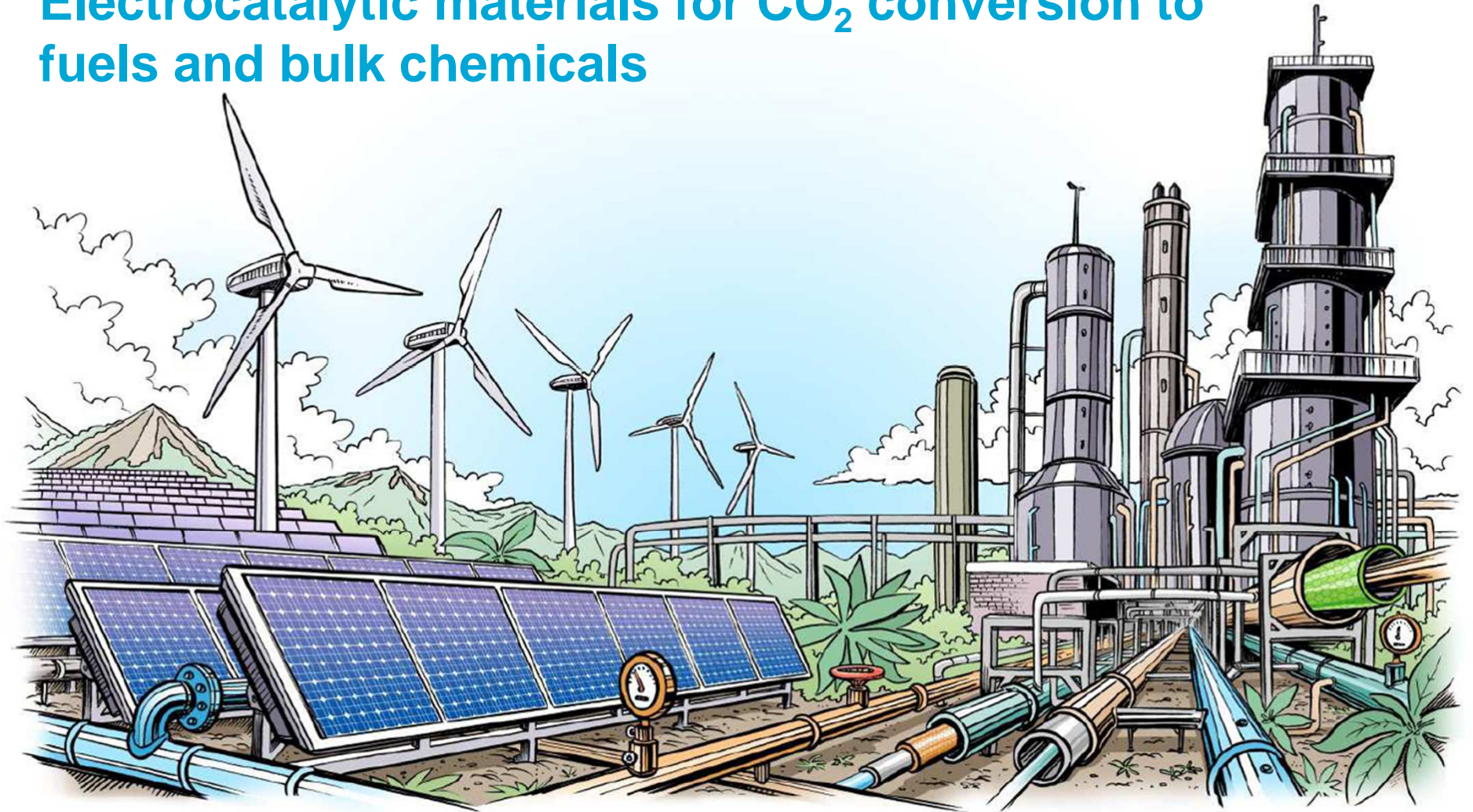


Electrocatalytic materials for CO₂ conversion to fuels and bulk chemicals



Dr. Ruud Kortlever

M2i Meeting Materials 2020 – 15-12-2020

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OUR CLIMATE IS CHANGING



+0.85°C

Average
temperature
increase from
1880 to 2012



-1.7 km

Arctic's sea ice
loss every decade
since 1979



+19cm

Average sea
level **rise** from
1901 to 2010



+50%

Greenhouse gas
emissions **rise**
than 1990



-5%

Grain yields
decline per
1°C increase



+400%

Increase of
natural disasters
since 1970



(Electro-)Catalysis for a sustainable future

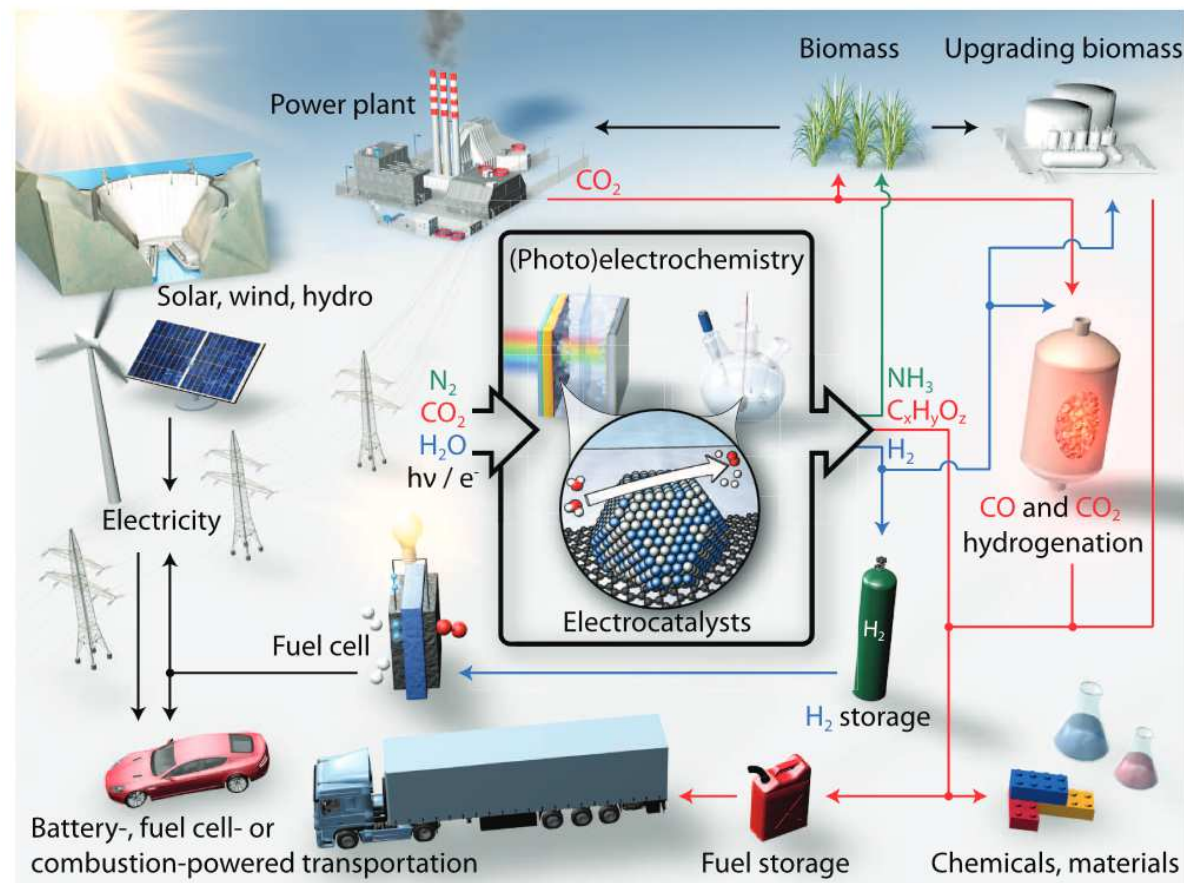


Fig. 1. Sustainable energy future. Schematic of a sustainable energy landscape based on electrocatalysis.

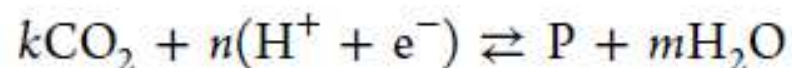
Seh, Z.W.; Kibsgaard, J.; Dickens, C.F.; Chorkendorff, I.; Nørskov, J.K.; Jaramillo T.F., *Science*, **2017**, 335, eaad4998.

Electrocatalytic challenges – CO₂ electroreduction

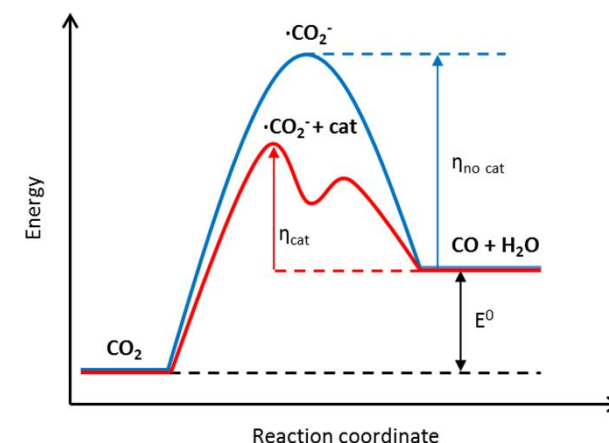
Table 1. Main Products of the Electrochemical Reduction of CO₂^a

product name and formula	<i>k</i>	<i>n</i>	<i>m</i>	<i>E</i> ⁰ (V versus RHE)
carbon monoxide, CO	1	2	1	−0.10
formic acid, HCOOH	1	2	0	−0.20 (for pH < 4); −0.20 + 0.059[pH-4] (for pH > 4)
formaldehyde, HCHO	1	4	1	−0.07
methanol, CH ₃ OH	1	6	1	0.02
methane, CH ₄	1	8	2	0.17
ethanol, CH ₃ CH ₂ OH	2	12	3	0.09
ethylene, C ₂ H ₄	2	12	4	0.08

^aThe coefficients *k*, *n*, and *m* in eq 1 are provided in each case together with the standard equilibrium potentials.



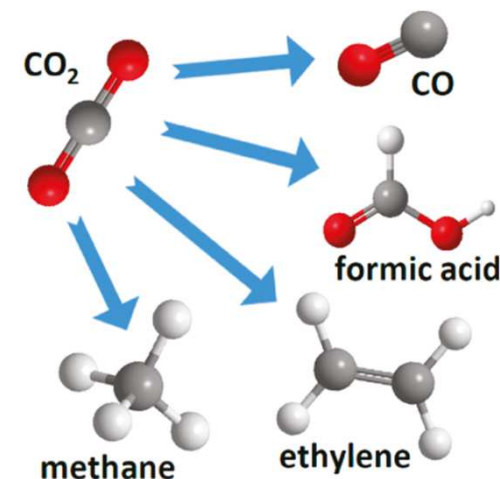
- Equilibrium potentials are far off from the actual onset potentials measured in CO₂ reduction.
- High overpotentials are the result of inappropriate adsorption energies of key reaction intermediates: need for better electrocatalysts.



Electrochemical CO₂ reduction on metal electrodes

Different electrocatalysts produce different products:

- **CO**: Au > Ag > Cu > Zn > > Cd > Sn > In > Pb > Tl = Hg
- **HCOOH**: Cd, Sn, In, Pb, Tl, Hg, Bi
- **C_xH_y's**: Cu



sp group metals

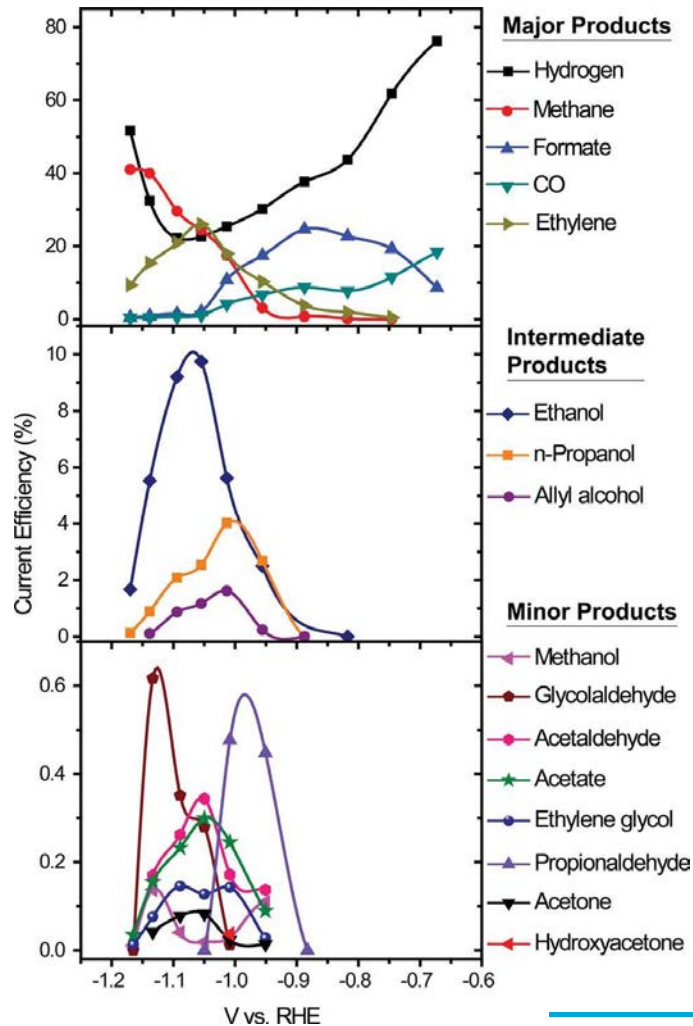
- Include the principal group metals and metals with a d¹⁰ electronic configuration.
- Make formic acid and oxalate (s²) and CO (d¹⁰).

d group metals

- Include transition metals with unfilled d orbitals.
- Produce CO_{ads} on surface.

Whipple, D.T.K.; Kenis P.J.A. *J. Phys. Chem. Lett.*, **2010**, 1, 3451.

Electrochemical CO₂ reduction on copper

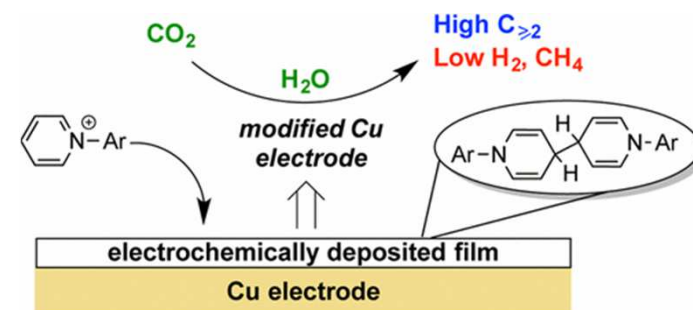
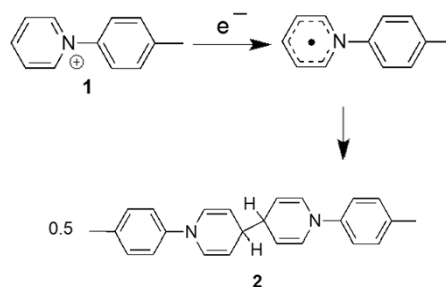


- Copper is the only catalytic material able to produce hydrocarbon products, such as methane and ethylene, with decent efficiencies.
- Recent observation of 16 different products from CO₂ reduction reveals the complexity of this reaction as well as its possibilities.
- Product formation is very potential dependent and copper shows an overall poor selectivity towards any product.

Kuhl, K.P.; Cave, E.R.; Abram, D.N.; Jaramillo, T.F., *Energy Environ. Sci.*, **2012**, 5, 7050-7059.

Altering product selectivity of Cu – Organic additive/film

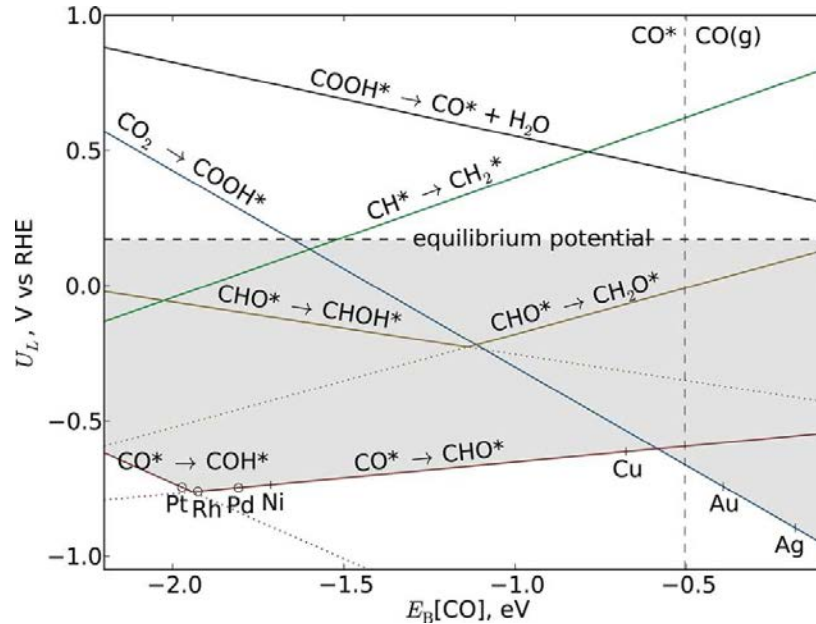
Without additive With additive



At -1.1 V _{RHE}	Faradaic Efficiencies (%)									C ₂ ⁺ / CH ₄	j (mA/cm ²)
Compound	CH ₄	C ₂ H ₄	C ₂ H ₅ OH	C ₃ H ₇ OH	CO	H ₂	HCOO ⁻	C ₂ ⁺	Total		
No additive	20.2	12.4	7.2	2.8	1.7	42.8	4.7	22.4	96.4	1	-4.59
1	1.1	40.7	30.5	10.0	1.0	18.1	7.1	80.2	107.8	70	-1.02

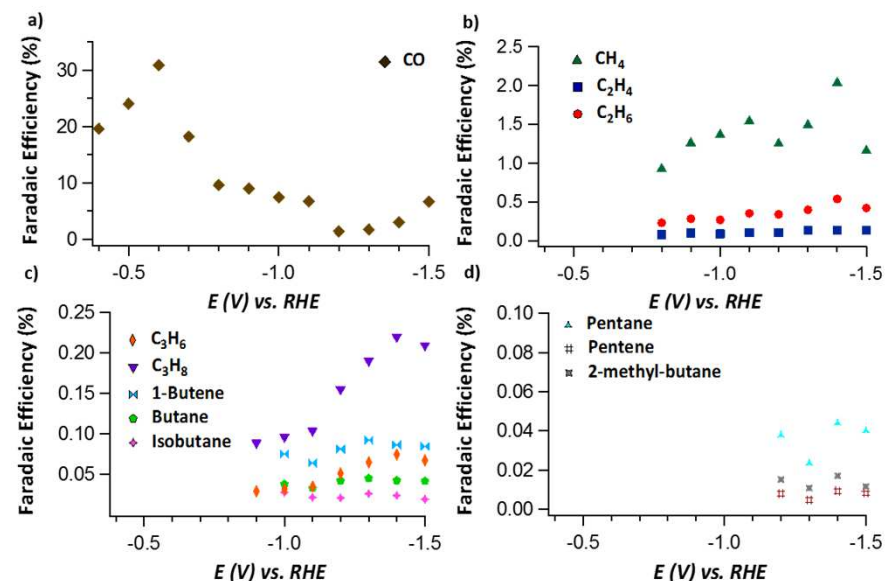
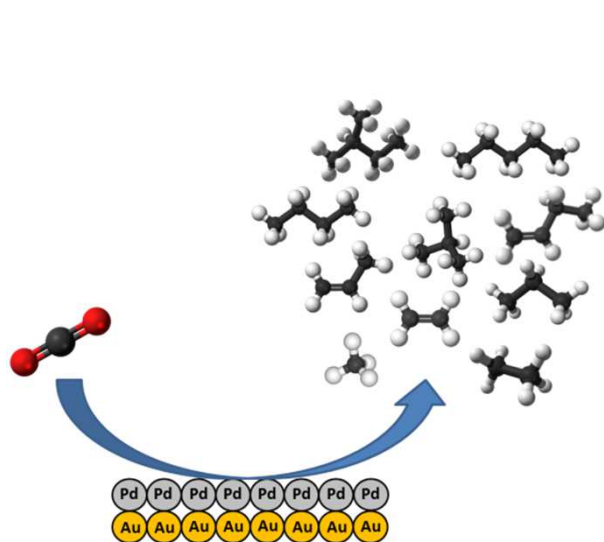
- N-aryl pyridinium additives were tested for their ability to promote electrochemical CO₂ reduction. The organic molecules were reduced and formed an organic film on the electrode surface.
- The organic film blocked the formation of hydrogen and C₁ products on the copper electrode, thereby increasing the selectivity of C₂⁺ products from 22% to 80%.

CO₂ reduction to hydrocarbons – Electrochemical Fischer-Tropsch?



- If a catalyst binds CO too weakly, CO will desorb before this protonation can take place, while if a catalyst binds CO too strongly, HCO or COH formation is thermodynamically unfavorable.
- Can we develop novel catalysts by combining a metal which binds CO too strongly (Pd) with a metal which binds CO too weakly (Au)?

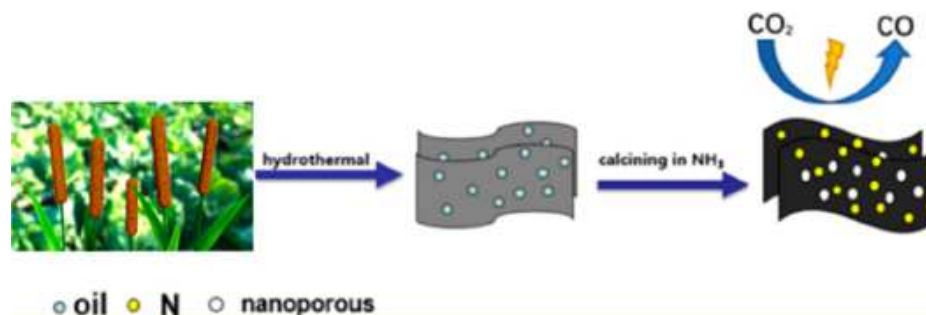
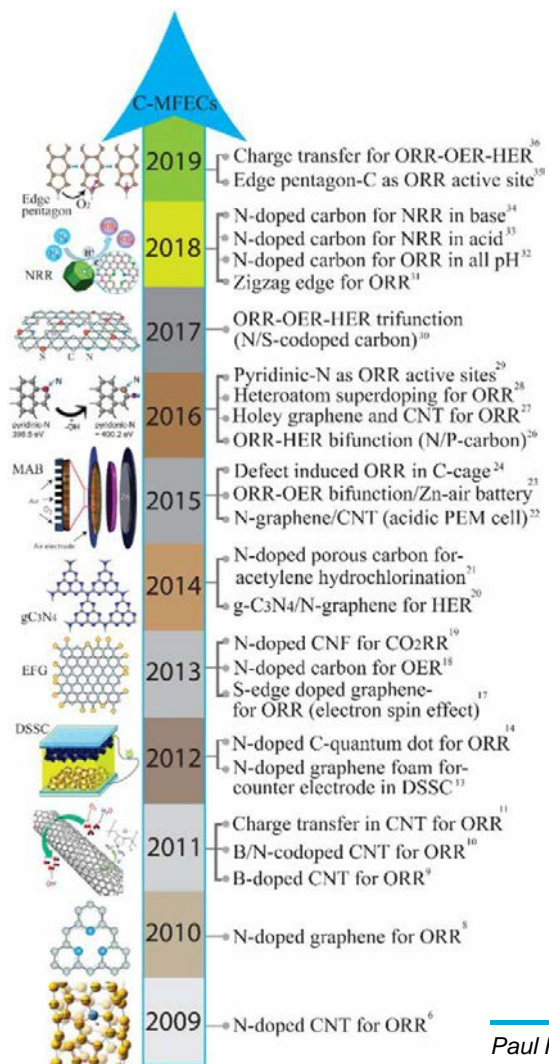
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- Can we develop novel catalysts by combining a metal which binds CO too strongly (Pd) with a metal which binds CO too weakly (Au)?
- By combining Pd with Au, we were able to create the first catalyst that is able to produce C₃-C₅ hydrocarbons.

Kortlever, R.; Peters, I.; Balemans, C.; Kas, R.; Kwon, Y.; Mul, G.; Koper, M.T.M., *Chem. Commun.*, **2016**, 52, 10229-10232.

N-doped carbon electrocatalysts for CO₂ conversion

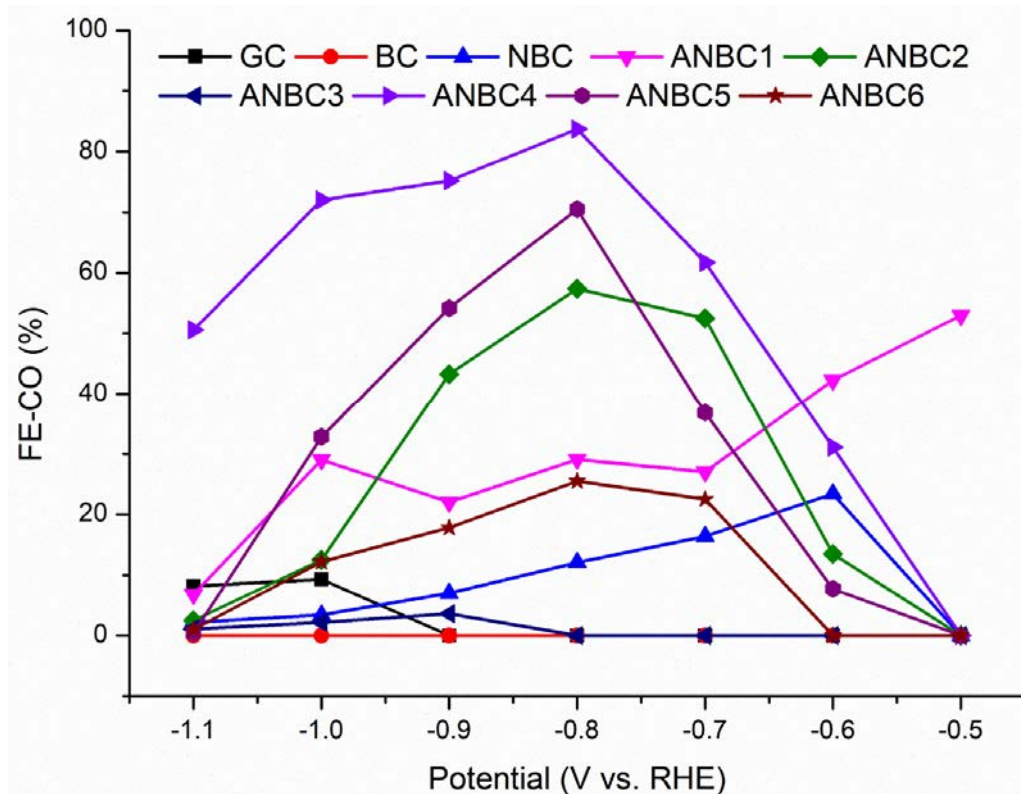


Shilong Fu



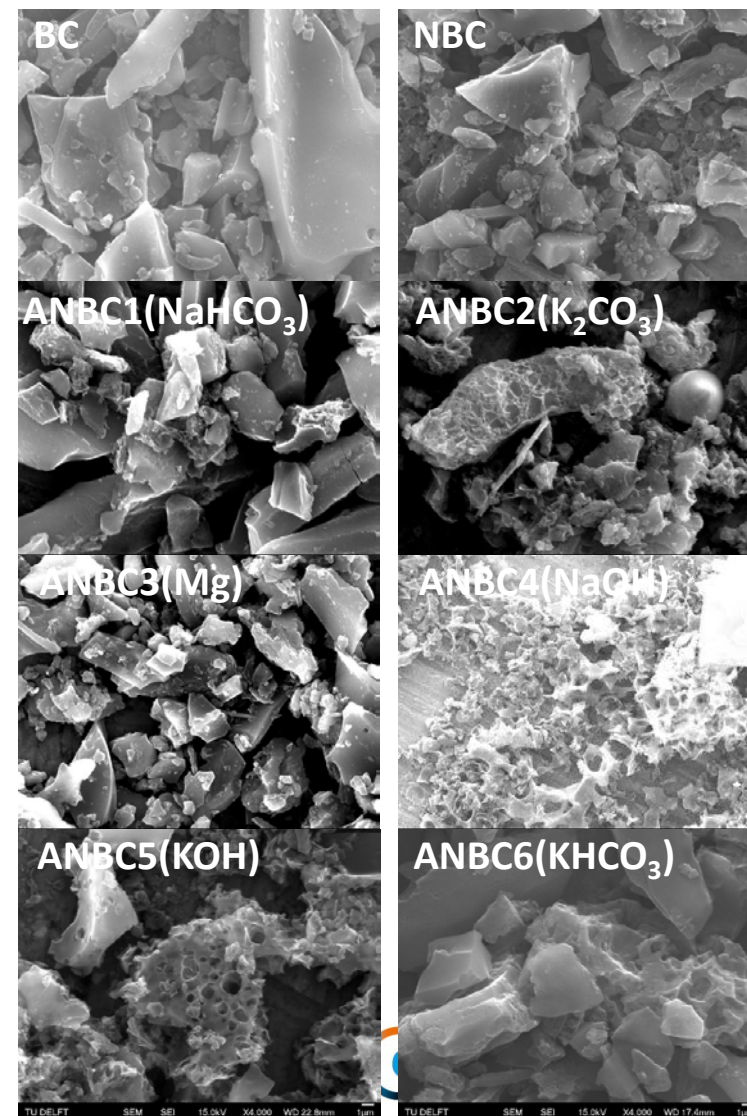
Prof. dr. ir.
Wiebren de Jong

Biomass-derived carbon-based catalysts for CO₂R performance

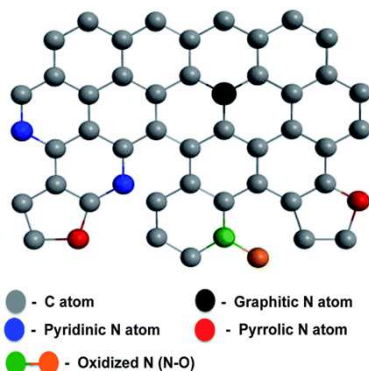
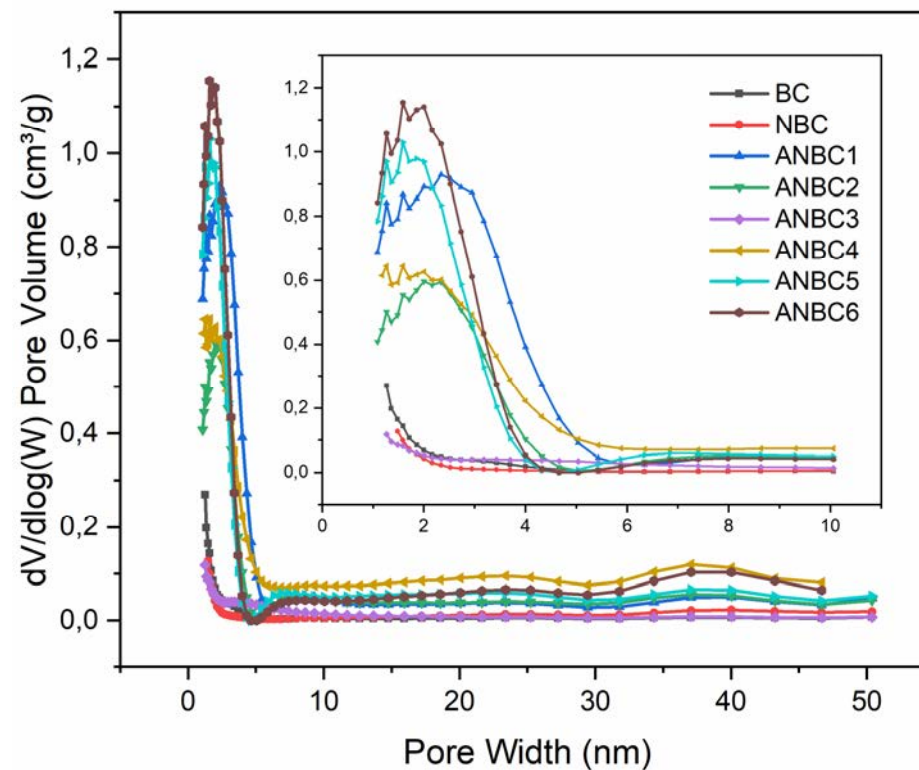
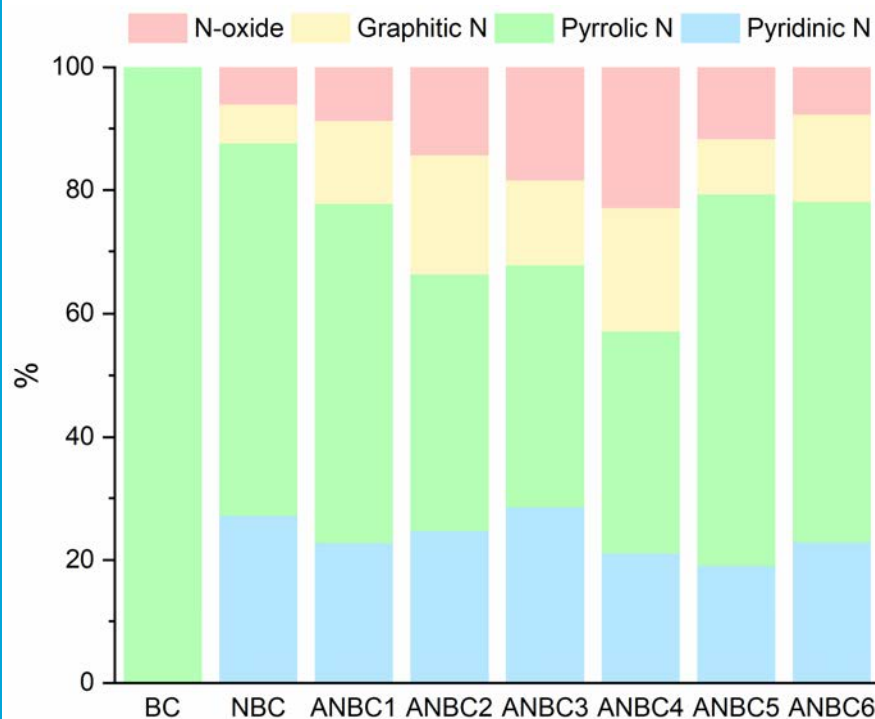


GC: Glassy Carbon
 BC: Biochar
 NBC: Nitrogen-doped biochar

ANBC1: NaHCO₃
 ANBC2: K₂CO₃
 ANBC3: Mg₅(OH)₂(CO₃)₄
 ANBC4: NaOH
 ANBC5: KOH
 ANBC6: KHCO₃



Biomass-derived carbon-based catalysts for CO₂R performance



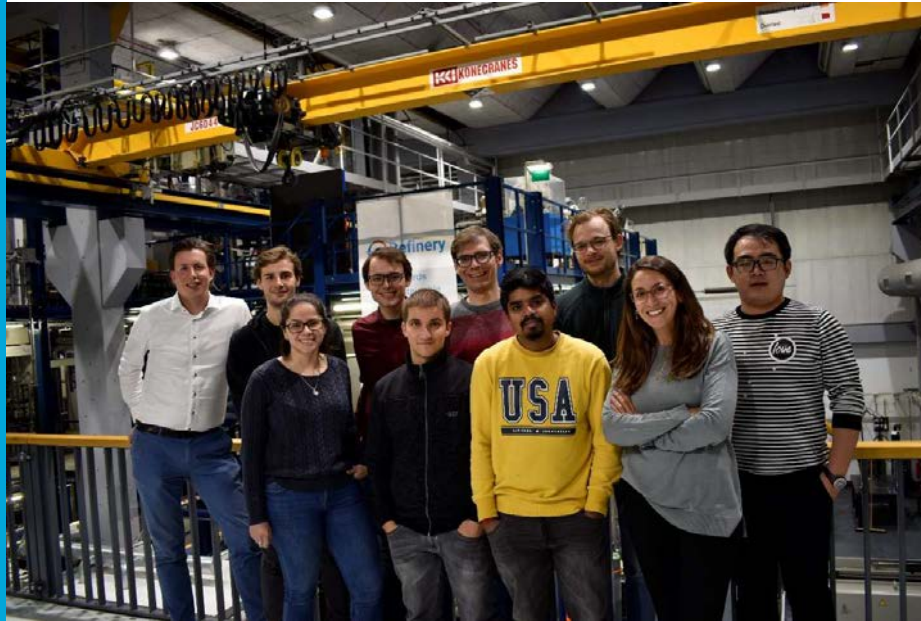
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Take-away messages

- The electrochemical reduction of CO₂ to valuable chemicals or fuels can close the carbon cycle, provide a means of energy storage and a route for renewable production of chemicals
- New electrocatalytic materials need to be developed for this reaction to be economically feasible.
- Bimetallic electrocatalysts can be used designed to alter product selectivities and, in some cases, alter the product distribution.
- Carbon-based catalytic materials, for instance biomass-derived, can provide cheap and stable alternatives and can produce CO with high selectivities.

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Nederland



Questions?

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