Fundamental Studies on CO_2 and CO Reduction

SurfCat Summer School
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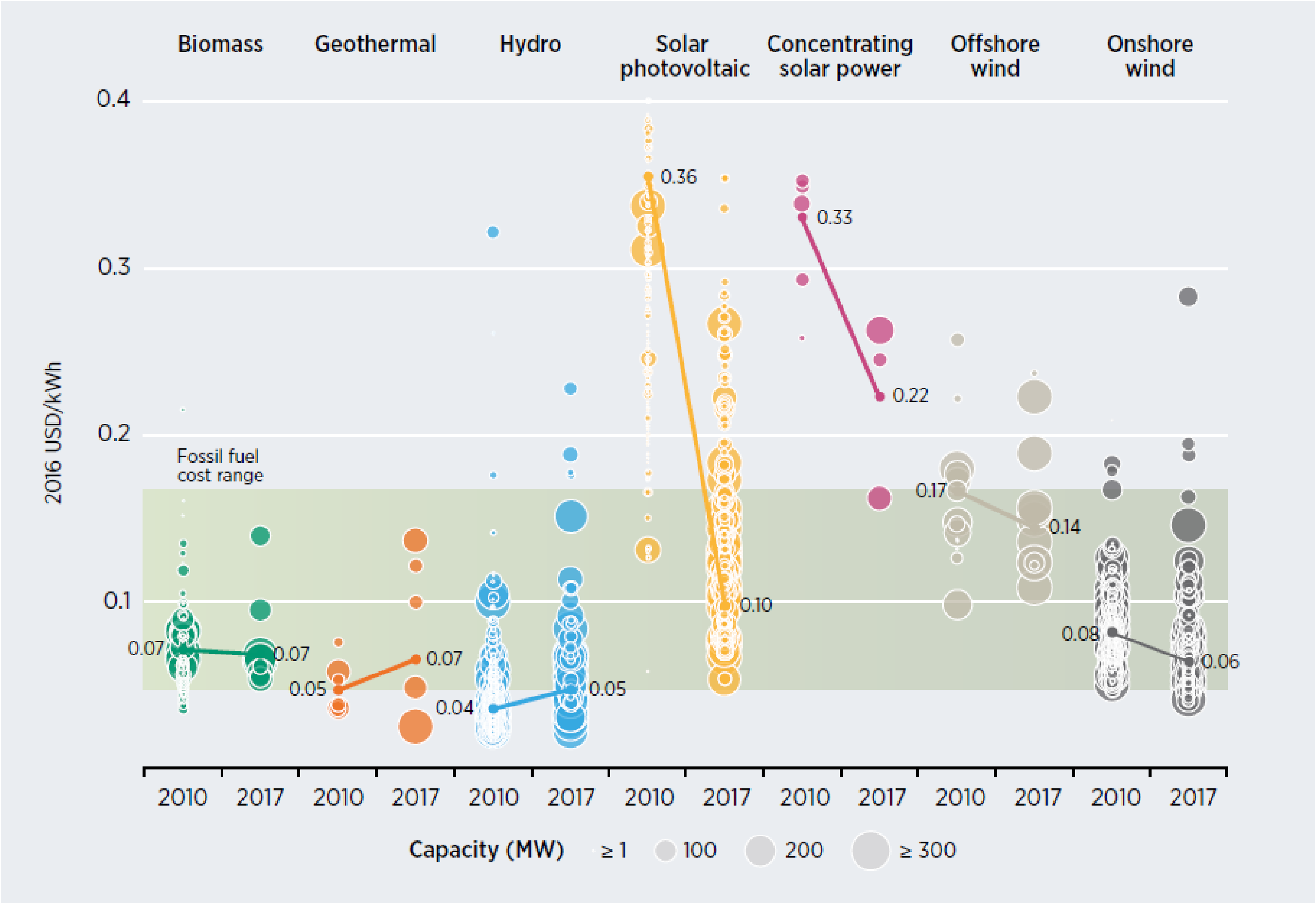
Why an Electrochemical Approach



Source: IRENA Renewable Cost Database.

Note: The diameter of the circle represents the size of the project, with its centre the value for the cost of each project on the Y axis. The thick lines are the global weighted average LCOE value for plants commissioned in each year. Real weighted average cost of capital is 7.5% for OECD countries and China and 10% for the rest of the world. The band represents the fossil fuel-fired power generation cost range.

Chemicals Before Fuels

- CO_2 reduction to chemicals starts with 1 carbon, whereas fossil fuels break down 10-20 carbon materials.

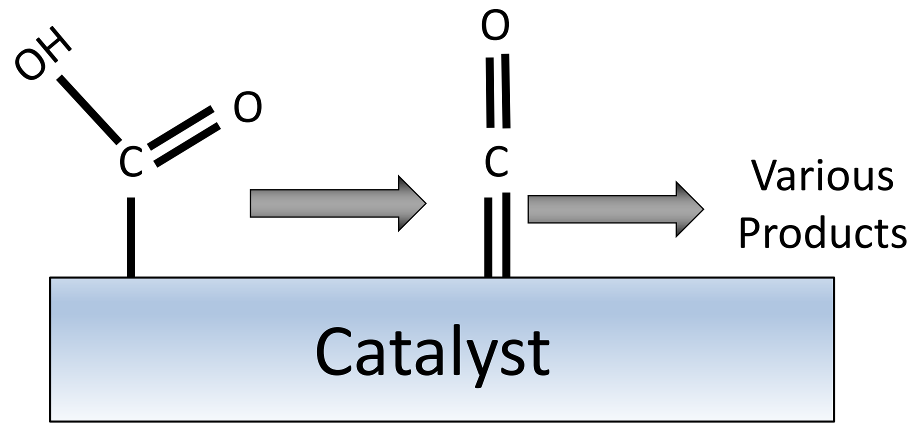
Material	# of e^-	(\$/ton)	(\$/MC)	World Prod. (megaton)
Hydrogen	2	1000	**0.010**	60
Carbon Monoxide	2	743	**0.110**	3.8
Formic Acid	2	650	**0.150**	0.8
Formaldehyde	4	530	**0.041**	10
Methanol	6	496	**0.027**	160
Methane	8	150	**0.003**	4000
Acetic Acid	8	460	**0.036**	12
Ethylene Glycol	10	1000	**0.065**	7
Acetone	16	700	**0.064**	6
Ethanol	12	600	**0.024**	110
Ethylene	12	1050	**0.025**	180

H_2- https://www.hydrogen.energy.gov/ CO- https://www.openpr.com/ COOH- A. A. N. Afshar, Chemical Profile: Formic Acid, *TranTech Consultants, Inc.*, (2014). CHOOH - https://www.icis.com CH_3OH Methanex.com CH_4- EIA (www.eia.gov), Acetic Acid- Prnewswire.com/ , Ethylene Glycol- https://www.intratec.us/ , Ullmann's Encyc. of Ind. Chem. Acetone- Platts , Ullmann's Encyc. of Ind. Chem, Ethanol- Nasdaq, http://www.ethanolrfa.org Ethylene- Platts

- Technoeconomic analysis: *Jouny et. al, Ind. Eng. Chem. Res.*, 2018, 57 (6), pp 2165–2177

Talk Outline

- All CO_2 reduction intermediates go through CO (except formate).



- A 2-step process allows us more flexibility in catalysis and better fundamental understanding.
- Thus this talk has 2 parts:

  Part 1: Fundamental studies on Au for CO_2 to CO

  Part 2: Syncrotron studies of CO reduction on Cu

CO_2 to CO Catalyst Electrocatalysis

Applied: *<u>goal</u>*- get highest current possible at a given potential

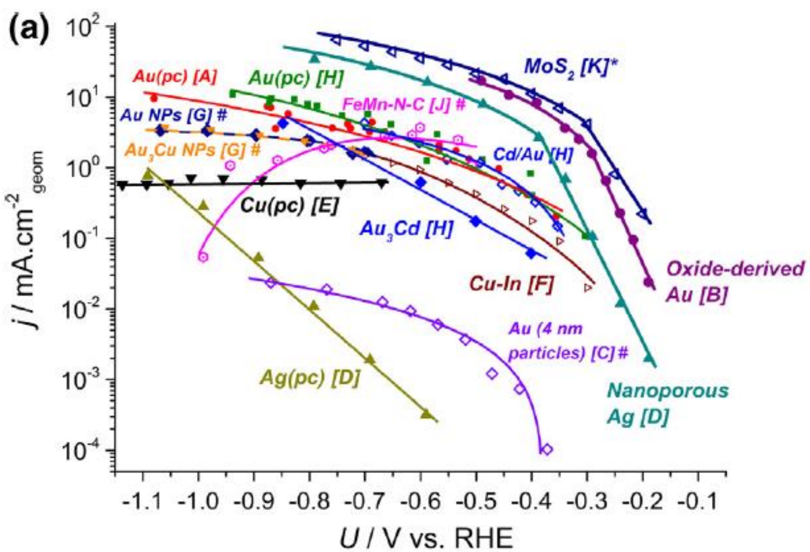
<u>catalyst</u>- high surface area, 3-dimensional

But report results in mA/cm^2 for some reason

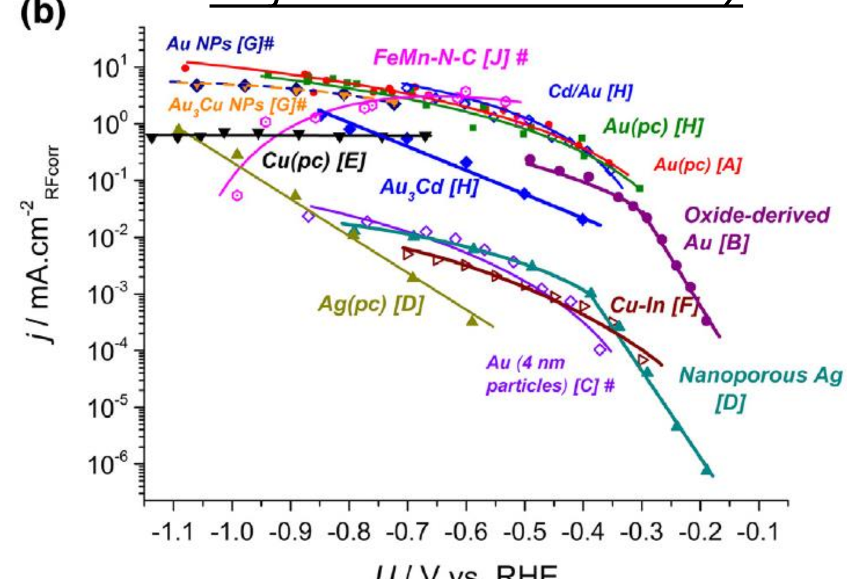
Fundamental: *<u>goal</u>*- determine intrinsic catalytic activity

<u>catalyst</u>- well defined, low surface area

<u>Electrocatalytic Activity</u>

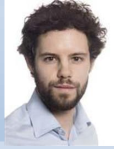


<u>Surface Normalized Activity</u>

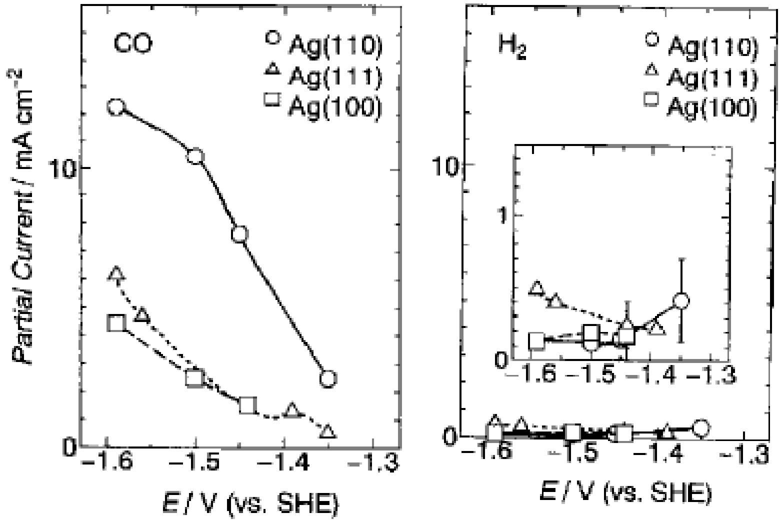


[Jonanov et al., 2016, J. Catalysis]

Single Crystal CO_2 to CO

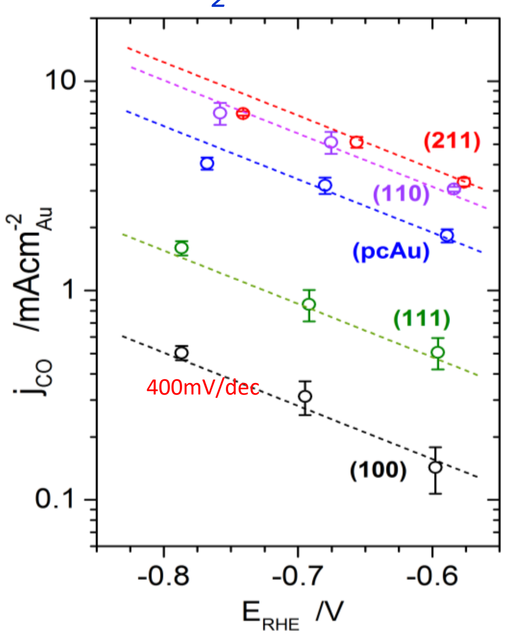


- Highly undercoordinated Au sites have the highest activity.
- H_2 evolution is about same on all Au catalysts.
- Ag is not as good as Au, but suppresses H_2 better.

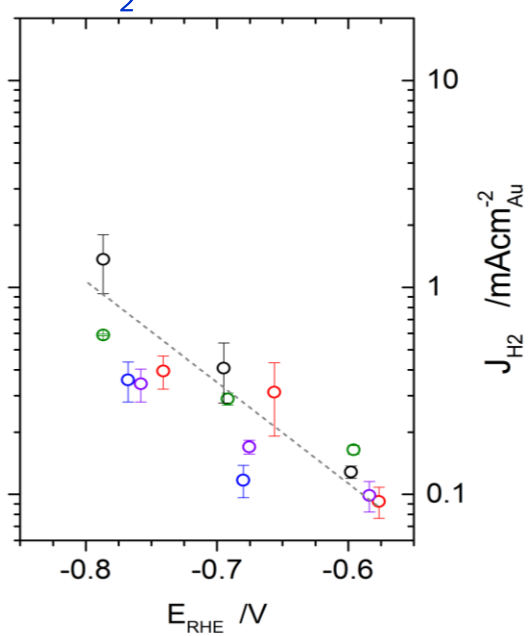


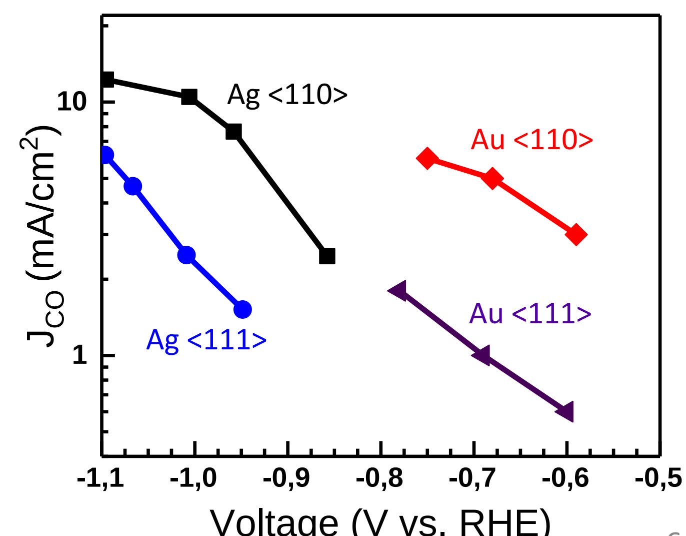
Ag single crystal data, [Hoshi et. al, 1997]

CO_2 evolution



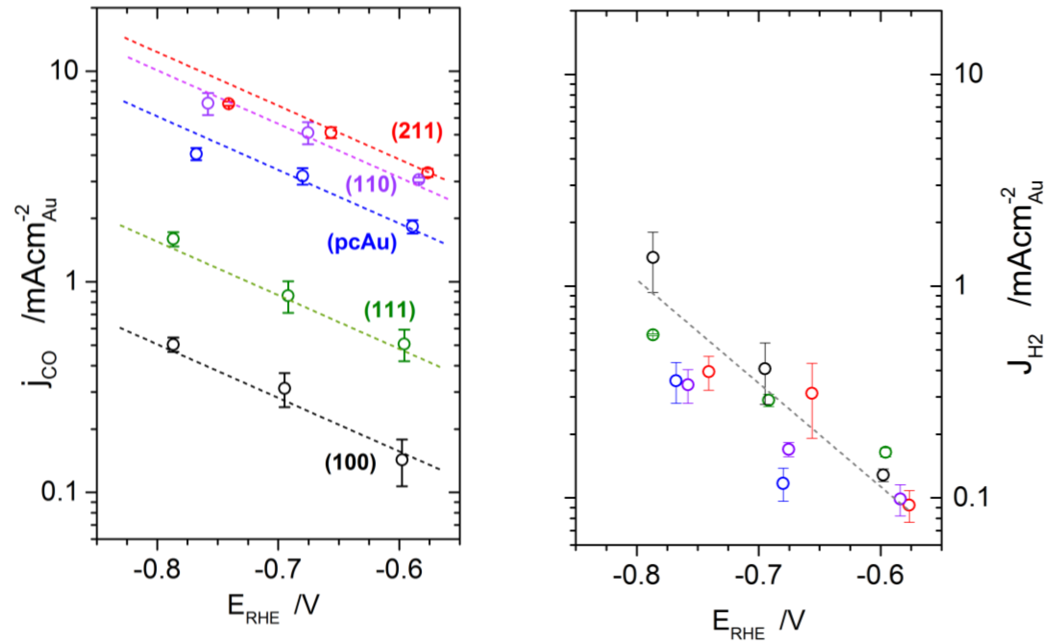
H_2 evolution

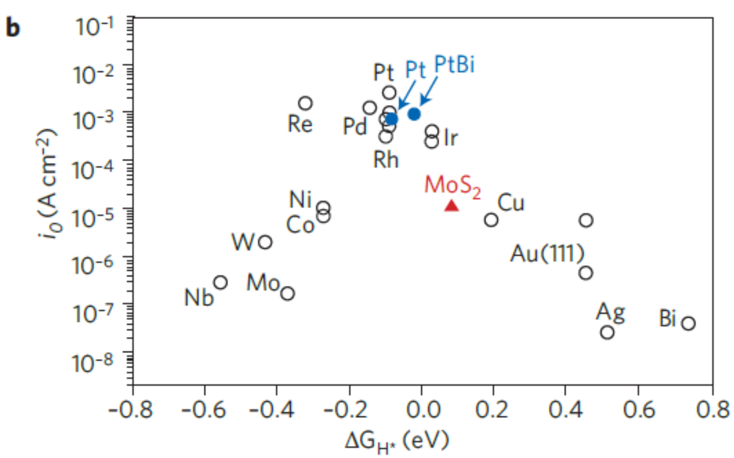




H_2 issues

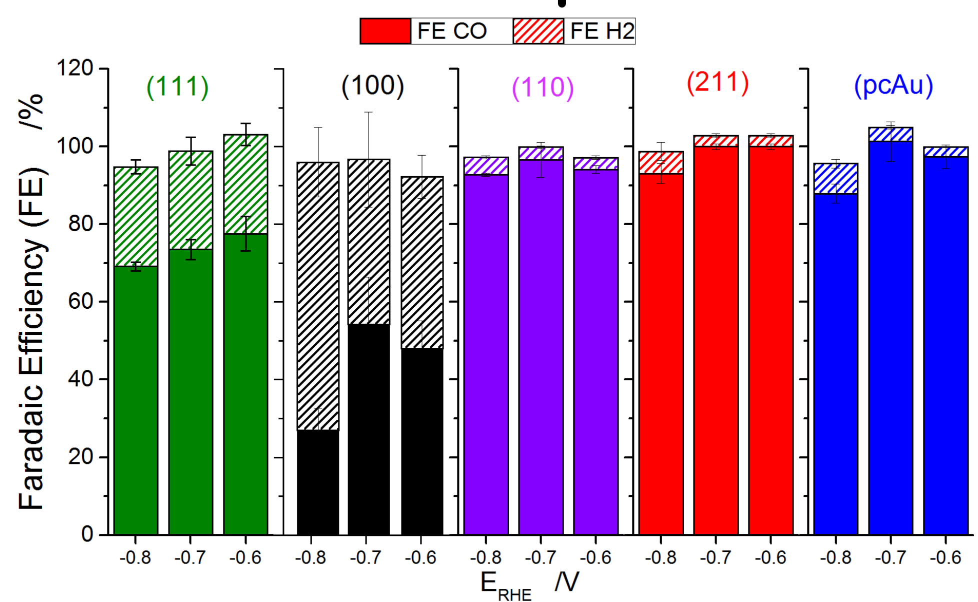
- The Au<111> and Au <100> has major H_2 issues.
- Au is a much better H_2 catalyst than Ag.



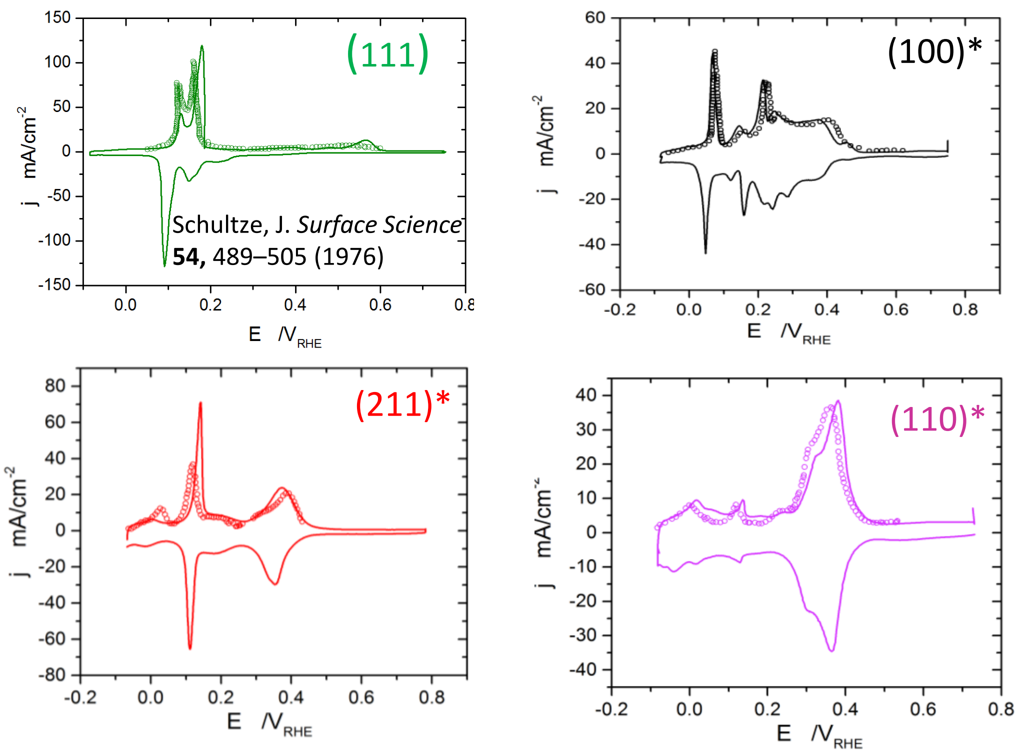


[Norskov et al., Nat. Chem, 2009]

Data Replotted



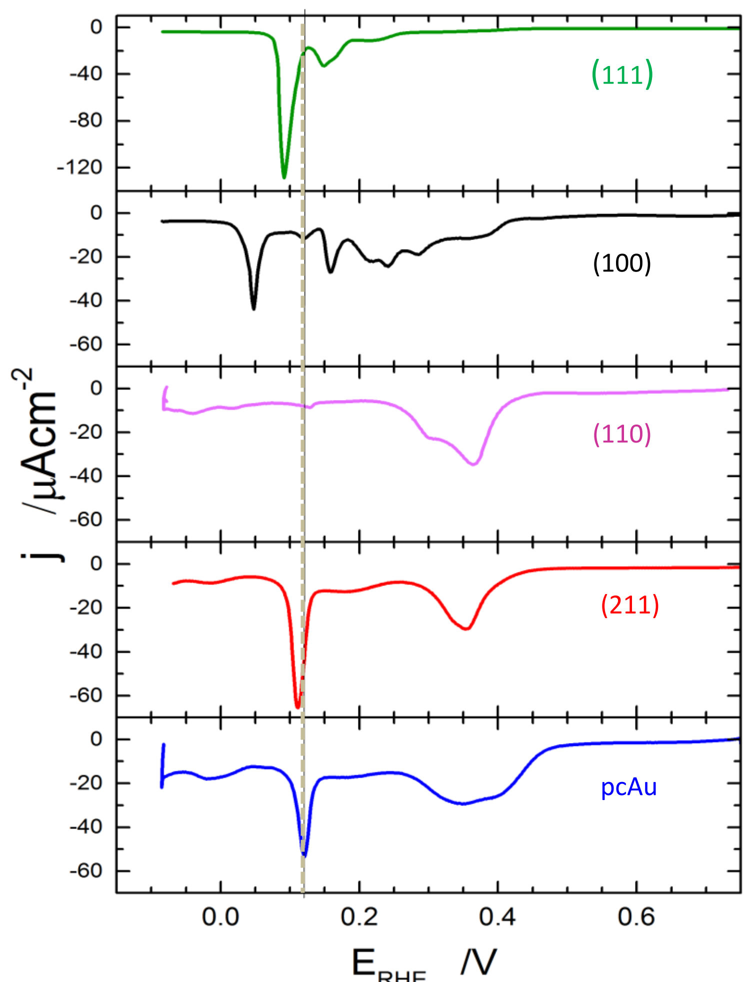
Pb Underpotential Deposition



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

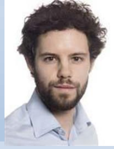
- Calculating surface area for Au

UPD for Au



	Pb Deposition (cathodic)		Pb Stripping (anodic)		Double layer capacitance
Electrode	Q (µCcm^{-2})	Rf (/)	Q (µCcm^{-2})	Rf (/)	C (µFcm^{-2})
(111)	295	1	266	1	20 ± 5
(100)	292	1	280	1	20 ± 5
(211)	293	1	270	1	25 ± 5
(110)	258	1	210	1	30 ± 5
pc Au	492	1.7	435	1.6*	60 ± 5

Partial Pb UPD – Polycrystalline Au

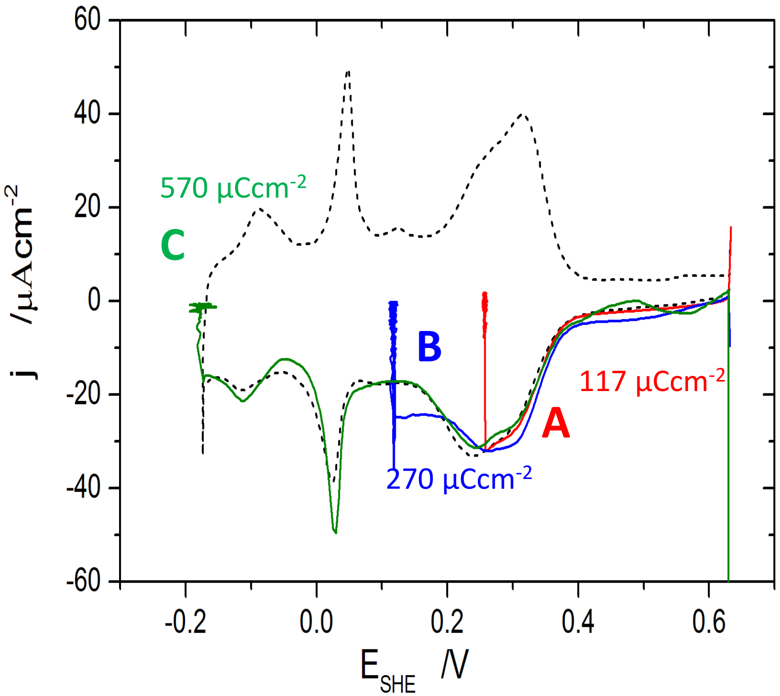


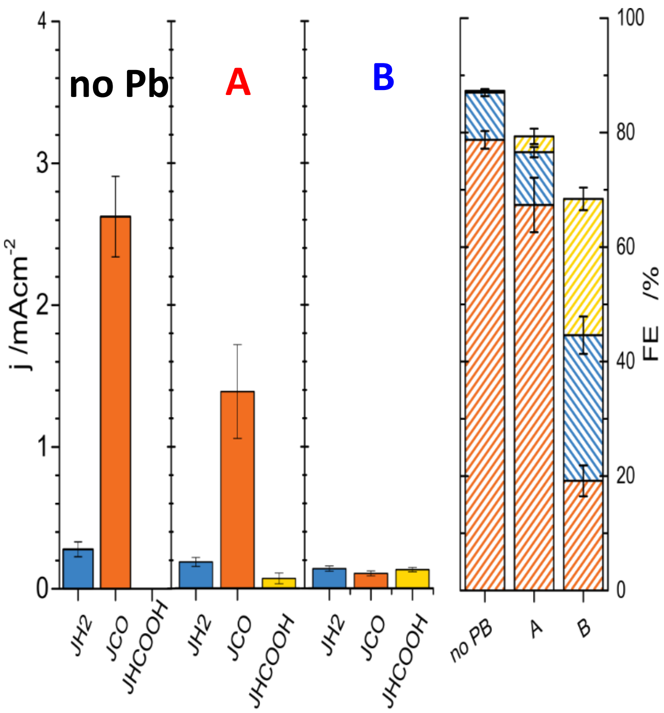
- We partially UPD lead onto Au and measure activity.
- We had Pb coverage of:

  A: 20% Pb coverage, about half undercoordinated peak

  B: 47% Pb coveage, all undercoodinated peak

  C: 100% Pb coverage (negligible current)

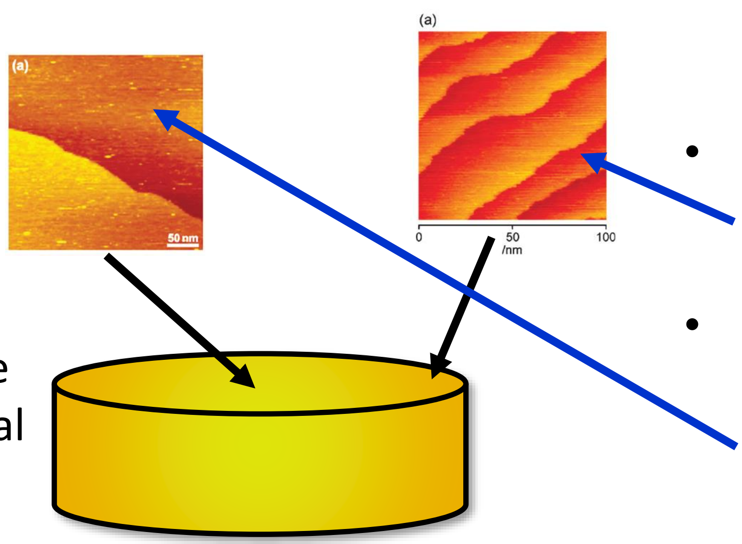




All experiments done at -0.7 V vs, RHE in 0.1M $KHCO_3$

Issues with Single Crystals

- Single crystals are very flat in the middle, but at the edges they tend to curve slightly, and have edge sites.
- Inactive facets (<100> & <111>) could be dominated by edge sites, thus hiding the intrinsic activity.

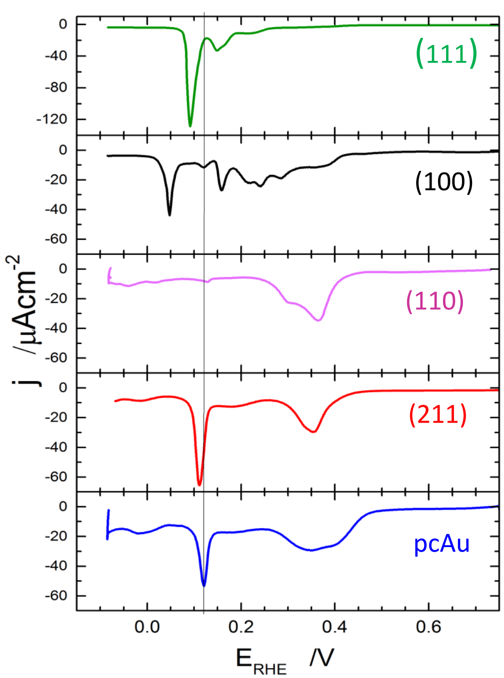


Single Crystal Au

- Use Pb UPD to block these edge sites
- We can then see the intrisic activity of these sites

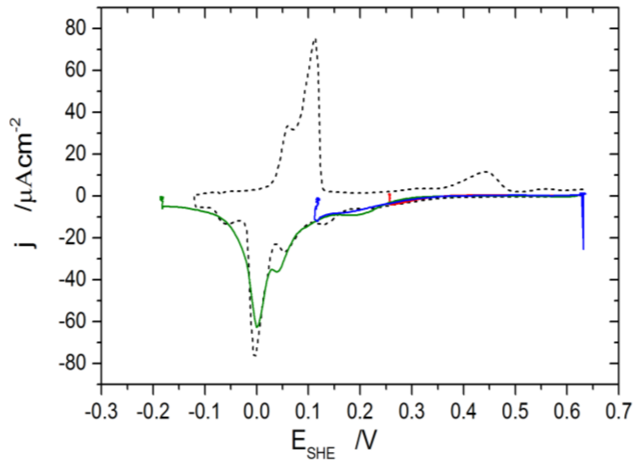
Images of flat and roughend Au from [Yoshimoto, et al., 2012](#)

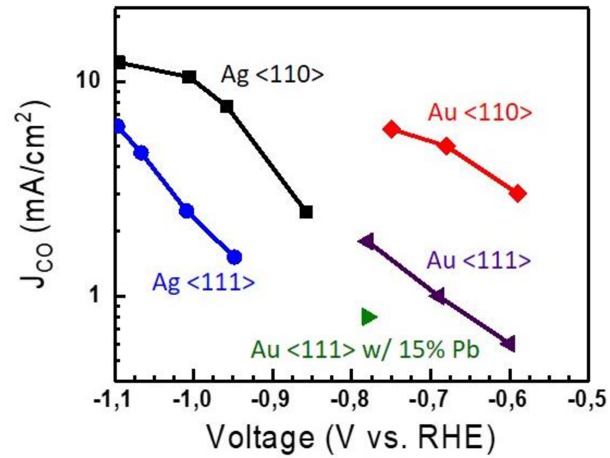
UPD for Au

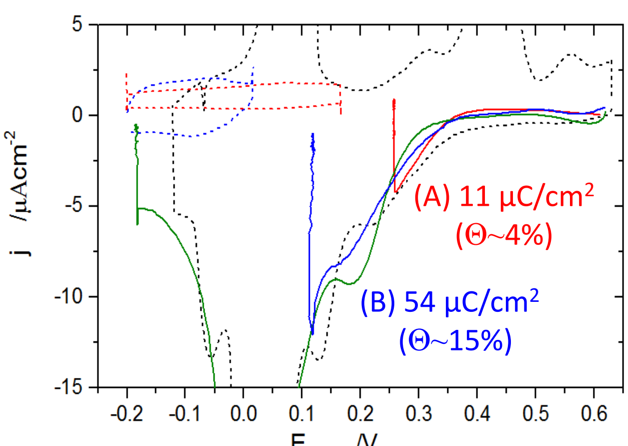


Partial Pb UPD –Au <111>

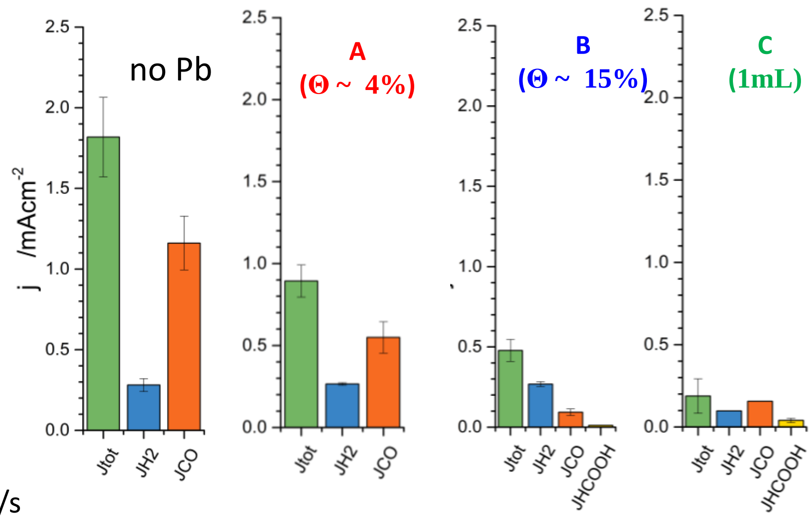
- We had Pb coverage of:
  - A: 4% Pb coverage, about half undercoordinated peak
  - B: 15% Pb coveage, all undercoodinated peak
  - C: 100% Pb coverage

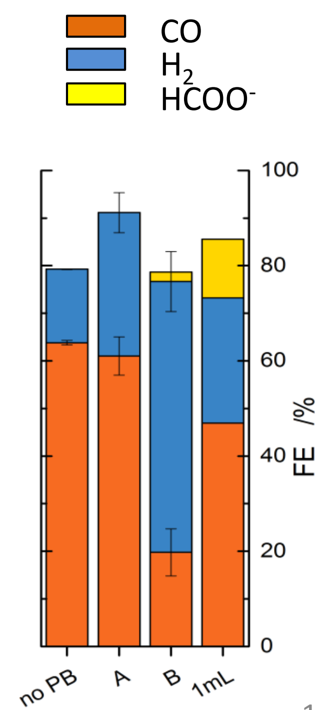






1 mmol Pb^{2+} 20 mV/s





Part 2

Syncrotron Studies on Cu

DTU

Erlend Betheussen

Søren Scott

Thomas Maagard

Thomas Hogg

Stanford

John Lin

Alan Landers

Christopher Hahn

Drew Higgins

Thomas Jaramillo

SLAC

Ryan Davis

Apurva Mehta

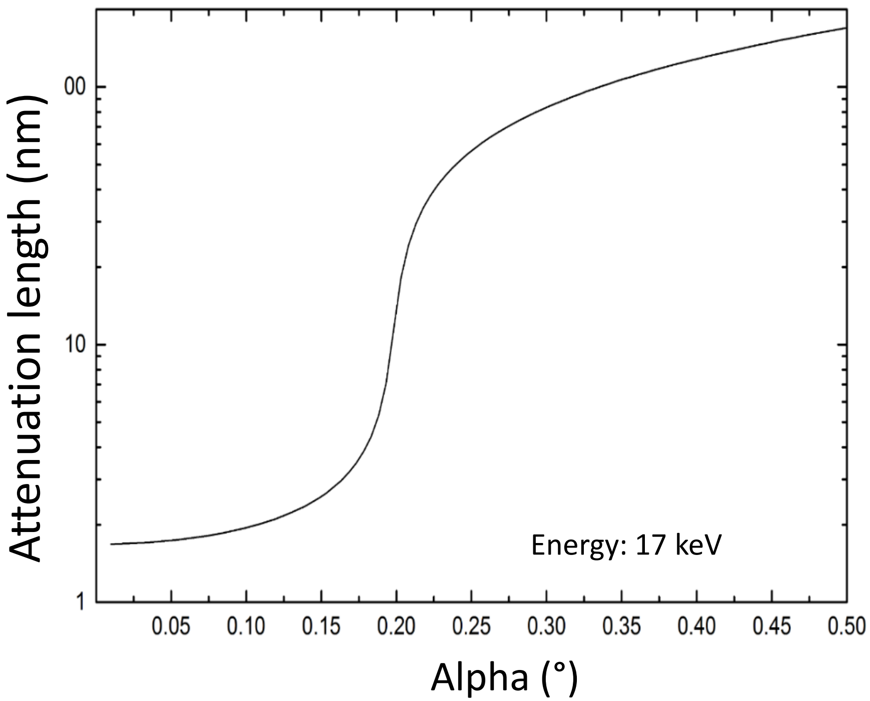
LBL

Walter Drisdell

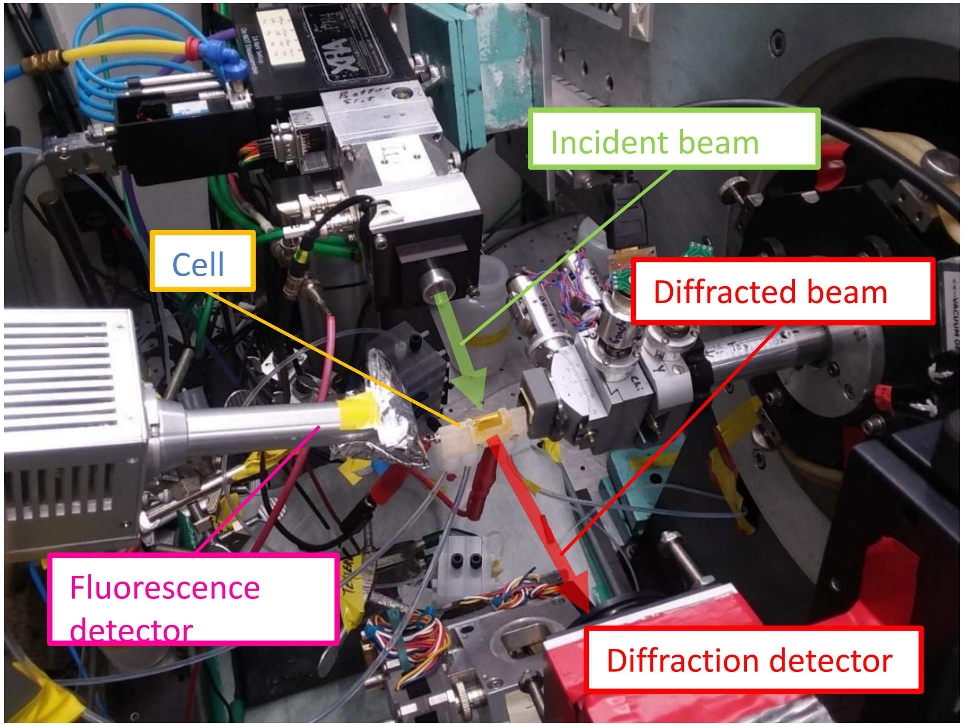
Jeff Beeman

Fundamental Studies on CO

- Our goal is to understand Cu's *in-situ* structure.
- Synctron measurements at SLAC was needed to do this.

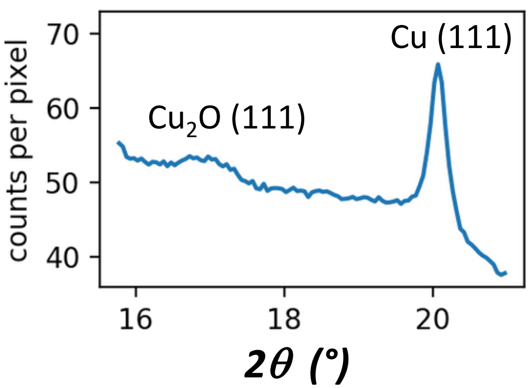


http://henke.lbl.gov/optical_constants/atten2.html

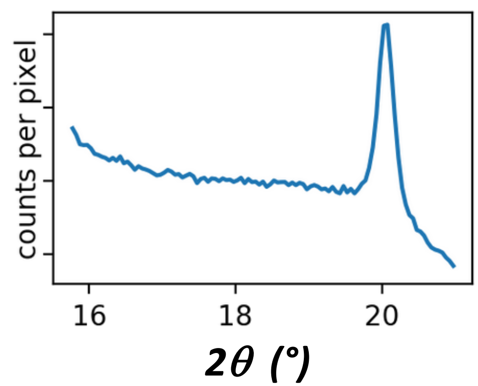


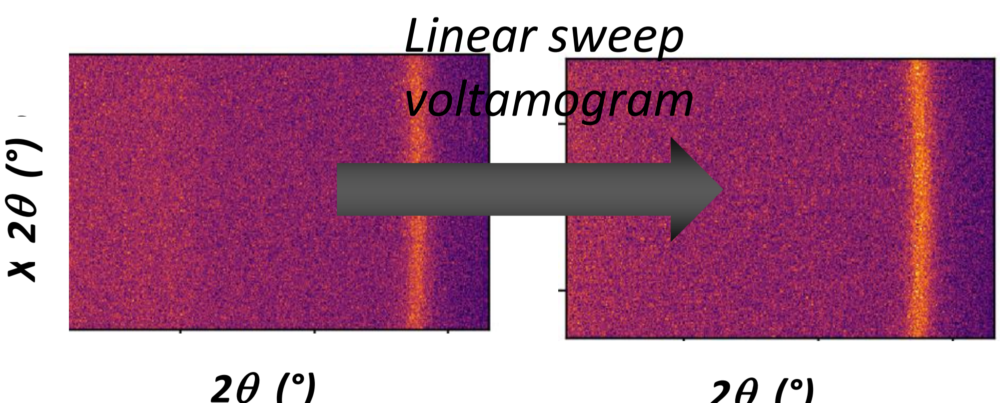
- Cu (111) has a peak at 20° and Cu_2O (111) at 17°.
- For sufficient signal we operated at α =0.15°.

U = OCV

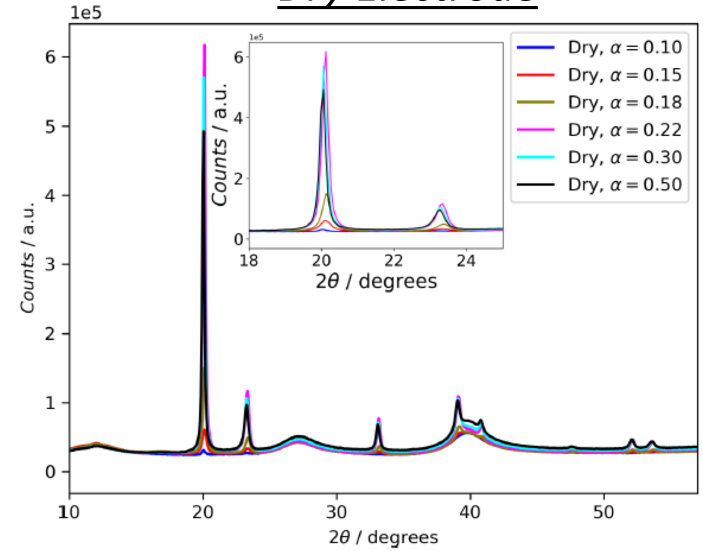


U = 0 V vs RHE

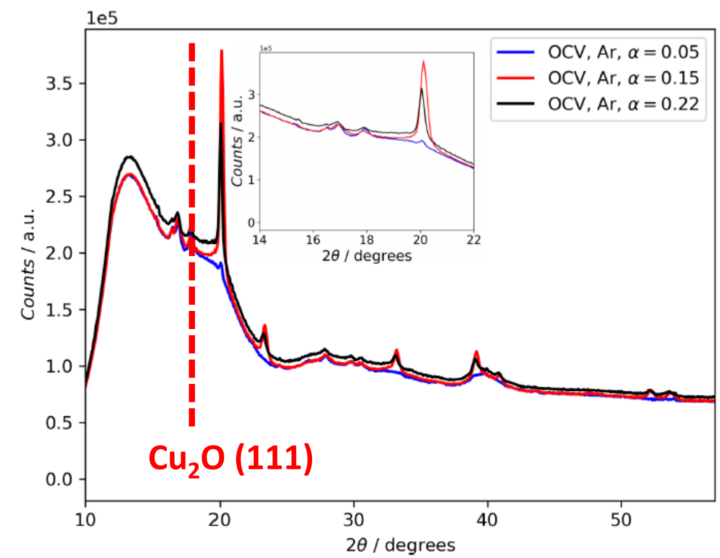




Dry Electrode



Aqueous Electrode

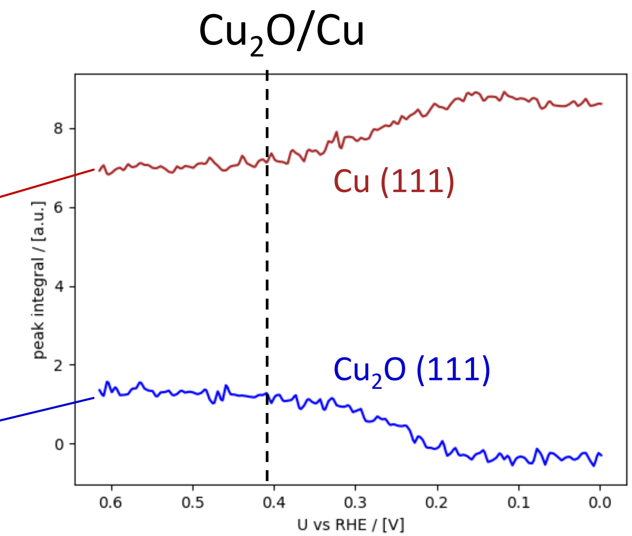


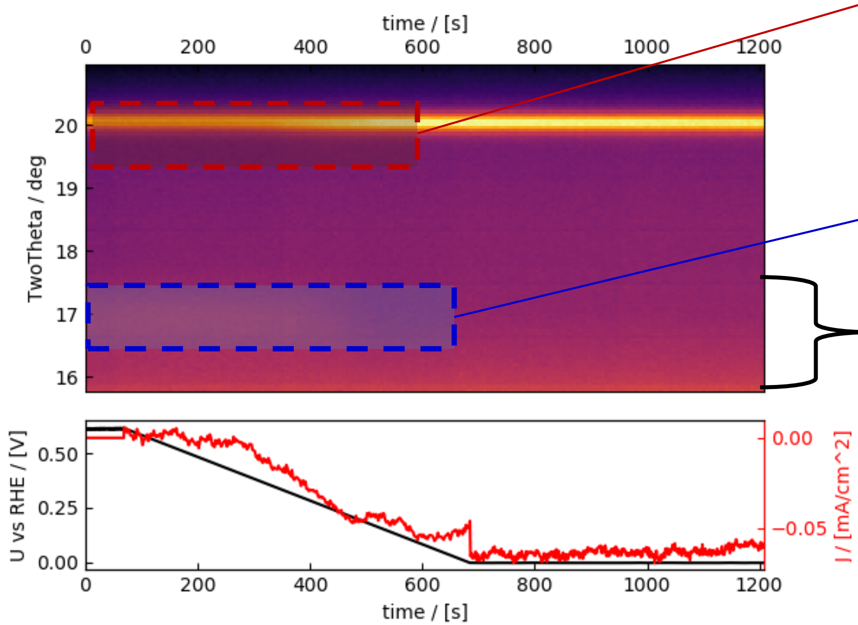
Electrode: Cu polycrystal
Electrolyte: 0.1 M KOH

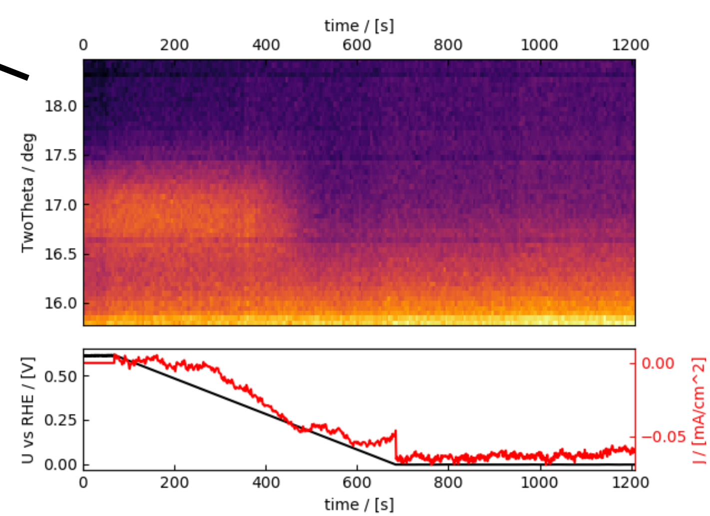
Reduction of Native Oxide in CO

- We set the detector at a given angle range and did a linear sweep voltammogram.

- We attribute the current to oxygen reduction reaction on Cu.







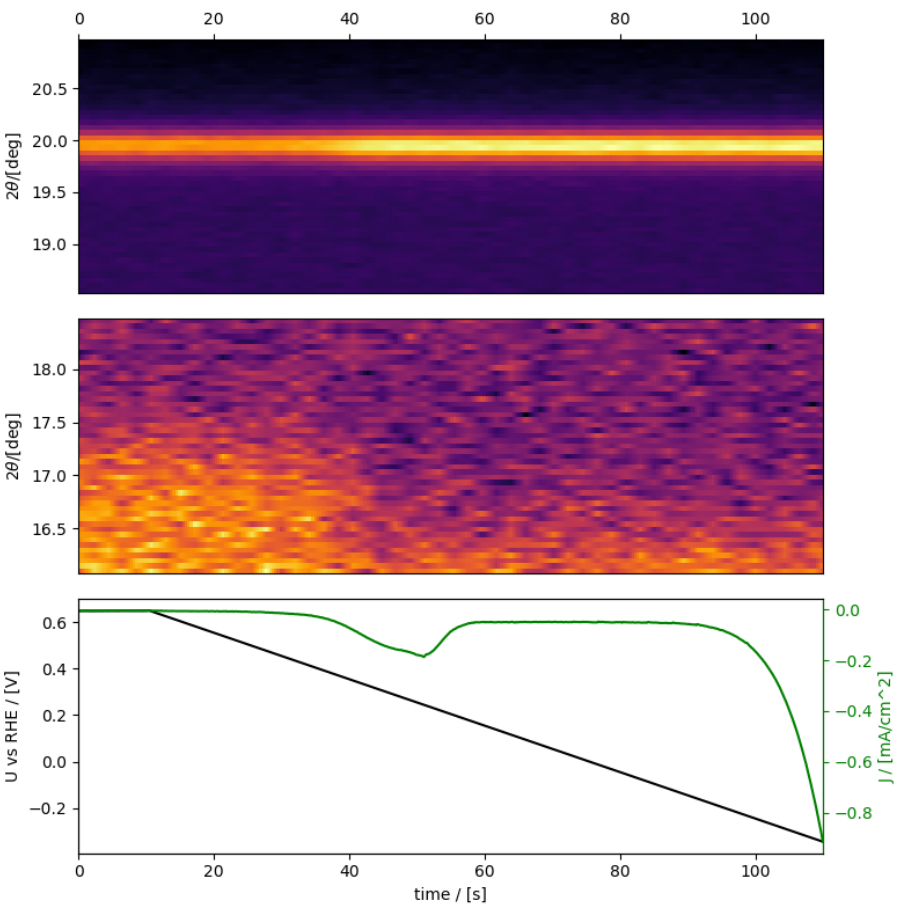
α: 0.15°

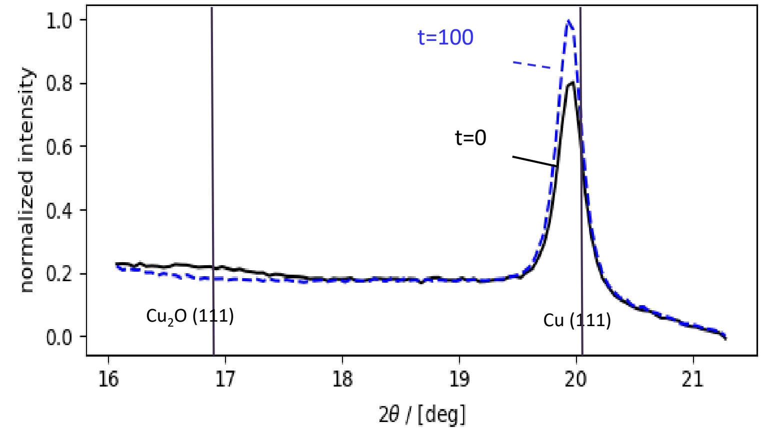
Scan rate: 1 mV/s

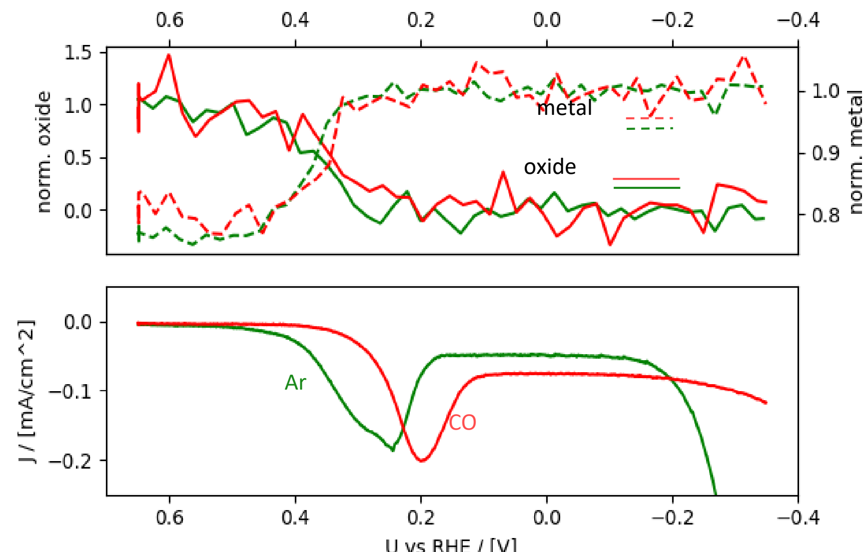
Electrolyte: CO Sat. 0.1 M KOH

Comparing CO Reduction in Ar and CO

- We have an earlier reduction onset in Ar, but the same XRD change w.r.t. potential.



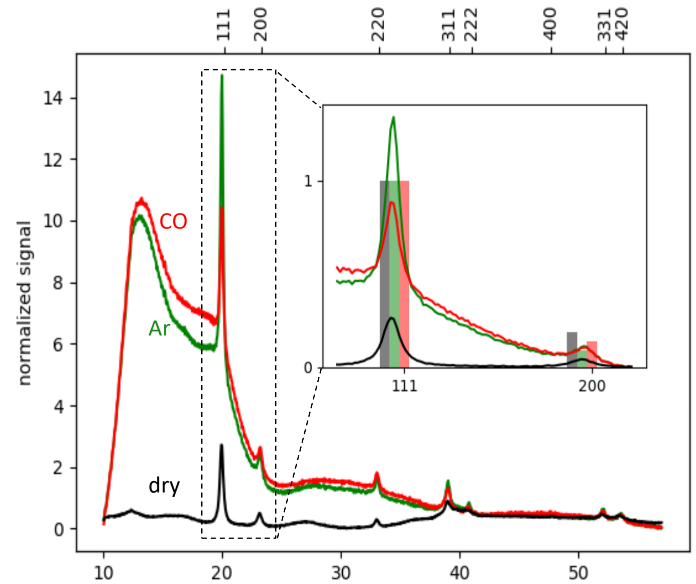


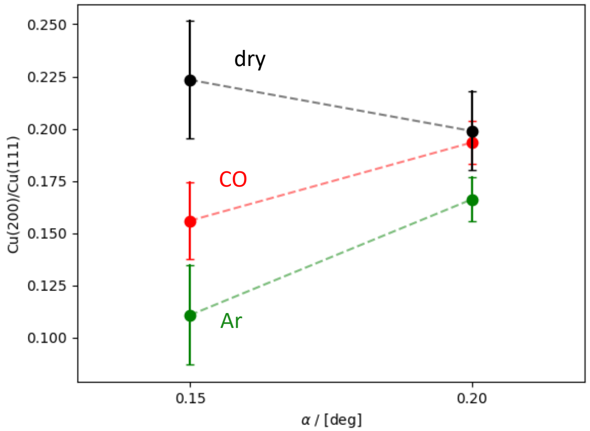


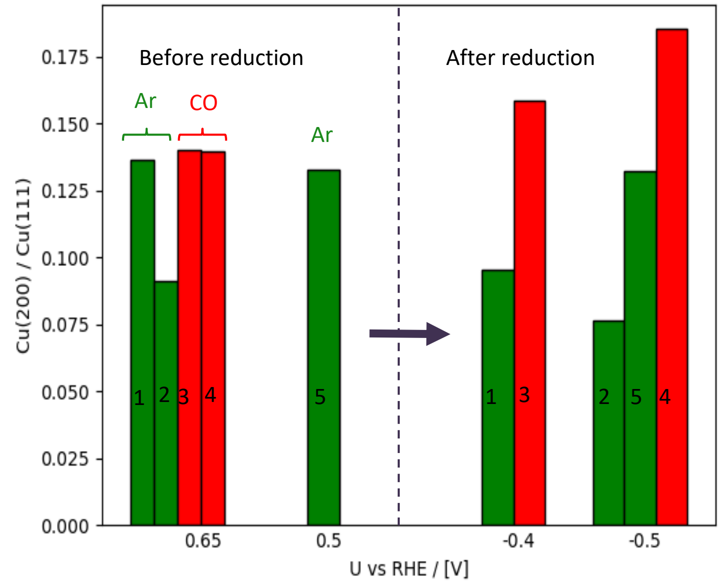
Cu reduction in 0.1M KOH in argon. Scan rate = 10 mV/s

Variations in Faceting

- We took XRD scans before and after the reduction to allow us to see all XRD peaks.
- Reduction in CO increased our Cu <200> peaks.
- Variation in XRD angle/depth shows this is just a surface effect.

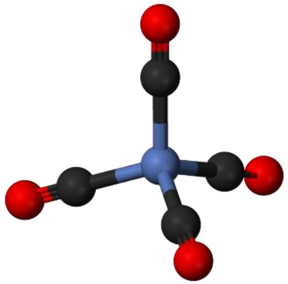




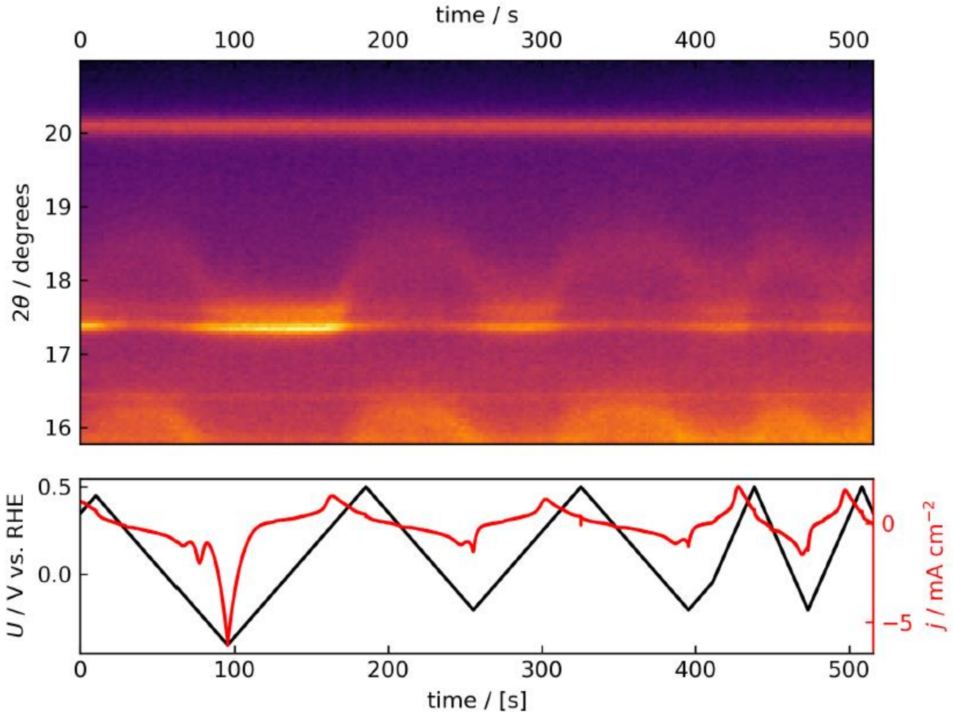


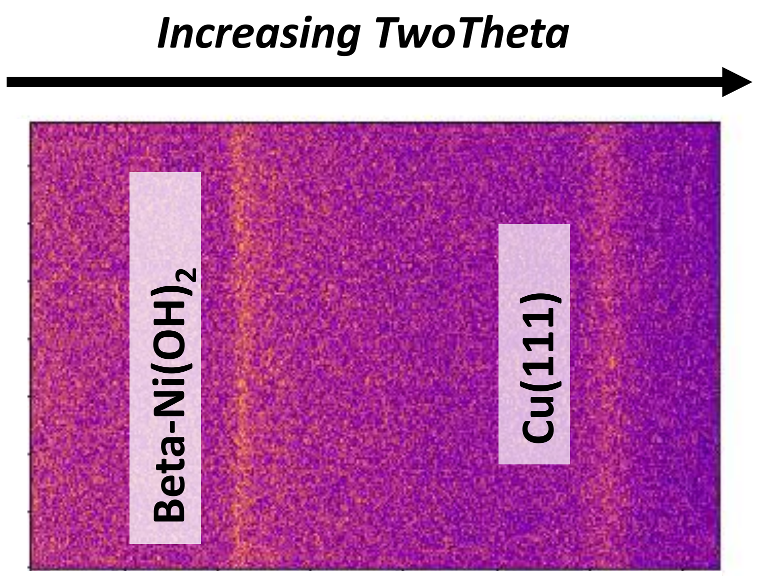
Interesting Mistake

- Nickel carbonyl is a common contaminant in CO.
- The actual performance of this sample is ineffective due to Ni producing H_2.
- We believe the variations is due to stress within the $Ni(OH)_2$.



$NiCO_4$, from CO + Steel





Acknowledgements

- I would like to acknowledge both the funding agencies and the DTU CO_2 reduction group.

Stefano Mezzavilla

Erlend Betheussen

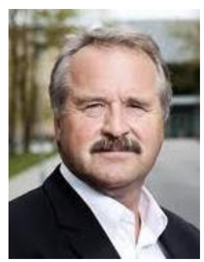
Søren Scott

Thomas Hogg

Thomas Maagard

Gaston Larrazabal

Sebastian Horch



Ib Chorkendorff

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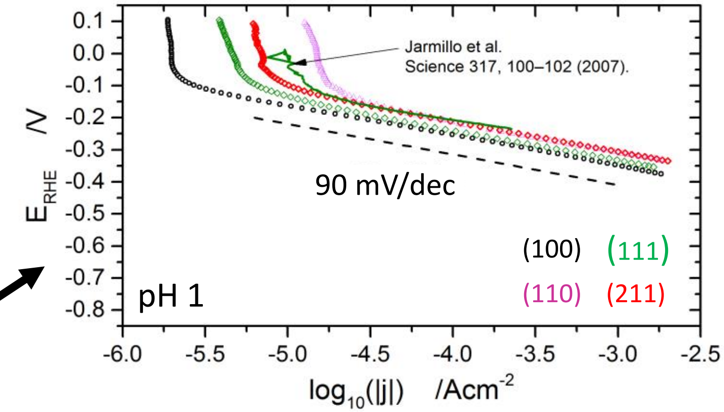
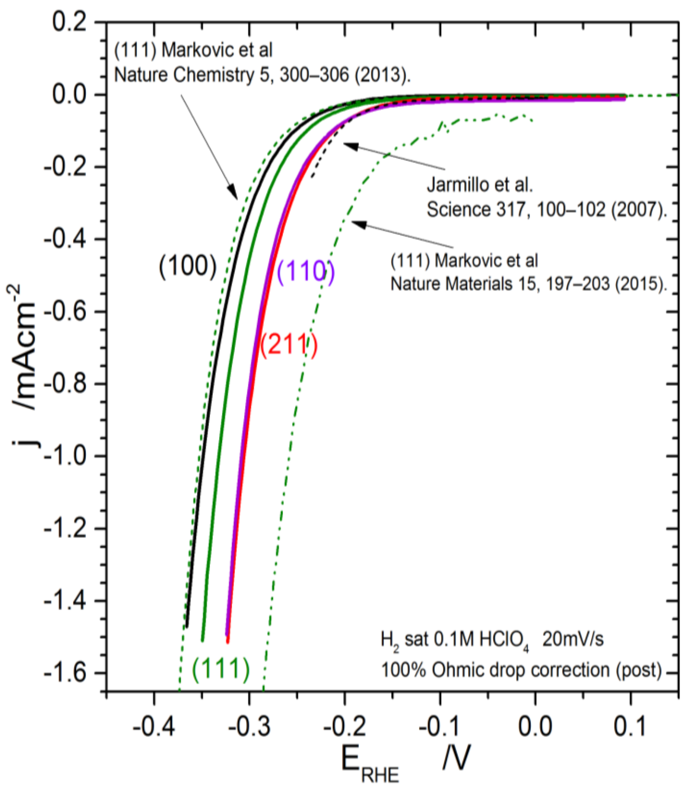
H_2 evolution on Au single crystals

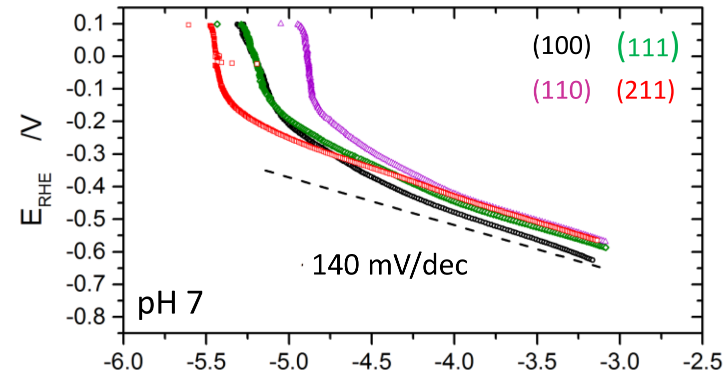
- H_2 evolution on Au is minor function of crystal facet.
- Au <211> is 3 times larger than Au <100>, but 20 time larger in CO evolution.



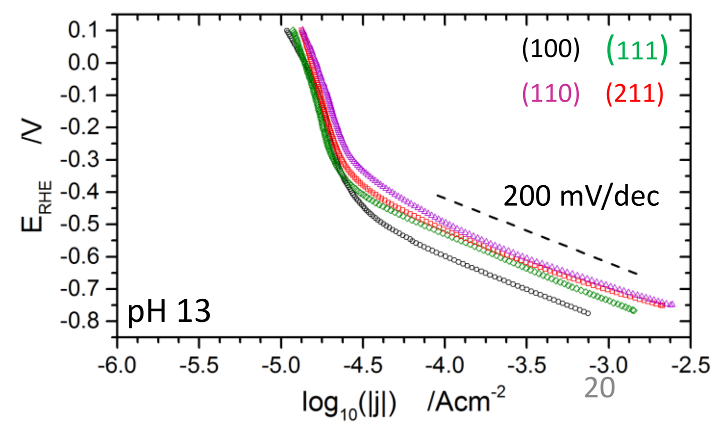
0.1 M $HCLO_4$ (pH 1)



0.1M phosphate buffer

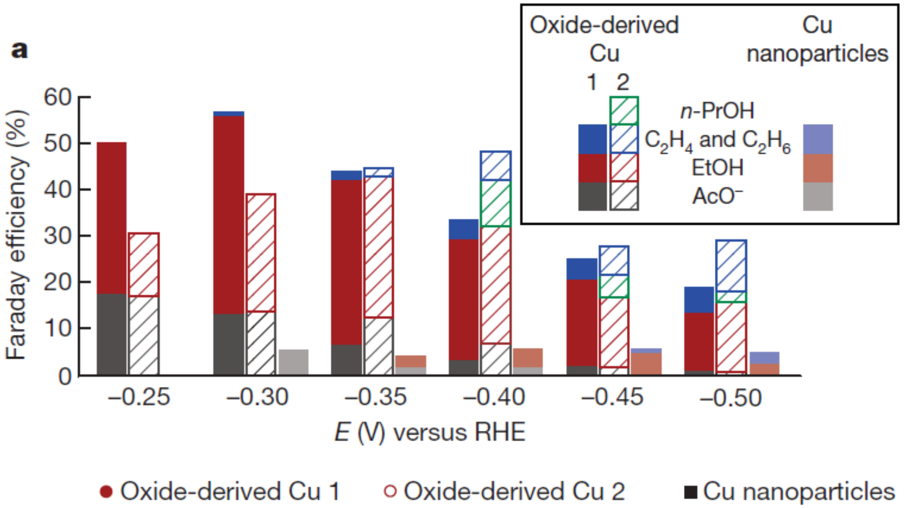


0.1M KOH



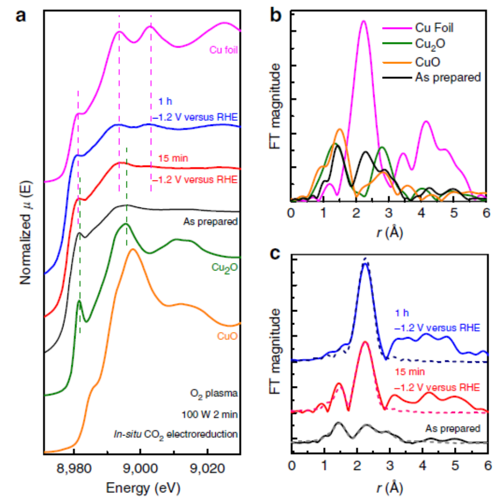
Does oxidized Cu Play a Role in CO Reduction?

Oxide derived copper in CO reduction



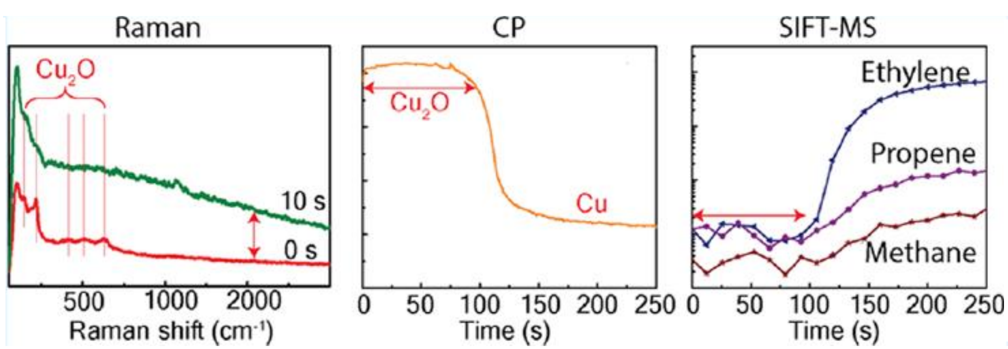
Lee et. al, Nature, 2014, 508, 504-507

XANES Studies



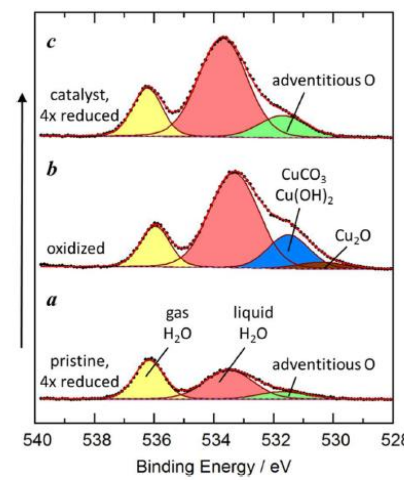
Mistry et. al, Nat. Comm., 2016, 7, 12123

Raman Specrtra



Mandal et. al, ACS Appl. Mat Int., 2018, 10, 8574-8584

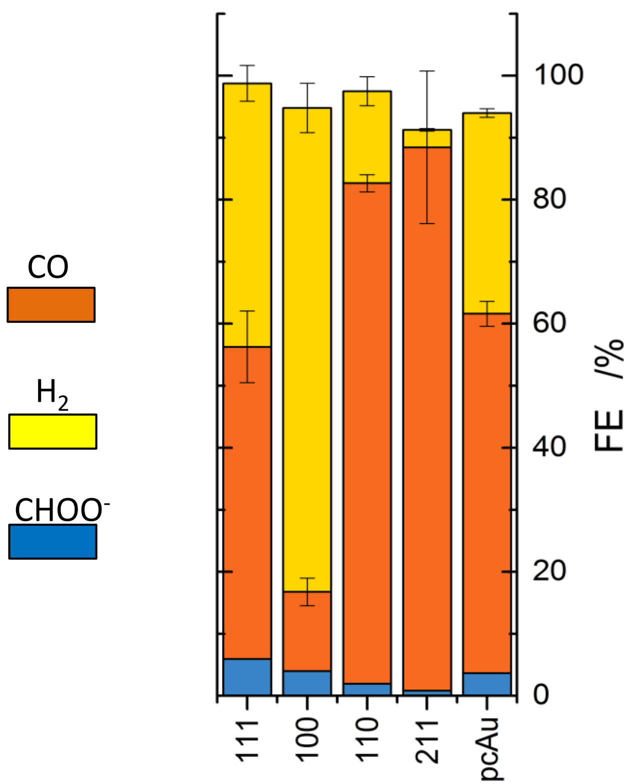
In-situ XPS

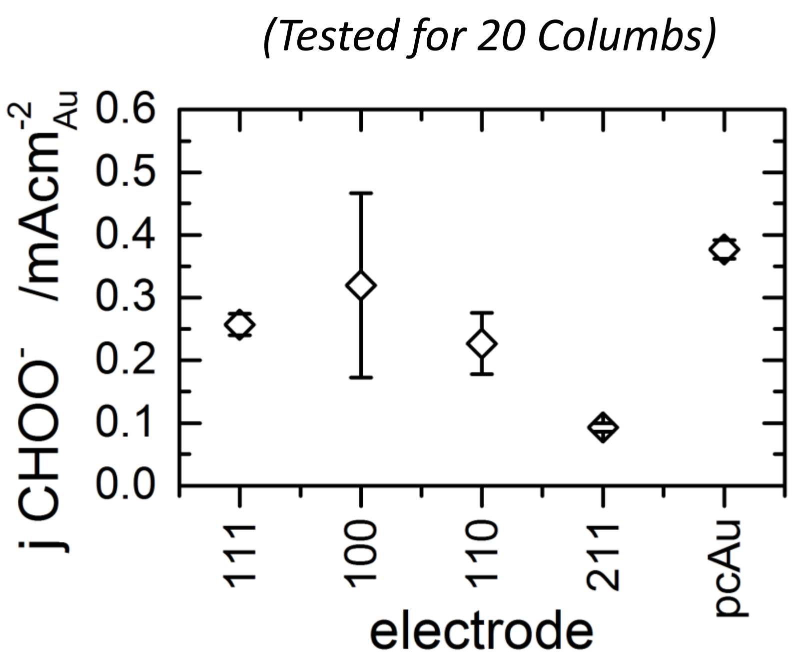


Eilert et. al, JPC-L, 2017, 8, 285-290

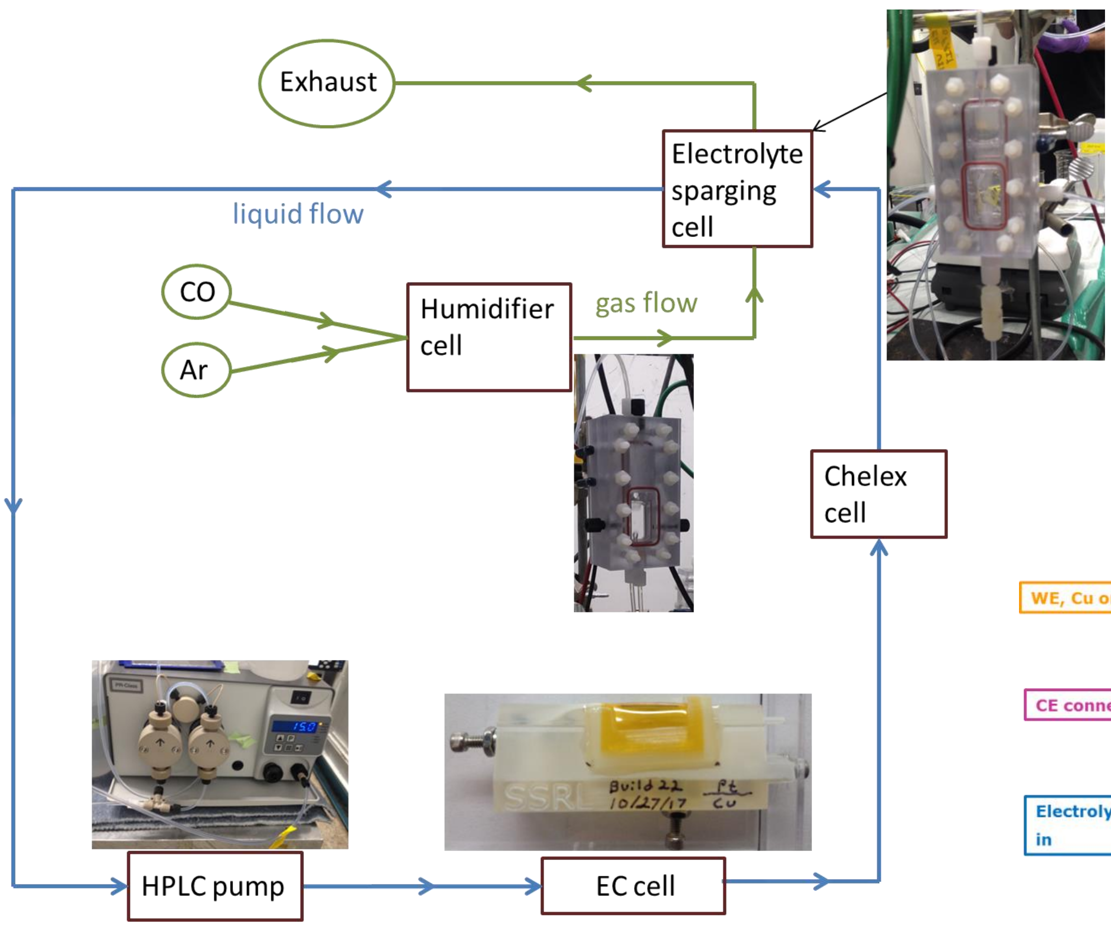
Formate on Au?

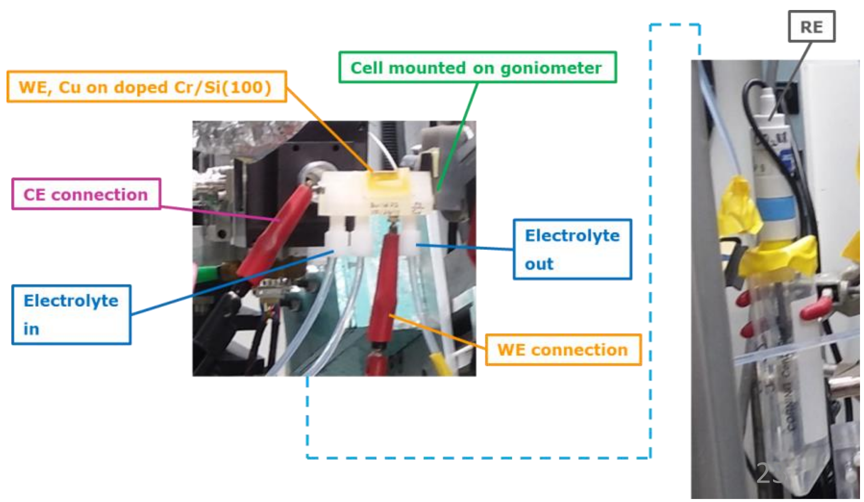
- The electrodes were taken to -1.0V vs RHE to look for formate.
- HPLC & NMR was used for detection.
- We also looked for methanol, but did not see anything.

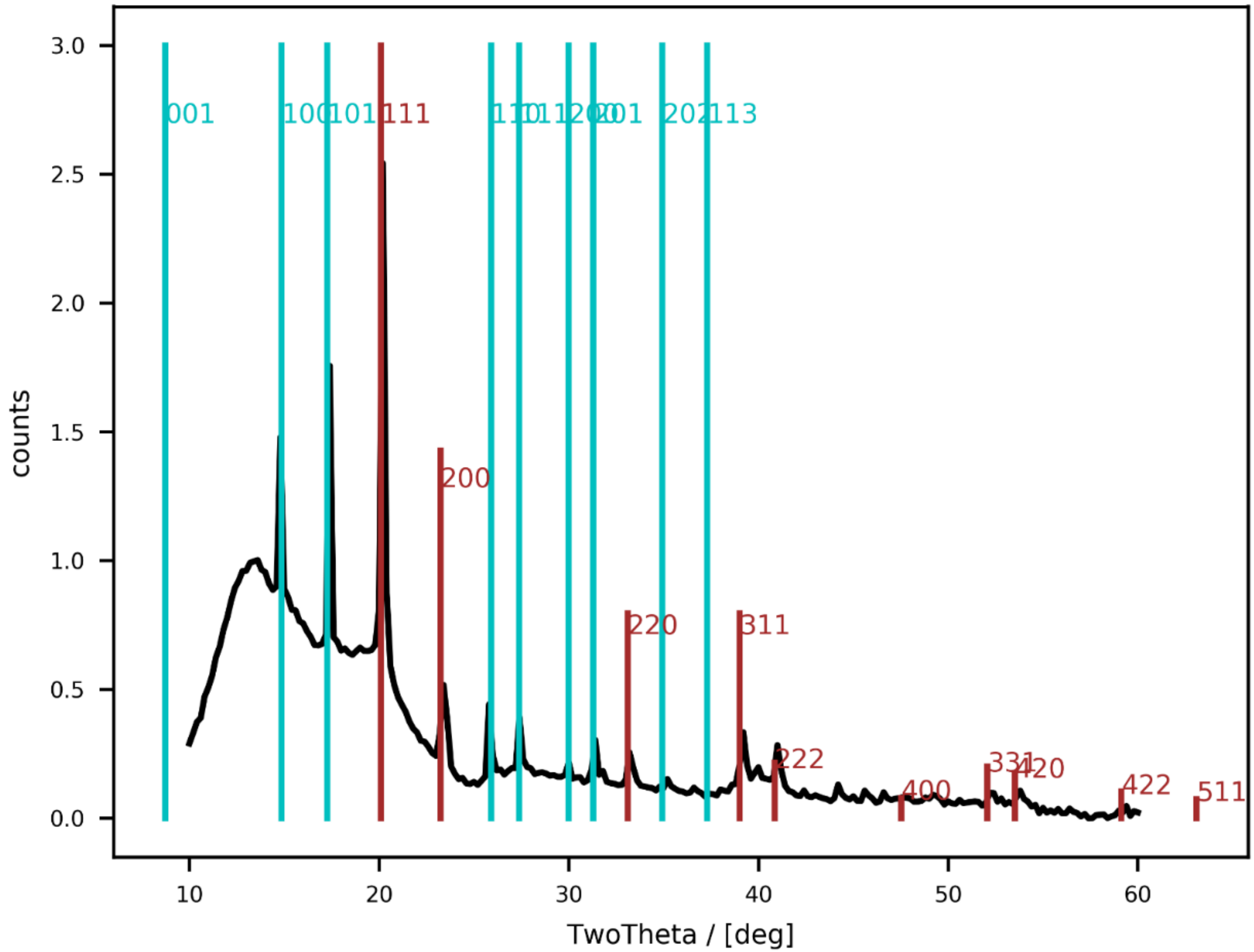




Setup Schematic







counts
TwoTheta / [deg]
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2.5
2.0
1.5
1.0
0.5
0.0
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20
30
40
50
60
001
100
101
111
200
110
112
200
201
202
113
220
311
222
400
331
420
422
511

The Team

- Below is the CO_2 reduction team at DTU.

Stefano Mezzavilla

Erlend Betheussen

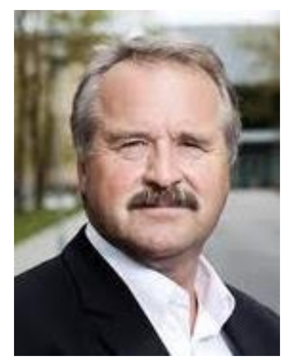
Søren Scott

Thomas Hogg

Thomas Maagard

Gaston Larrazabal

Sebastian Horch



Ib Chorkendorff

The Team

- There are many people that work on our projects, but below are the major contributors.

DTU

Stefano Mezzavilla

Erlend Betheussen

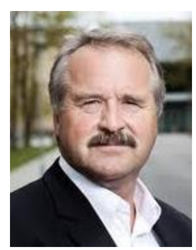
Søren Scott

Thomas Hogg

Thomas Maagard

Gaston Larrazabal

Sebastian Horch



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John Lin

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