Analyzing olefin production with Cu Nanocubes during CO_2 electrolysis

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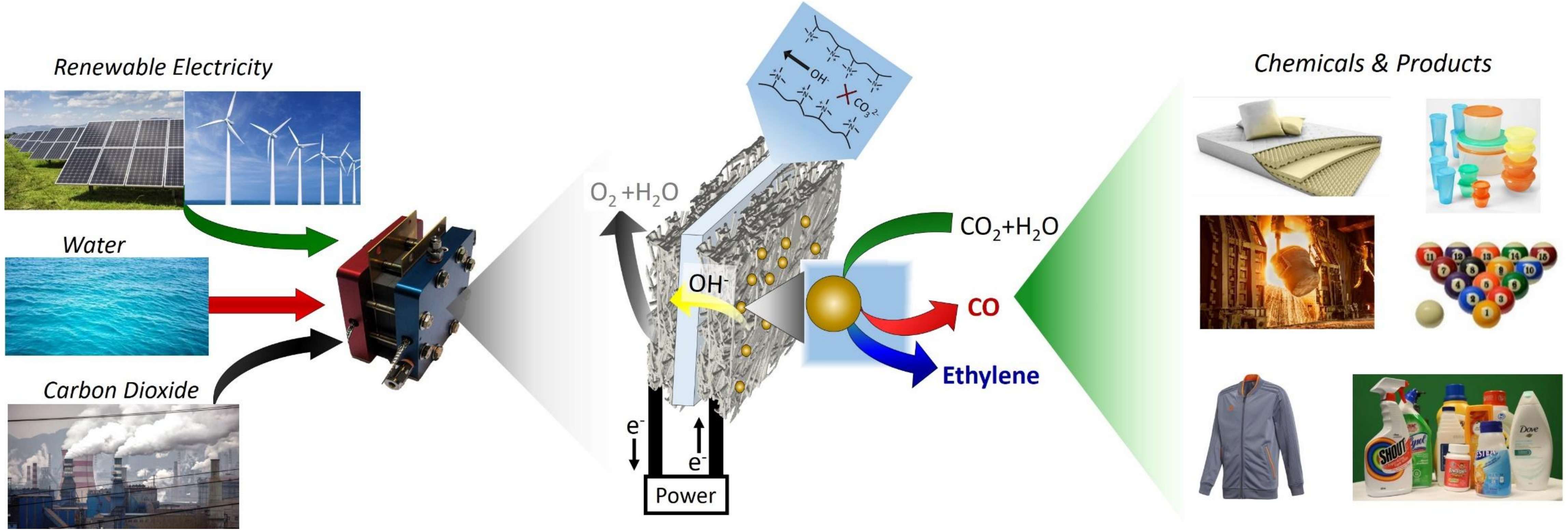
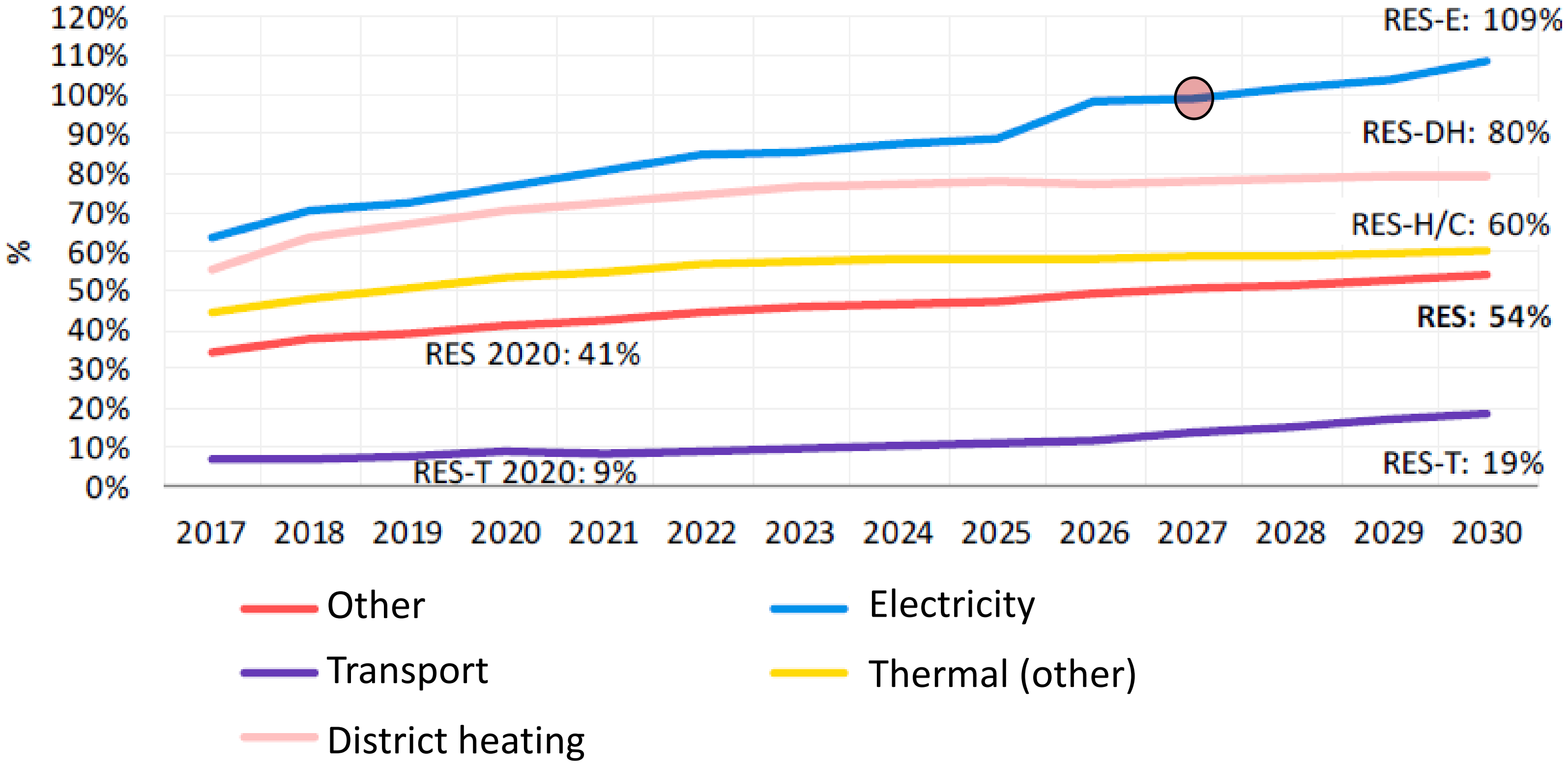
ICEM Conference

Nov 6, 2021



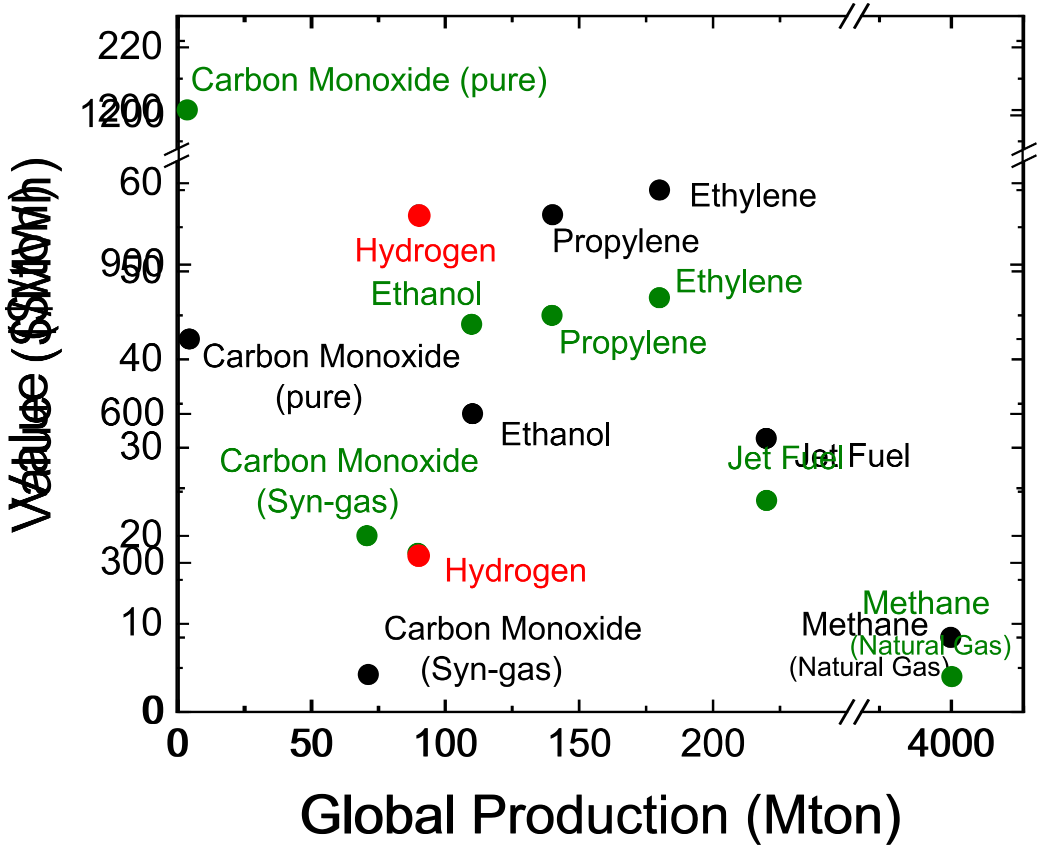
Too much electricity- A very real issue in Denmark

- Denmark will reach 100% renewables by 2027
- We are already in the process of building greater than 100% electricity



What are we trying to do it

- Chemicals are 7% of EU's greenhouse gasses emissions



Applications of chemicals

Ethylene → Plastics

Propylene → Plastics

Ethanol → Fuel, Solvent

Methane (Natural gas) → Burning

- *If all of Europes's electricity went to ethylene production (@ 2V electrolysis), we would only produce 67% of world's ethylene.*

CO_2 Reduction Basics

Table 1. Various products from the electroreduction of CO_2

Electrode	Potential (V) vs. *nhe*	Current density (mA cm^{-2})	Faradaic efficiency/% CH_4	C_2H_4	EtOH	PrOH	CO	$HCOO^-$	H_2	Total
Cu	−1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5*
Au	−1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	−1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	−1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	−1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	−1.24	5.0	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Pb	−1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	−1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
In	−1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	−1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	−1.63	5.0	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Tl	−1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
Ni	−1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4†
Fe	−0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	−1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	−1.60	5.0	0.0	0.0	0.0	0.0	tr.	0.0	99.7	99.7

Electrolyte: 0.1 M $KHCO_3$; temperature: 18.5 ± 0.5°C.

* The total value contains C_3H_5OH (1.4%), CH_3CHO (1.1%) and C_2H_5CHO (2.3%) in addition to the tabulated substances.

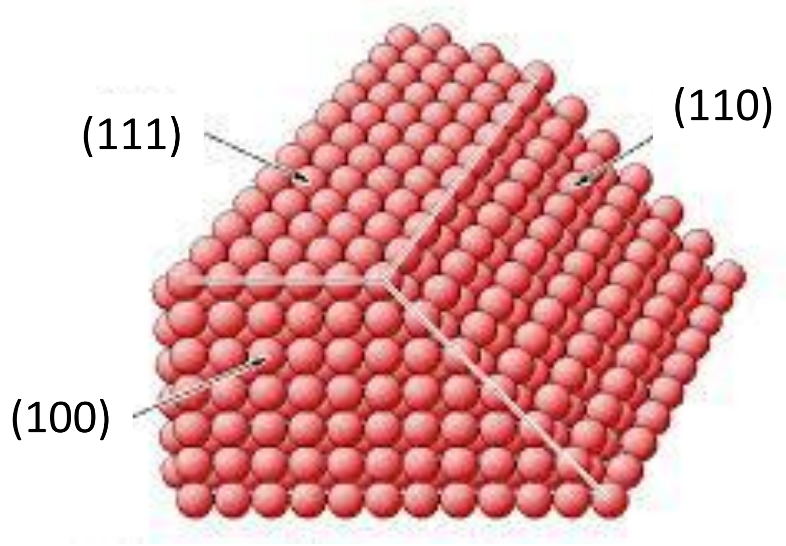
† The total value contains C_2H_6 (0.2%).

Hori, ECA, 1994

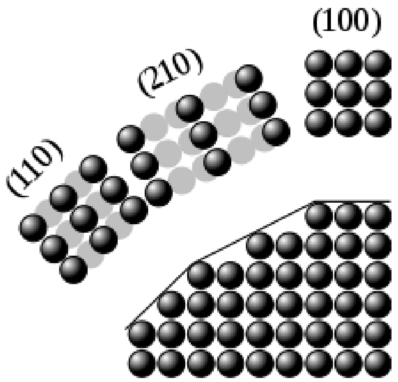
CO_2 Reduction Basics

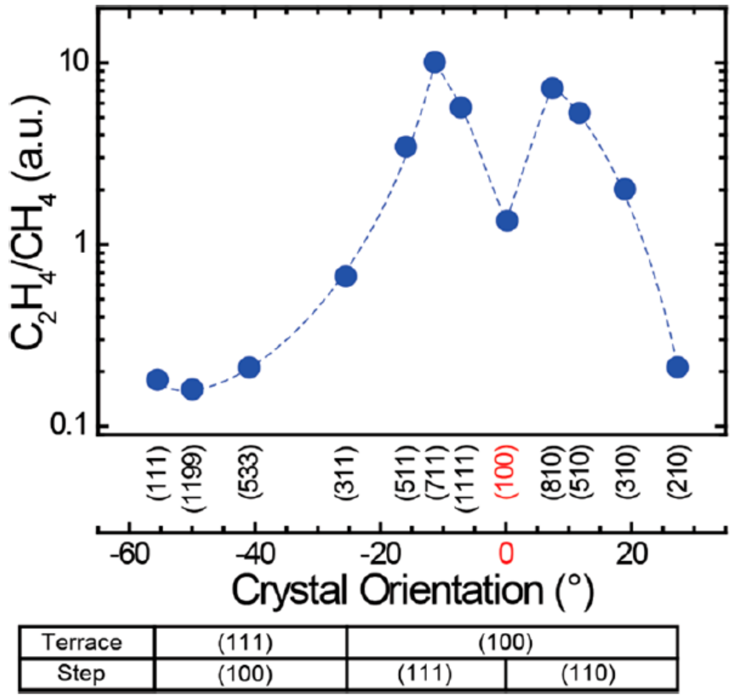
- It is well known that the <100> facet of copper is more active than the <111> facet.

- It is also believed that step sites improve performance



J. Mol. Catal. A: Chem. **2003**,





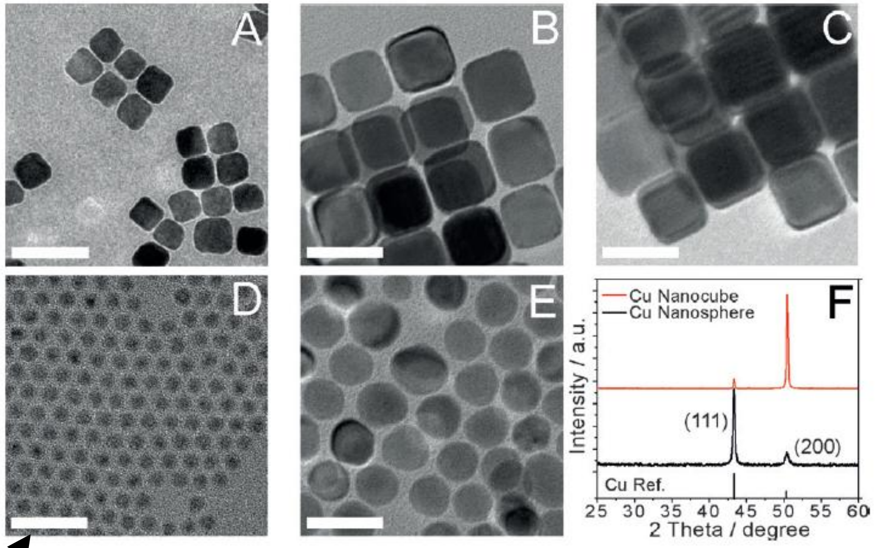
Data: Hori et al, J. Mol. Catal. A:Chem, 2003
Figure: Nitopi et al. Chem. Rev. 2019

Making Nanocubes

- Copper Nanocubes are <100> faceted.
- After ligand removal, these can be tested for CO_2 electrolysis

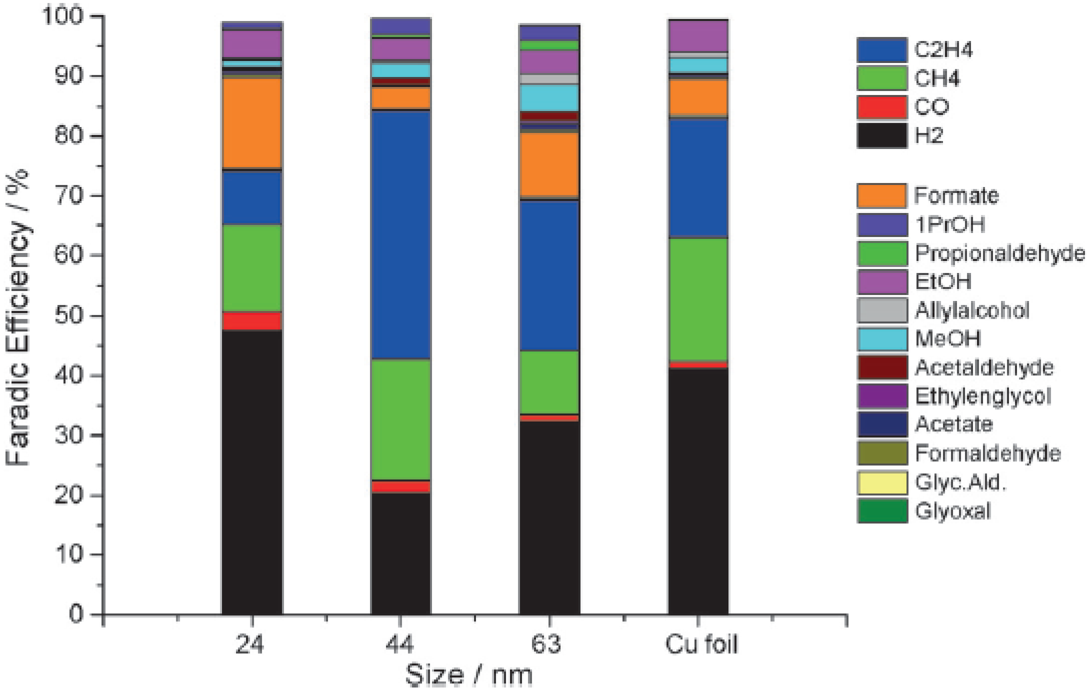
EPFL

Rafaella Buonsanti



50nm

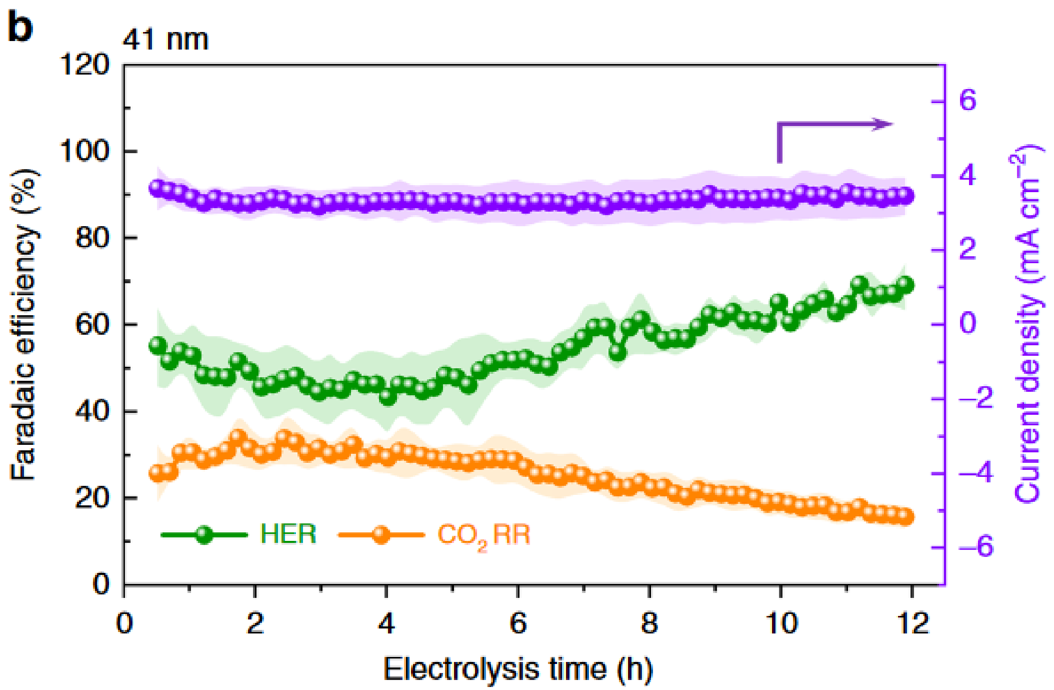
Louidice et al., 2016 Ang. Chem. Int.

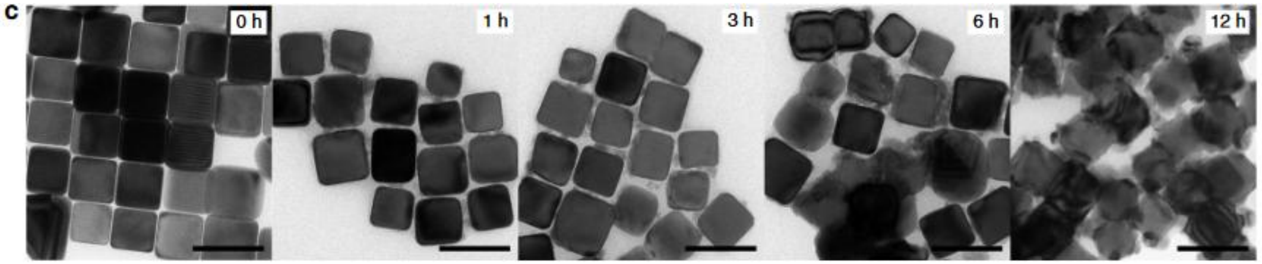


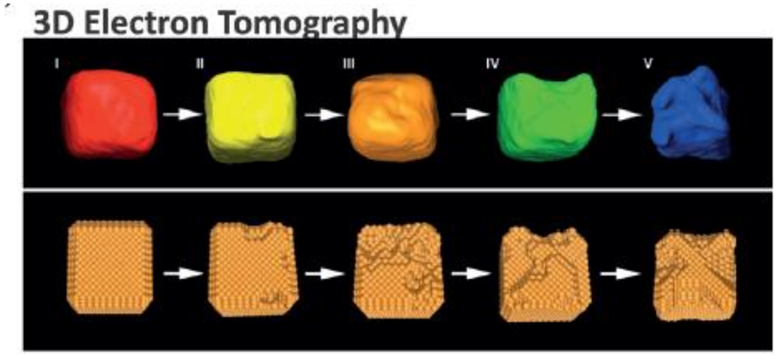
Stability issues

- The catlaysts were not stable over time
- MEA type cells have less water, which may effect catalyst stability.

Rafaella Buonsanti

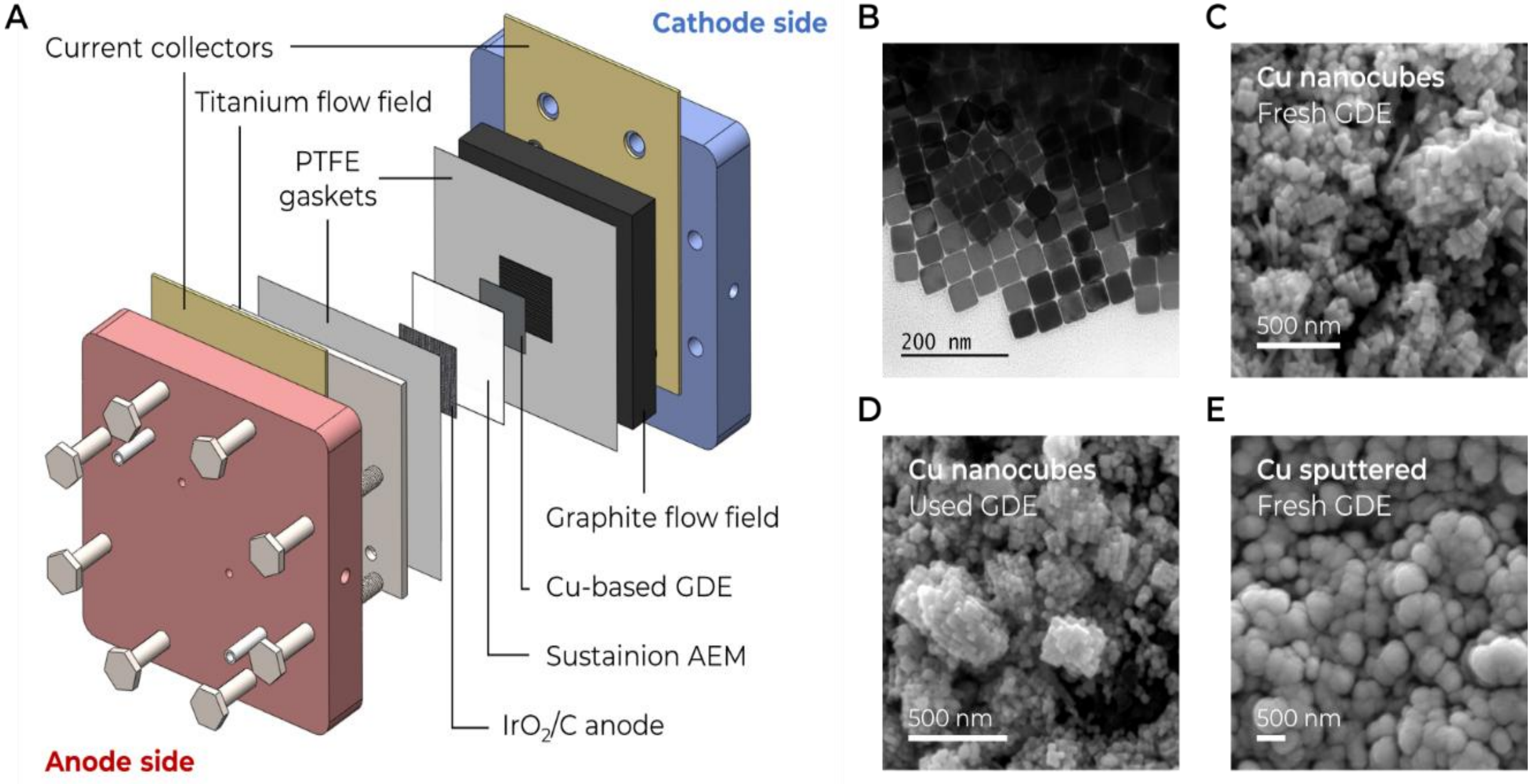






Goal of this work

- We wanted to analyze copper nanocubes versus sputtered copper.



Issues with outlet flow rate

- It is not straightforward to measure outlet flow rate

Inaccurate

(? Δ in conductivity)

Inaccurate

(? Δ in viscoscity)

Accurate

(Positive Displacement)

MESA Labs- Defender 530

Soap bubble

(painfully manual)

Accurate (Buoyancy)

Bioprocess Control µFlow

Product Line

N_2 Bleed line

(known flowrate)

CO_2 Reduction Basics

- CO_2 that goes into the reactor can do multiple things.
  1) React to form
     - Liquid products, thus will not be in the gas flow
     - C2 products, which will ½ the gas flow rate
  2) Equilibrate into the electrolyte

$$CO_2 + OH^- \rightarrow HCO_3^-$$

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$$

Cathodic reactions

$CO_2 + H_2O + 2\ e^- \rightarrow CO + 2\ OH^-$

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

$CO_2 + H_2O + 2\ e^- \rightarrow HCOO^- + OH^-$

$CO_2 + OH^- \rightarrow HCO_3^-$

$HCO_3^- + OH^- \rightarrow CO_3^{2-}$

Anodic reactions

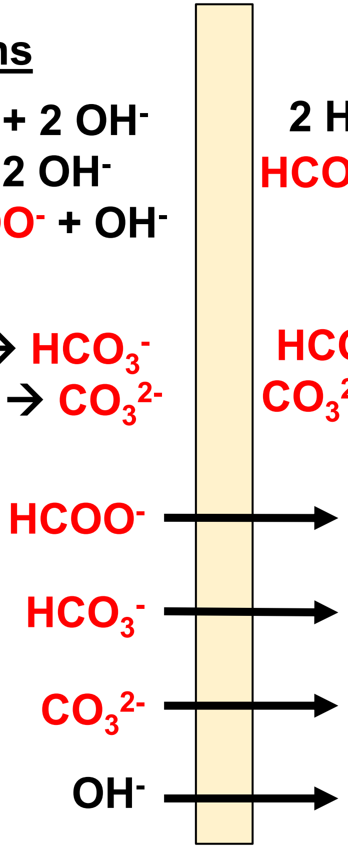
$2\ H_2O \rightarrow O_2 + 4\ e^- + 4\ H^+$

$HCOO^- \rightarrow CO_2 + 2\ e^- + H^+$

$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$

$CO_3^{2-} + 2\ H+ \rightarrow CO_2 + H_2O$

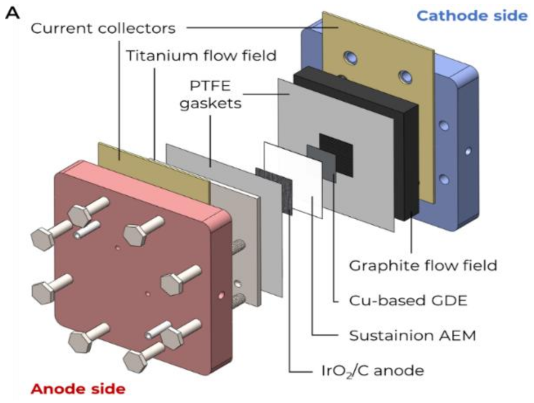
$OH^- + H+ \rightarrow H_2O$

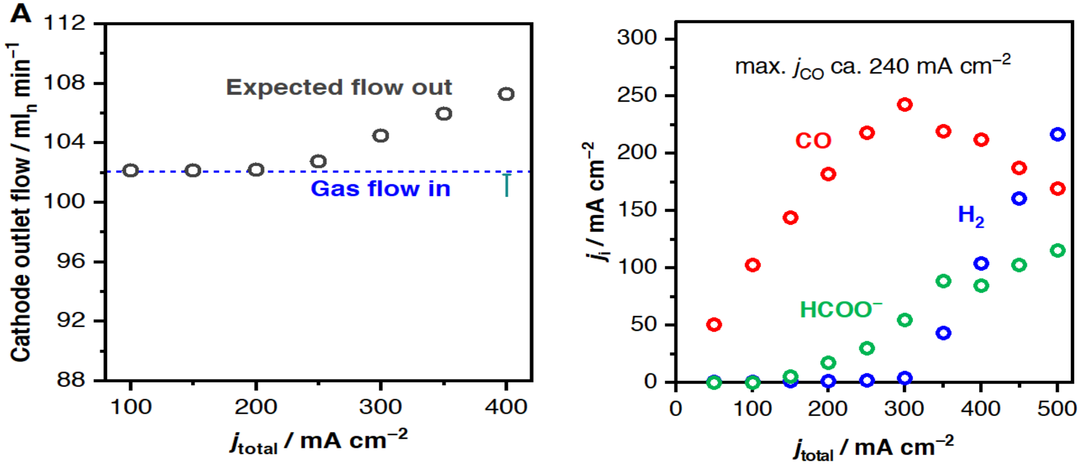


Anion exchange membrane

Issues with outlet flow rate

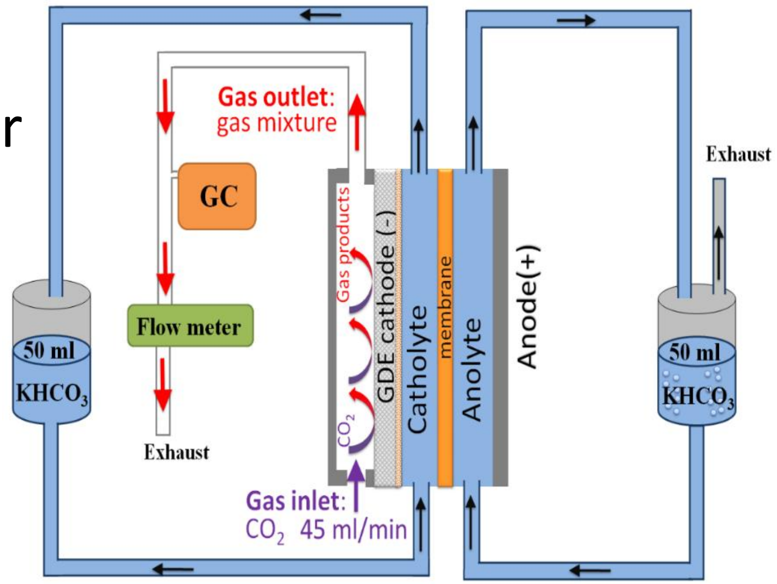
- Zero-Gap MEA cell
- Ag catalyst

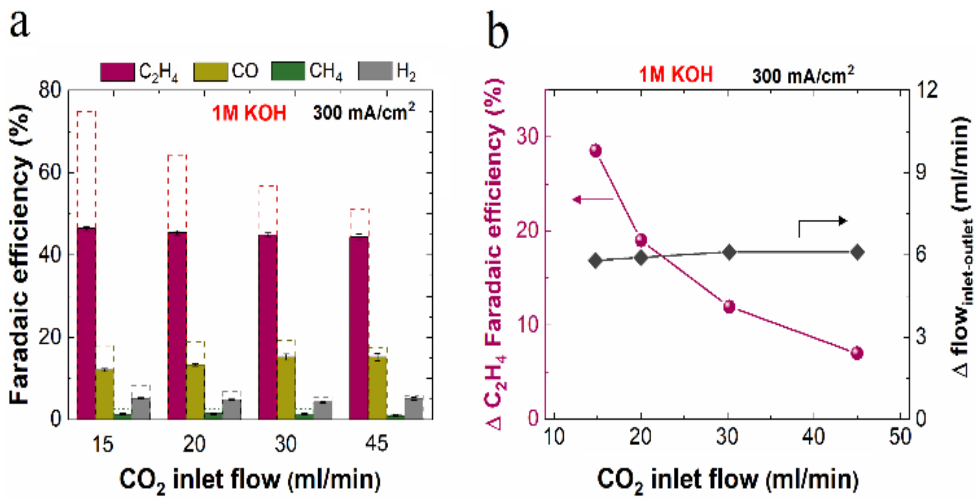




Larrazabal, G., et al., *ACS Appl. Mat & Int., 2019*

- 'Gapped' cell with a catholyte layer
- Cu catalyst

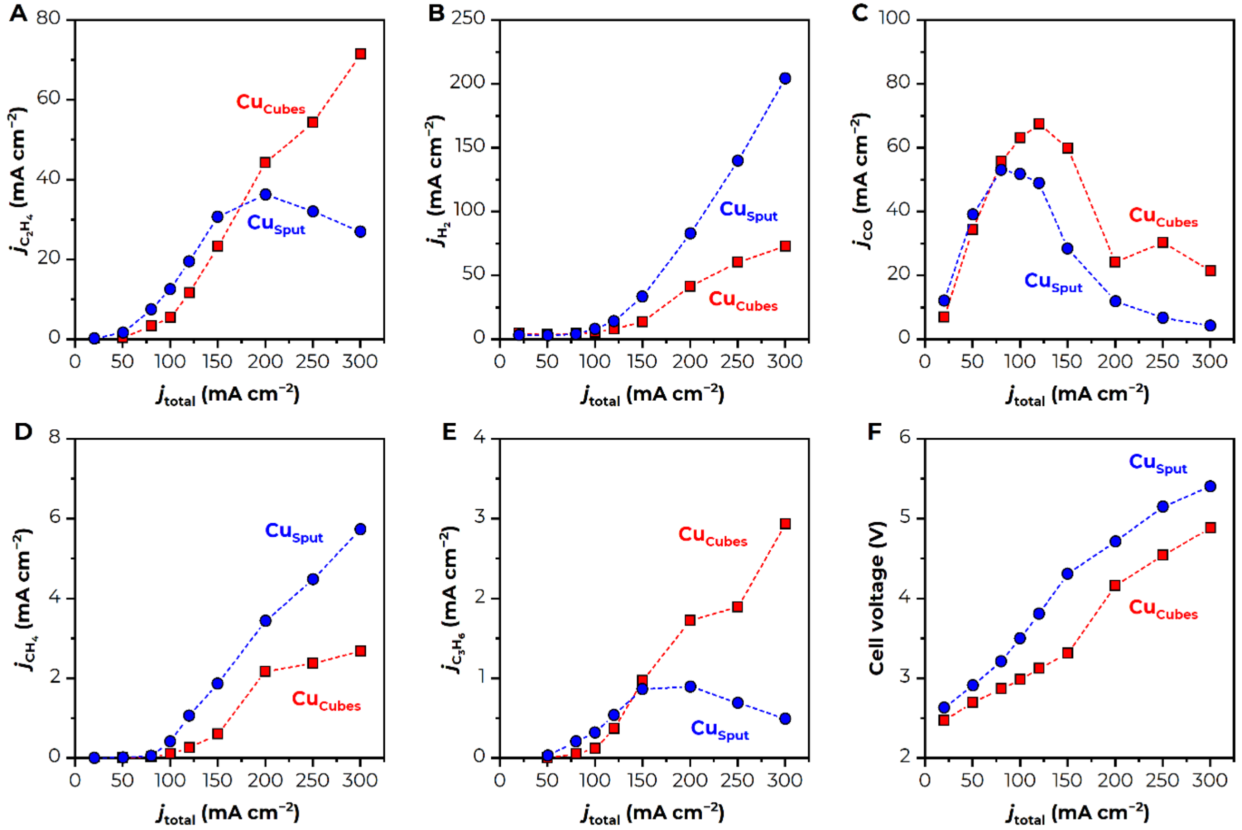




Ma, M., et al E&ES 2020.

Testing nanocubes in a zero gap cell

- Our results showed that the initial activity was mostly the same until we reached higher current densities.
- Our reactors tend to flood at high current densities



Conditions

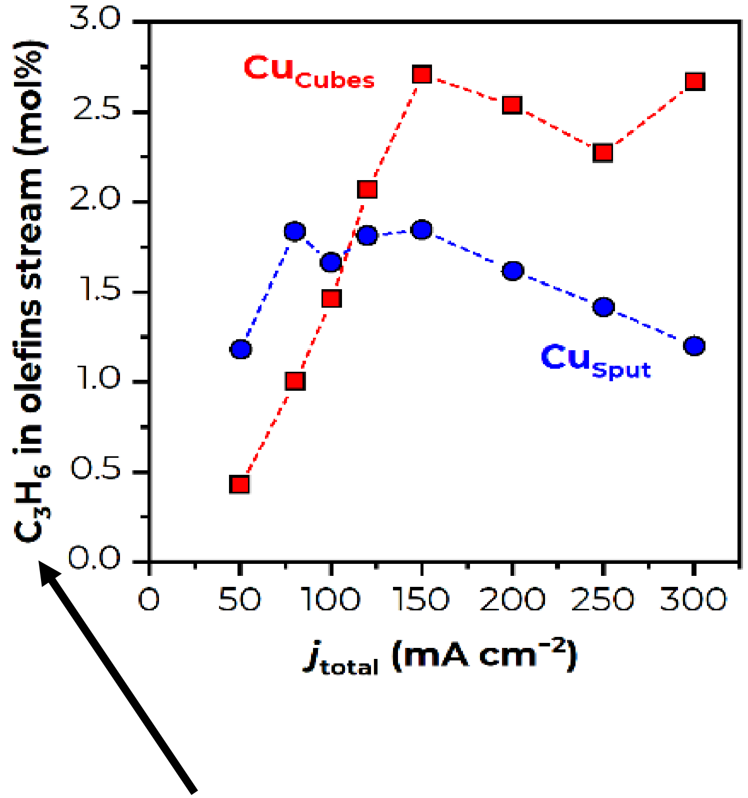
Nanocubes: 440 µg/cm^2 Cu
Dispersed
44nm size

Sputtered: 520 µg/cm^2 Cu
Concentrated (100 nm sputter)

Anolyte: 0.1M $KHCO_3$

Propene – Is it worth it?

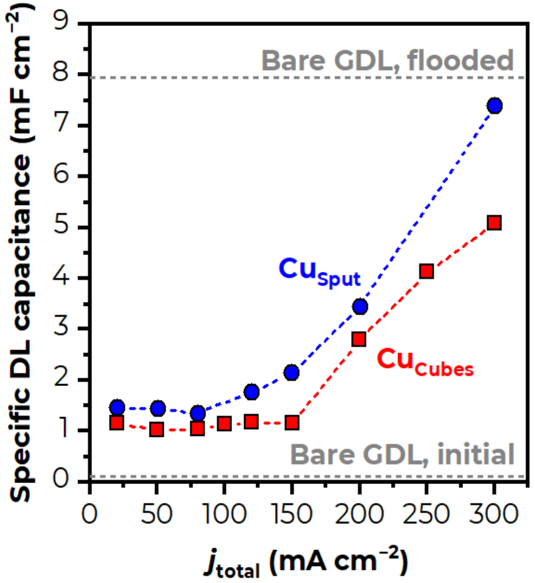
- Few researchers have ever seen propene, most likely because they never looked for it.
- Propylene is 2nd largest organic chemical globally (2,000 $/ton)
- Separating ethylene and propylene is not easy (goes through cryogenic distillation).
- Polymer grade ethylene needs <15 ppm propylene in it.

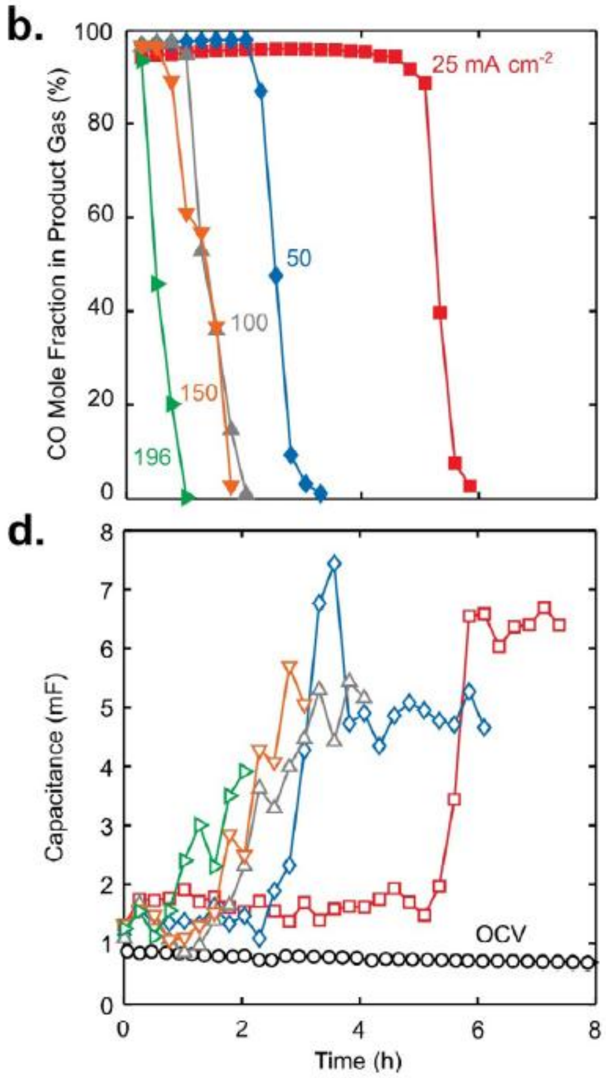


$$\frac{\text{propylene}}{\text{propylene + ethylene}}$$

Flooding

- The Bruschett group realized increased water into the GDL meant increased capacitance.
- We used this technique to see whether water was penetrating into our device

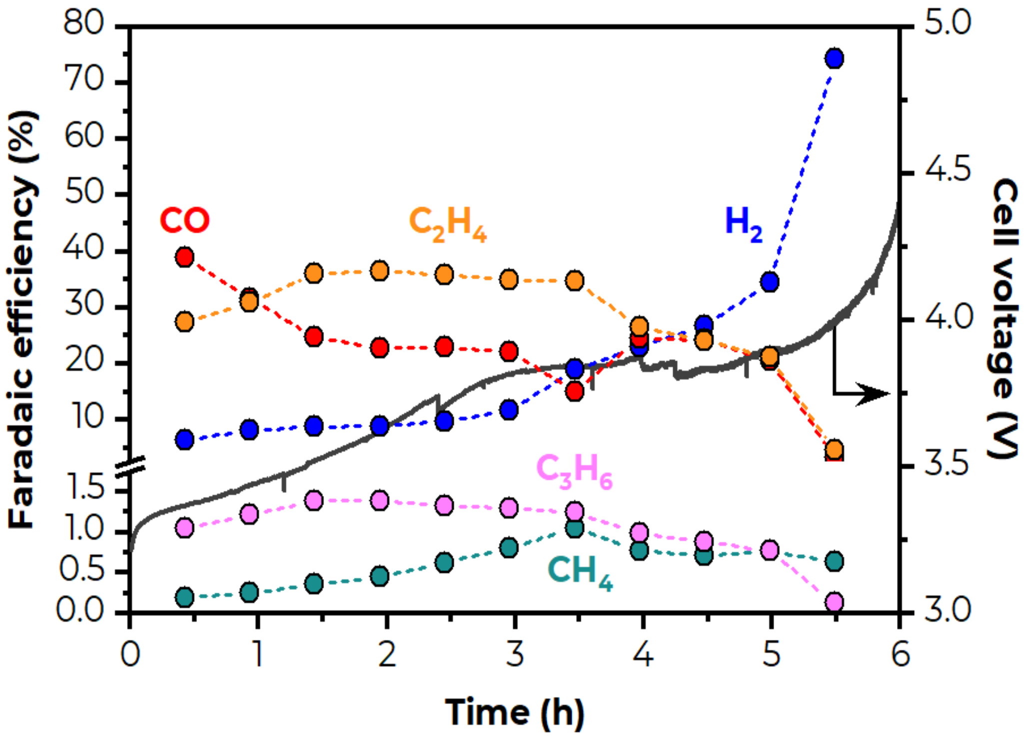




Leonard et al., ChemSusChem, 2019

Durability

- We are slowly flooding our gas diffusion layer (GDL) due to the increase in cell voltage
- With dispersed catalysts in the GDL, it takes longer until all the copper becomes flooded.



Conditions

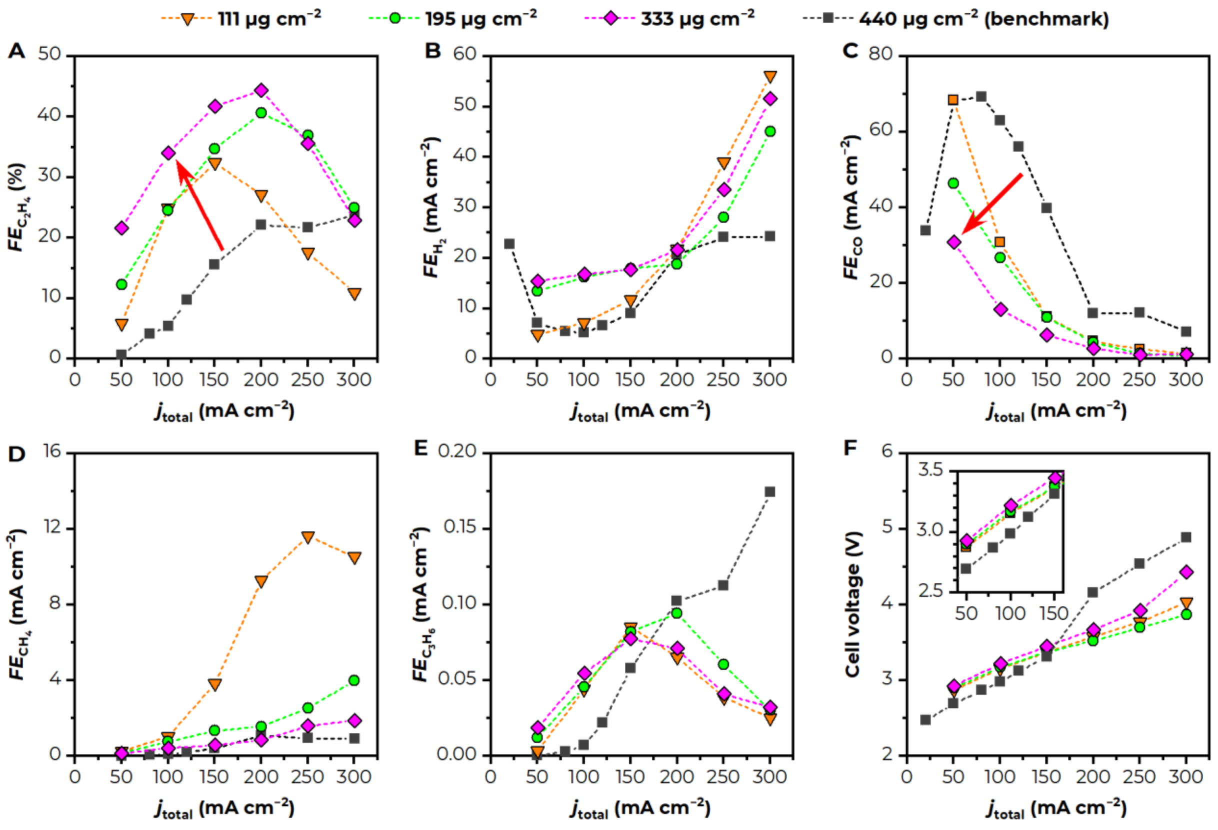
Nanocubes: 440 μg/cm^2 Cu Dispersed

Current Density: 250 mA/cm^2

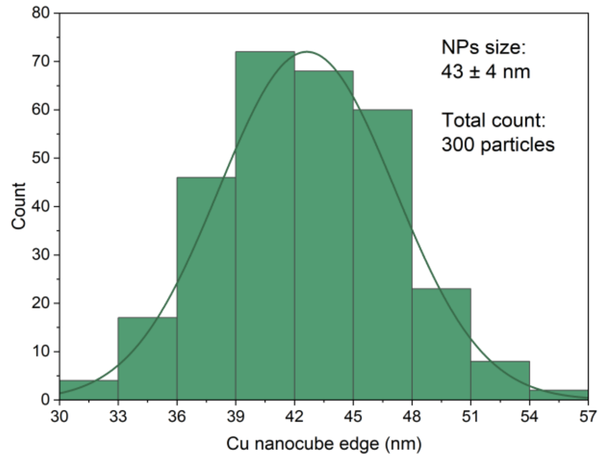
Anolyte: 0.1M $KHCO_3$

Loading and particle distribution

- We also tried varying the loading.
- We see a varying trend between CO and ethylene with loading



Particle Distribution



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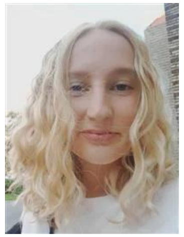
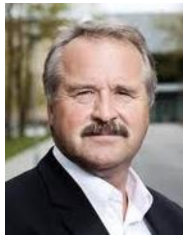


Clara Jensen



Ib Chorkendorff