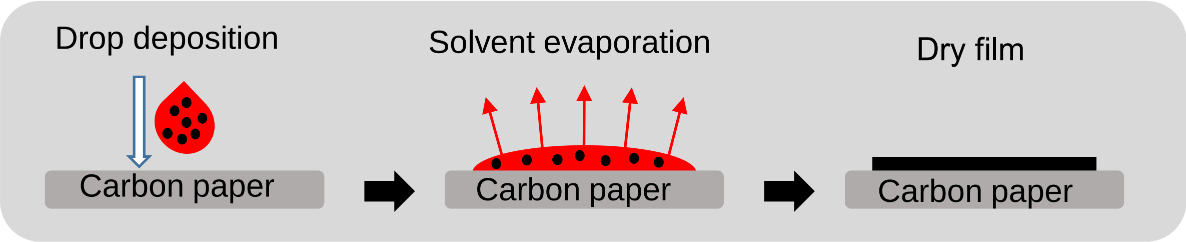


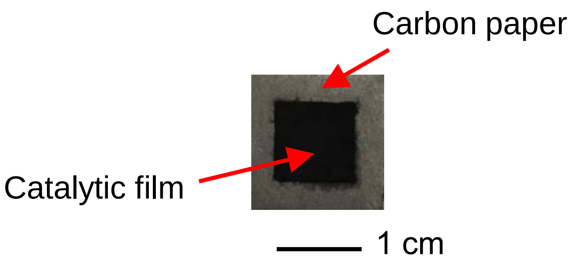




Molecular electrocatalysts can mediate fast, selective CO_2 reduction to CO in a flow cell

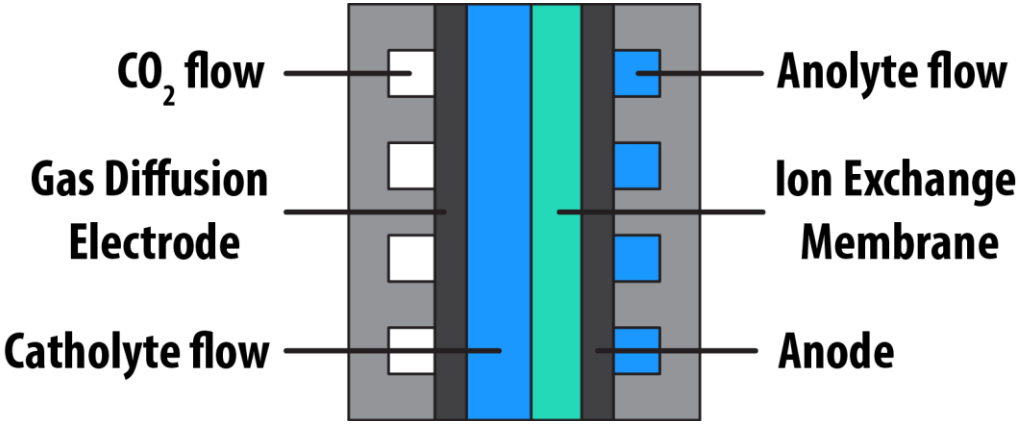






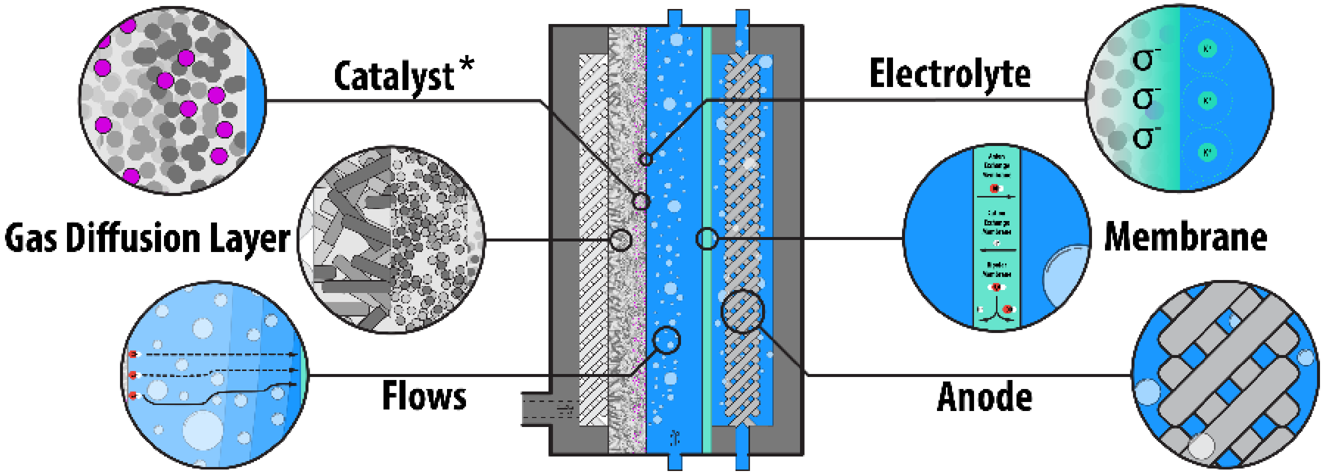
Flow cell optimisation comprises:

- CO_2 (flow, humidity)
- GDL
- Catalyst
- Electrolyte (cation, flow, temperature)
- Membrane



the CO_2 electrolyzer

Ultra-efficient CO_2 to CO conversion : **j_{CO} > 450 mA cm^{-2} in a flow cell @ pH 7**



**metal (Fe, Co) complex deposited at carbon paper*

Science **2012**, *338*, 90
Science **2019**, 365, 367-369
Nature Commun. **2019**, 10:3602
6 patents – 1 start-up (*Carboneo*)

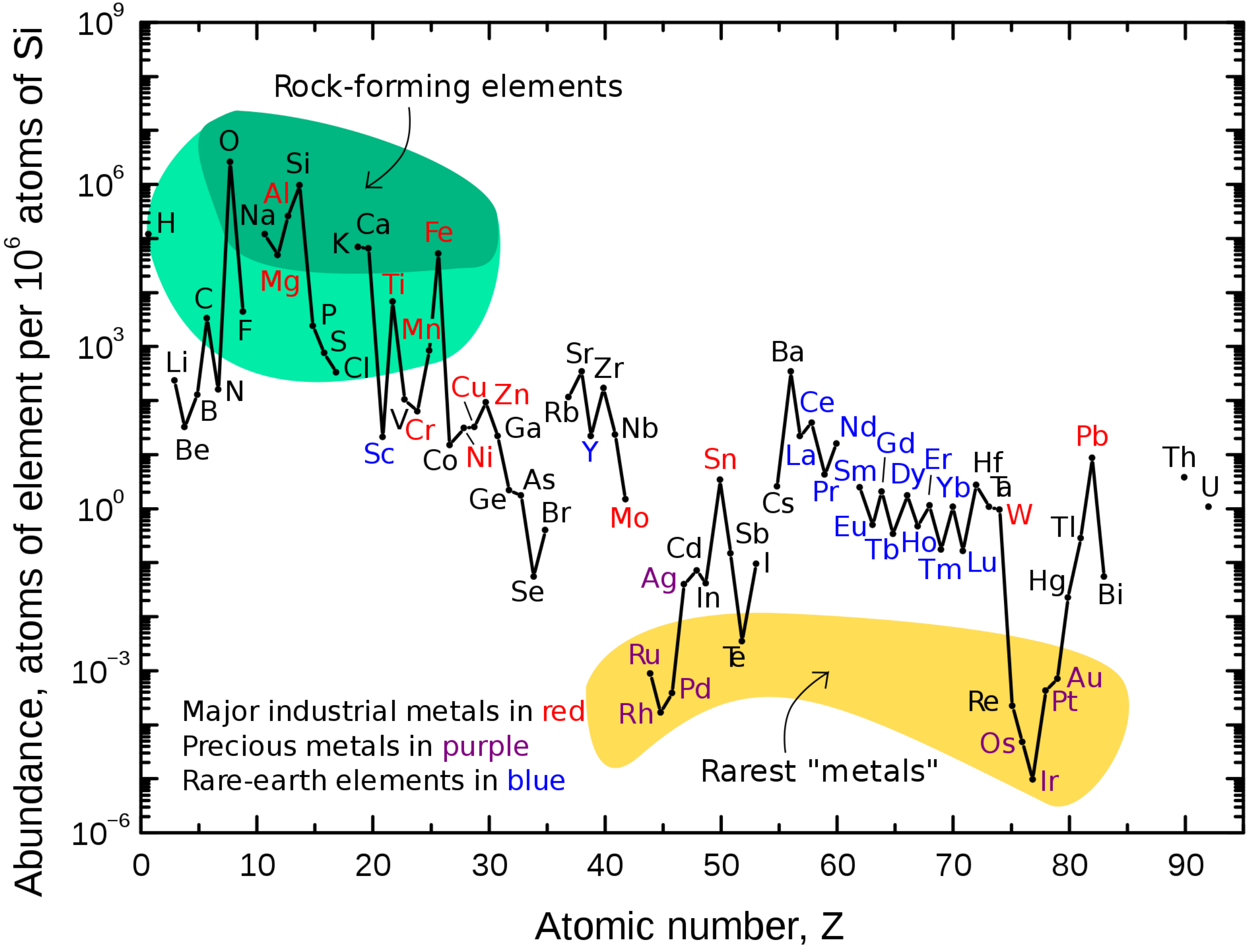
next step, the CO_2 electrolyzer to CH_4

Ruwen Wang
Daniela Mendoza
Julian Guerrero
Jaya Bharti
Aude Salamé
Jeremy de Freitas
Junming Shao
Francesco Crisanti
Giulia Raffaeli
Victoria Bloquert
Cecilia Albanese
Dr. Duobin Chao
Dr. Deba Sarkar
Dr Etienne Boutin (former student)

Dr. Niklas Von Wolff
Dr. Julien Bonin
Dr. Elodie Anxolabéhère

Prof T. C. Lau (City Univ., Hong-Kong)
Dr. G. Chen, L. Chen (Dongguan University of Technology)
Prof O. Ishitani (Tokyo Institute of Technology)
Prof. G. Granozzi, Dr. L. Calvillo (Padova University)
Dr. Fabrice Odobel (U Nantes)
Dr. Negar Naghavi (IPVF, Saclay)
Dr. Nicolas Mézailles (U Toulouse)

GRTgaz
Air Liquide
ANR
IdEx Université de Paris
CNRS
IUF institut universitaire de France
JST Japan Science and Technology Agency
GRDF
Teréga
ERGANEO L'AVENIR EST FAIT D'AUDACE
MAKE OUR PLANET GREAT AGAIN
SOLEIL SYNCHROTRON
Région îledeFrance
China Scholarship Council



Rock-forming elements
Rarest "metals"
Major industrial metals in red
Precious metals in purple
Rare-earth elements in blue
Abundance, atoms of element per 10^6 atoms of Si
Atomic number, Z
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

Global scale energy demand

« Global energy demand is projected to increase by 57% in 26 years, from 14.9 terawatt (TW) in 2004 to 23.4 TW in 2030. »

« Towards these ends, numerous technologies will have valuable application within the local context. However, at the global scale, sunlight is one of the few energy sources that can meet projected human energy demands in an environmentally and socially responsible manner. Solar energy reaches the surface of the earth at a rate of 120 000 TW, far exceeding the global rate of human energy consumption. »

A. L Moore et al., Chem. Soc. Rev. **2009**, *38*, 25.

Use solar energy ?
So we need being able to store it !

Molecules are ideal candidates to do so

… in particular CO_2

Renewable (Solar) fuels before the renewable (solar) fuels …

SCIENCE

THE PHOTOCHEMISTRY OF THE FUTURE[1]

MODERN civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy and wealth.

The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us, and a proof of this may be seen in the fact that the subject was treated last year almost at the same time by Sir William Ramsay before the British Association for the Advancement of Science at Portsmouth and by Professor Carl Engler before the Versammlung deutscher Naturforscher und Aerzte at Karlsruhe. According to the calculations of Professor Engler Europe possesses to-day about 700 billion tons of coal and America about as much; to this must be added the coal of the unknown parts of Asia. The supply is enormous but, with increasing consumption, the mining of coal becomes more expensive on account of the greater depth to which it is necessary to go. It must therefore be remembered that in some regions the deposits of coal may become practically useless long before their exhaustion.

Is *fossil* solar energy the only one that may be used in modern life and civilization? That is the question.

Even making allowances for the absorption of heat on the part of the atmosphere and for other circumstances, we see that the solar energy that reaches a small tropical country—say of the size of Latium—is equal annually to the energy produced by the entire amount of coal mined in the world! The desert of Sahara with its six million square kilometers receives daily solar energy equivalent to six billion tons of coal!

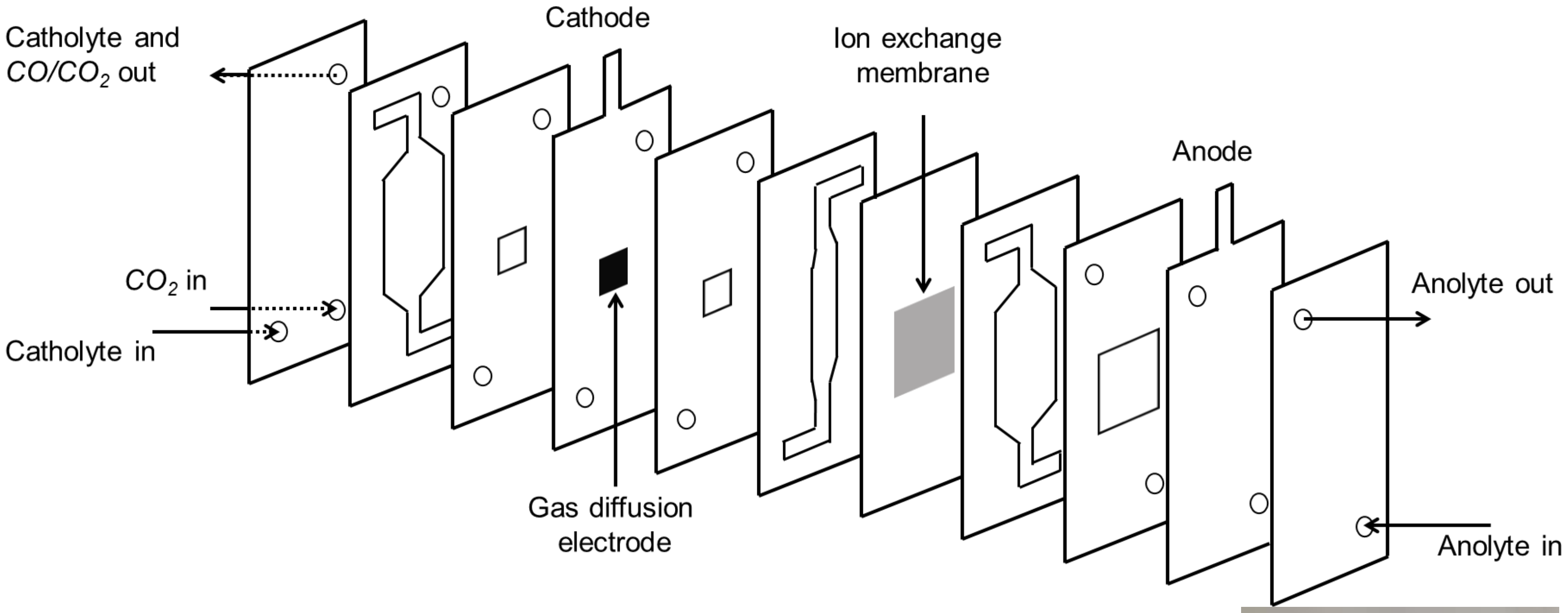
(...) With convenient modifications could not this now actually be done on the tropical highlands? Yet the true solution consists in utilizing the radiations that pass through the entire atmosphere and reach the surface of the earth in large amounts. That a way of accomplishing this exists is proved by the plants themselves. By using suitable catalyzers, it should be possible to transform the mixture of water and carbon dioxide into oxygen and methane, or to cause other endo-energetic processes. The desert regions of the tropics, where the conditions of the soil and of the climate make it impossible to grow any ordinary crops, would be made to utilize the solar energy which they receive in so large a measure all the year, that the energy derived from them would be equal to that of billions of tons of coal.

Besides this process, which would give new value to the waste products of combustion, several others are known, which are caused by ultraviolet radiations and which might eventually take place under the influence of ordinary radiations, provided suitable sensitizers were discovered.

By using suitable catalyzers, it should be possible to transform the mixture of water and carbon dioxide into oxygen and methane

Ciamician, *Science* **1912**, 36, 385

Molecular electrocatalysts can mediate fast, selective CO_2 reduction to CO in a flow cell



Micro Flow Cell® electrolyzer
(ElectroCell, Denmark)