



A closer analysis of CO₂ electrolysis catalysts and their upscaling

Brian Seger University of Deleware Seminar Oct 21, 2020



Chemicals before fuels

- Chemicals need functionality, and purity.
- Fuels just need to burn

Material	# of e⁻	Valu	World Prod.	
		(\$/ton)	(\$/MC)	(megaton)
Hydrogen	2	1000	0.010	60
СО	2	750	0.110	75
Formic Acid	2	650	0.150	0.8
Formaldehyde	4	530	0.041	10
Methanol	6	496	0.027	160
Methane	8	150	0.003	4000
Ethanol	12	600	0.024	110
Ethylene	12	1050	0.025	180

H₂- <u>https://www.hydrogen.energy.gov/</u>CO- <u>https://www.openpr.com/</u>COOH- A. A. N. Afshar, Chemical Profile: Formic Acid. *TranTech Consultants, Inc.*, (2014). CHOOH - <u>https://www.icis.com</u> CH₃OH <u>Methanex.com</u> CH₄- EIA (<u>www.eia.gov</u>), Acetic Acid- <u>Prnewswire.com/</u>, Ethylene Glycol-<u>https://www.intratec.us/</u>, <u>Ullmann's Encyc. of Ind. Chem</u>. Acetone- <u>Platts</u>, <u>Ullmann's Encyc. of</u> <u>Ind. Chem</u>, Ethanol- <u>Nasdaq</u>, <u>http://www.ethanolrfa.org</u> Ethylene- <u>Platts</u> Denmark will reach 100% renewables by 2027



This is 100 times Denmark's electricity consumption

CO₂ Reduction Basics

Table 1. Various products from the electroreduction of CO₂

	Potential (V)	Current density	Faradaic efficiency/%							
Electrode	vs. nhe	$(mA \ cm^{-2})$	CH4	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
Рb	- 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	1 3.9	78.4	9.4	103.0
TI	-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 KHCO₃; temperature: $18.5 \pm 0.5^{\circ}$ 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%).

<u>Hori, ECA, 1994</u>

CO₂ to CO Catalyst Electrocatalysis

Applied:goal-get highest current possible at a given potential
catalyst- high surface area, 3-dimensional
But report results in
mA/cm² for some reasonFundamental:goal-determine intrinsic catalytic activity
catalyst- low surface area, well defined



Jonanov et al., 2016, J. Catalysis

Single Crystal CO₂ to CO

- Highly undercoordinated Au sites have the highest activity.
- H₂ evolution is about same on all Au catalysts.
- Ag is not as good as Au, but suppresses H₂ better.



Mezzavilla, S. et. al, 2019, Ang. Chem. Int. Ed., doi: 10.1002/anie.201811422



Ag single crystal data, Hoshi et. al, 1997



H₂ issues

• The Au<111> and Au <100> has major H_2 issues.

Au is a much better H_2 catalyst than Ag. •





Formate on Au?

- The electrodes were taken to -1.0V vs RHE to look for formate.
- We also looked for methanol, but did not see anything.





Mezzavilla, S. et. al, 2019, Ang. Chem. Int. Ed., doi:<u>10.1002/anie.201811422</u>

CO

 H_2

CHOO-

Issues with Single Crystals

- Single crystals are flat in the middle, but at the edges have many step sites.
- Inactive facets (<100> & <111>) could be dominated by step sites, thus hiding the intrinsic activity.



• We can then see the intrisic activity of these sites







Images of flat and roughend Au from <u>Yoshimoto, et al., 2012</u>

Partial Pb UPD – Polycrystalline Au

• We had Pb coverage of:

A: 20% Pb coverage, about half undercoordinated peak

- B: 47% Pb coveage, all undercoodinated peak
- C: 100% Pb coverage (negligible current)



All experiments done at -0.7 V vs, RHE in 0.1M KHCO₃

Partial Pb UPD –Au <111>

• We had Pb coverage of:

0.1 0.2

E_{SHE} N 0.3

0.4

0.5 0.6

1 mmol Pb²⁺ 20 mV/s

-0.2 -0.1 0.0

A: 4% Pb coverage, about half undercoordinated peak

B: 15% Pb coveage, all undercoodinated peak



10 J 20

101 SCO

100

80

60

%

40世

20

BIML

A

NOPB

Can this be done with copper?

- There is a slight difference between UPD potentials on the <111> and <100> facets.
- Cu's facile oxidation makes this much more difficult.





Industrial relevant approaches to eCO₂ reduction



CO,





Ohmic Losses in Electrolyte (V) 0.1 M KHCO3 M KHCO3 0.8 KCI KOH /linimum CD 0.6 0.4 0.2 50 200 0 100 150 Current Density (mA/cm²)

3 mm anolyte & catholye

Burdyny and Smith, E&ES, 12, 1442-1453, (2019)

Disadvantages:

Kibria, et. al, Adv. Mat., 1807166, (2019)

Electrochemical set-up





Anode: IrO₂ on carbon paper Membrane: Sustainion 37-50 AEM Temperature: 30 C



Cathode: silver membranes of 50 µm thickness



Characterization & performance data

- SEM shows uniform pores of varying size.
- We did not see any significant performance difference between membranes.



?? Faradaic Efficiency Partial Current Density

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



Issues with outlet flow rate

• It is very hard to measure outlet flow rate



(? Δ in conductivity)





Accurate (Positive Displacement) MESA Labs- Defender 530



Soap bubble (painfully manual)



Product Line N₂ Bleed line (known flowrate)



Inaccurate (? Δ in viscoscity)

Accurate (Buoyancy) Bioprocess Control µFlow

Reactions for CO₂ to CO Electrolysis

- CO₂ 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 $CO_2 + OH^- \rightarrow HCO_3^ CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$
 - 3) Get transferred across the membrane



Anion exchange membrane



Cathodic reactions	Δ in outlet flow/2e-
$CO_2 + H_2O + 2 e^- \rightarrow CO + 2 OH^-$	0 mol
$2 H_2O + 2 e^- \rightarrow 2 H_2 + 2 OH^-$	1 mol
$CO_2 + H_2O + 2 e^- \rightarrow HCOO^- + OH^-$	-1 mol

We clearly have lots of CO₂ transferring over to the anode.



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

- A further analysis of anode gas flow gives insights into membrane crossover.
- This can give us details relating to:
 - Local pH
 - Membrane conductivity



 $\underline{\text{Anode reactions:}} \qquad \underline{\text{CO}_2/\text{O}_2 \text{ ratio}} \\ 4HCO_3^- \to 4CO_2 + O_2 + 2H_2O + 4e^- \longrightarrow 4 \\ 2CO_3^{2-} \to 2CO_2 + O_2 + 4e^- \longrightarrow 2 \\ 4OH^- \to 2H_2O + O_2 + 4e^- \longrightarrow 0 \\ OH^- + COOH^- \to H_2O + CO_2 + 2e^- \longrightarrow 0 \\ \end{bmatrix}$



Analyzing our CO₂ crossover

02

H₂0

0.5

Jpn., 55, 660 (1982)

- Carbonate transfer allows us to learn 2 very important things.
 - 1. Carbonate is going through, hurting conductivity
 - 2. Locally we are highly basic



Liu, Z.;J. Electr. Soc.,165(15) J3371-J3377 (2018)

Total system analysis

• 100% faradaic efficiency is great to see

• Full carbon balance is just as important to see.



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

Copper



Modified from Nitopi, et.al., *Chemical Reviews* 2019, doi:<u>10.1021/acs.chemrev.8b00705</u>



Wang, et.al., ACS Catalysis 2018 Doi:10.1021/acscatal.8b01200

Analyzing copper for CO₂ reduction

- With copper producing liquid products, we decided to go with a GDE approach.
- 70 nm sputtered Cu on a gas diffusion layer.





Testing different electrolytes

- We tested in both neutral and basic electrolytes.
- Basic electrolytes are effectively 'CO₂ scrubbers'

 $CO_2 + OH^- \to HCO_3^-$ pKa (effective)=7.8 $HCO_3^- + 2OH^- \to CO_3^{2-} + H_2O$ pKa = 10.3

- Even at open-circuit, significant CO₂ is consumed.
- CO₂ reduction naturally produces OH⁻, thus increasing 'scrubbing' capability of catholyte gas

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



Ma, M., et al E&ES 2020 Doi:<u>10.1039/D0EE00047G</u>

Comparison of selectivites in different electrolytes



• How important is it to take into considration actual gas flow rate leaving reactor?



Liquid selectivites

- We see 8 different liquid products
- Minimal variation at different current regimes.
- We see significant products coming out the anode.





Understanding membrane crossover



Proposed carbon balance paths via CO_3^{2-} or HCO_3^{-} formation from CO_2 and a subsequent CO_2 production from CO_3^{2-} or HCO_3^{-}

Anode reactions:

<u>CO₂/O₂ ratio</u>



 $4COOH^- \rightarrow 4HCOOH + O_2 + 4e^- \longrightarrow 0$

 $4CH_3COO^- \rightarrow 4CH_3COOH + O_2 + 4e^- \longrightarrow 0$







pKa of $HCO_3/CO_2 = 7.8$

• Varying the current densities accelerates pH modifications.



- With basic electrolytes there is no CO₂ emitting from anolyte.
- A smaller reservoir shows CO₂ just needs to satruate the solution.



Stability

• The reactor's performance is relatively stable over a 2 hour time frame.



• We measured potential vs. current, but we can not plot this versus RHE.



Device analysis

• 100% faradaic efficiency

• Full carbon balance



Inlet CO₂ flow: 45 ml/min

 $\phi_{inlet CO_2} = \phi_{unused CO_2} + \phi_{CO_2 to gas} + \phi_{CO_2 to liquid} + \phi_{out the anode}$

J	Ø _{unused} CO ₂	$\phi_{CO_2 to gas}$	$\phi_{CO_2 to liquid}$	Ø _{Anode}	$\phi_{total \ CO_2}$
(mA/cm ²)	(ml/min)	(ml/min)	(ml/min)	(ml/min)	(ml/min)
200	40.806	0.922	0.3387	3.11156	45.178
250	39.735	1.169	0.3928	3.80596	45.103
300	38.616	1.379	0.4779	4.50385	44.977

Using 1 M KHCO₃ as initial electrolyte

How do CEM & Bipolar membranes compare ?

- Selectivity does not vary as long as you have a gapped cell (1cm for us).
- The CO₂ crossover is quite different.



Total cell voltage

- Ohmic resistance in electrolytes dominate cell voltage.
- Carbonate's pulls K⁺ through CEM's modifying conductivity
- Conductivity does not account for water-splitting in BPM.
- CO electrolysis does not have these issues.



Conclusions

CO₂ consumption (%)

0

200

- Even single crystal data can be deceiving with respect to activity and selectivity.
- 100% Faradaic efficiency and full carbon balance give a deeper insight into high current density reactions.
- CO₂ crossover is a huge issue for the CO₂ electroysis field.





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

250

Current density (mA/cm²)

300

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



Acknowledgements

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Kasper Therkildsen



Celia

Callioux

Competing Technologies

- Single-step CO₂ electrolysis to high value products:
 - 3 V operating potential



- Hydrogen electrolysis followed by thermal processes:
 - 1.8 2 V operating potential





Competing Technologies

- **Biomass:** •
 - Very complicated life-cycle analysis
 - Already dominant production for ethanol •



- Methane decomposition:
 - This will be cheap since methane is energy dense
 - This process needs heat though (its endothermic) ۲
 - Methane leakage is a greenhouse gas issue. ۲



Competing Technologies

- High-temp (700 °C) CO₂ to CO electrolysis
 - Topsoe Catalyst and Sunfire
 - Operate at 1.5V (plus thermal energy)

- Low-temp (60 °C) CO electrolysis
 - Operate at ~2.3 V



• Low temperature CO electrolysis has very high potential.

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lb Chorkendorff

Kasper Therkildsen



Celia

Callioux

Pb underpotential deposition

• Calculating surface area for Au

UPD for Au



		Pb Deposition		Pb Stripping		Double layer	
		(cath	odic)	(anoc	lic)	capacitance	
ſ	Flootrado	Q	Rf	Q	Rf	С	
	Electione	(µCcm⁻²)	(/)	(µCcm⁻²)	(/)	(µFcm⁻²)	
	(111)	295	1	266	1	20 ± 5	
	(100)	0) 292 1 1) 293 1		280	1	20 ± 5	
	(211)			270	1	25 ± 5	
	(110)	258	1	210	1	30 ± 5	
[pc Au	492	1.7	435	1.6*	60 ± 5	



* Hamelin, A. J Electroanal Chem Interfacial Electrochem 165, 167–180 (1984).

H₂ evolution on Au single crystals

