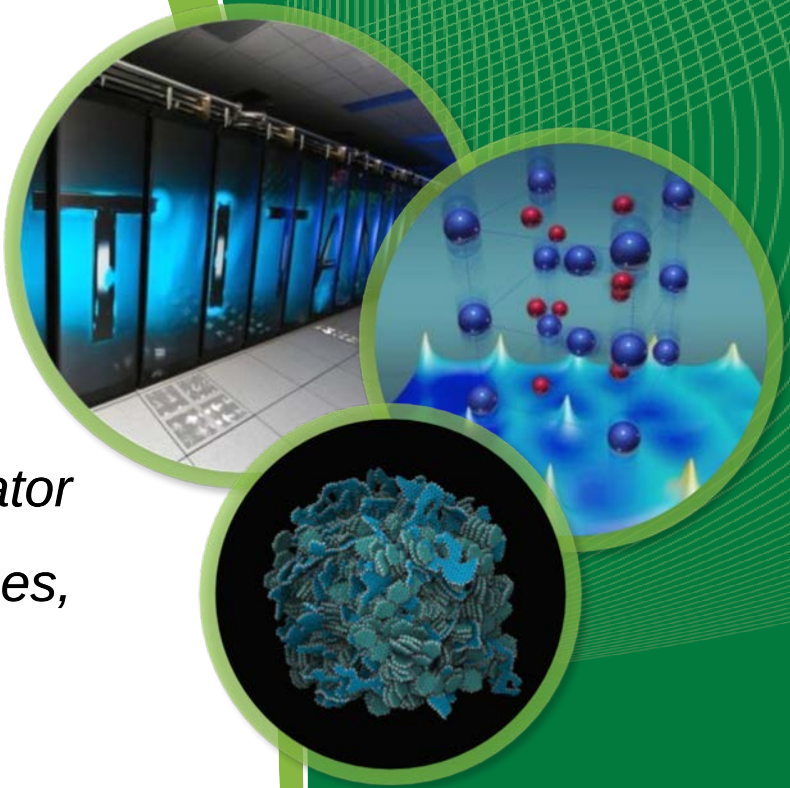
Maximizing Current Density for Electrochemical Conversion of Flue Gas CO_2 to Ethanol

Adam Rondinone

Senior Scientist and Outreach Coordinator

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory



NETL/DOE Field Work Proposal #FEAA132

NETL/DOE Project Manager Sai Gollakota

Project Kick-Off Meeting 27 October 2017

Outline

- Graphene is an Interesting Heterogeneous Catalyst
- Carbon Nanospikes and CO_2 Electrochemistry
  - Motivation
  - Mechanism of Reaction
- Economic Considerations
- Scale-Up Efforts to Date
- Fossil Energy Project
  - Objectives
  - Strategies

The Oak Ridge National Laboratory

Owned by DOE Office of Science

$1.6 billion per year

~4700 staff

Founded in Manhattan Project for U-235 enrichment and plutonium breeding

After WWII, transitioned to civilian nuclear technology and science

World-renowned expertise in neutron science, high performance computing, materials science

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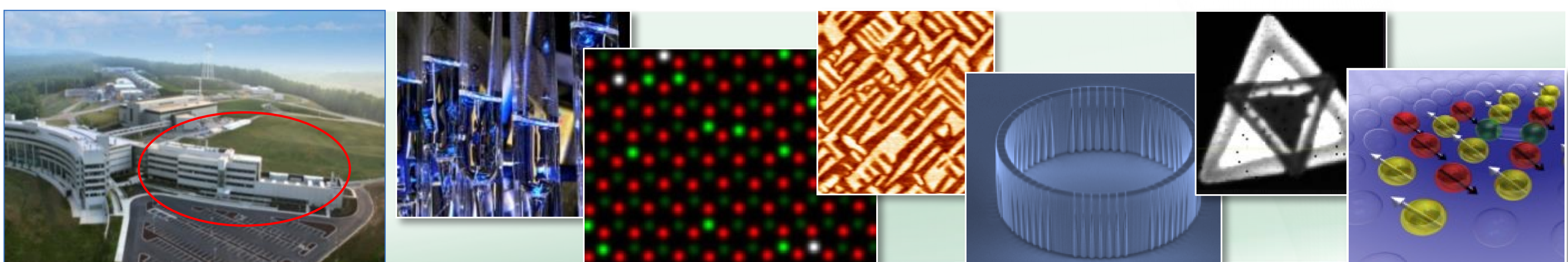
CNMS is a national user facility with a mission to advance nanoscience

About CNMS:

- **Unlike many user facilities, you don’t need to have samples to apply for time**
- **Two calls per year for continuous access; anytime for short-term projects**
- **Simple 2-page proposal**
- **Free access to laboratories, equipment and expertise if you agree to publish**
- **Proposal deadlines: early May and mid-October**
- **Joint proposals with neutron sources (SNS, HFIR)**

Research areas:

- **Synthesis –** 2D, precision synthesis, selective deuteration
- **Nanofabrication –** direct-write, microfluidics, cleanroom
- **Advanced Microscopy –** AFM, STM, aberration-corrected TEM/STEM, atom-probe tomography
- **Functional Characterization –** laser spectroscopy, transport, magnetism, electromechanics
- **Theory and Modelling –** including gateway to leadership-class high performance computing



CNMS is a Nanoscale Science Research Center supported by the U.S. Department of Energy, Office of Science, Scientific User Facilities Division

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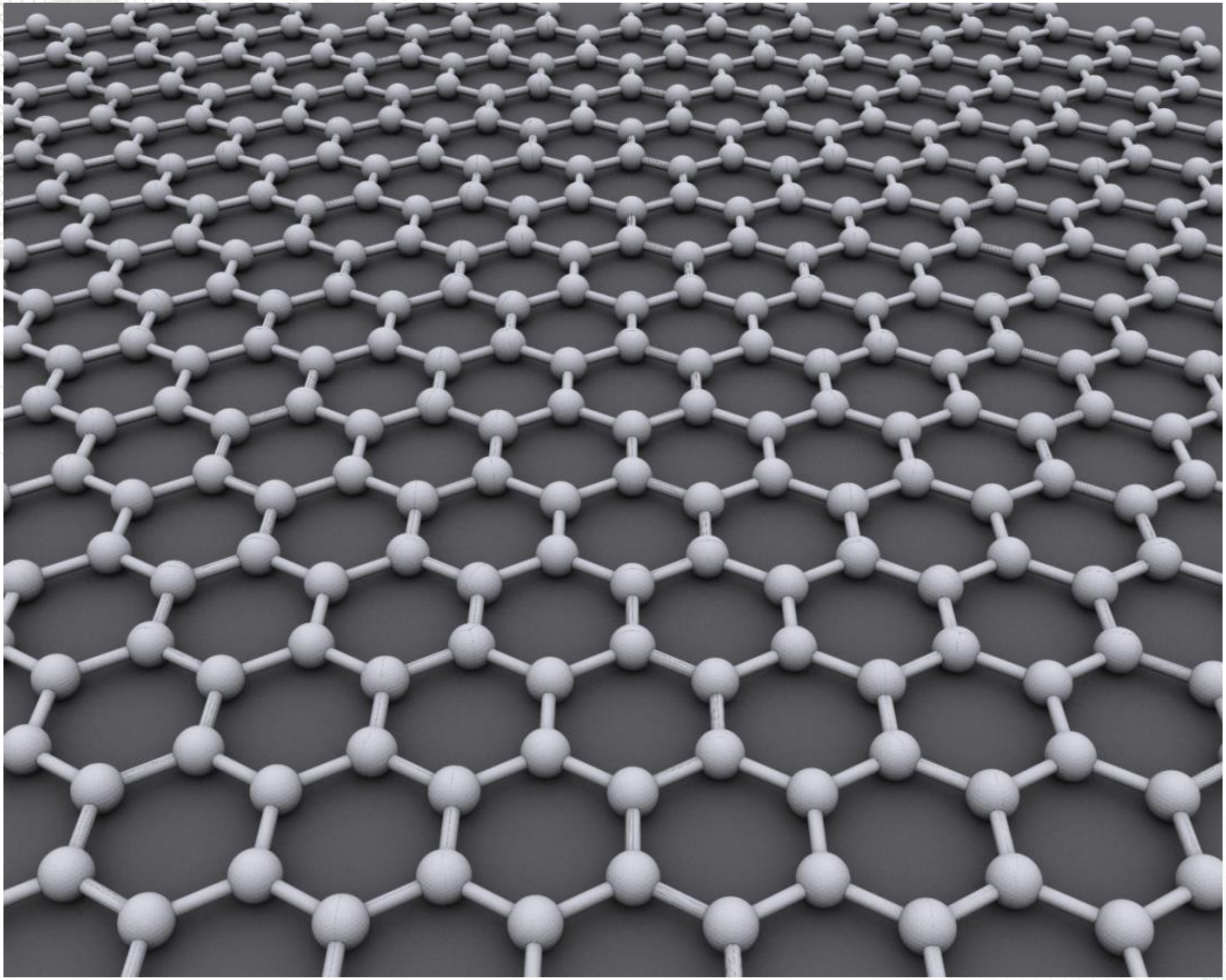
Graphene: Single Layer, Hexagonal Carbon



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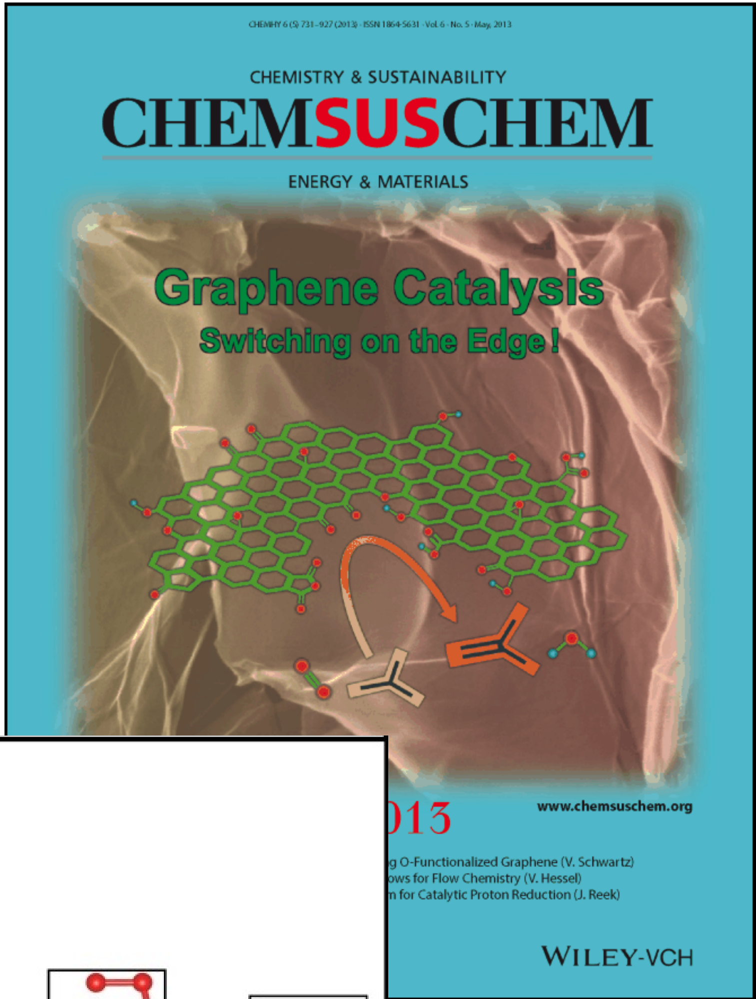
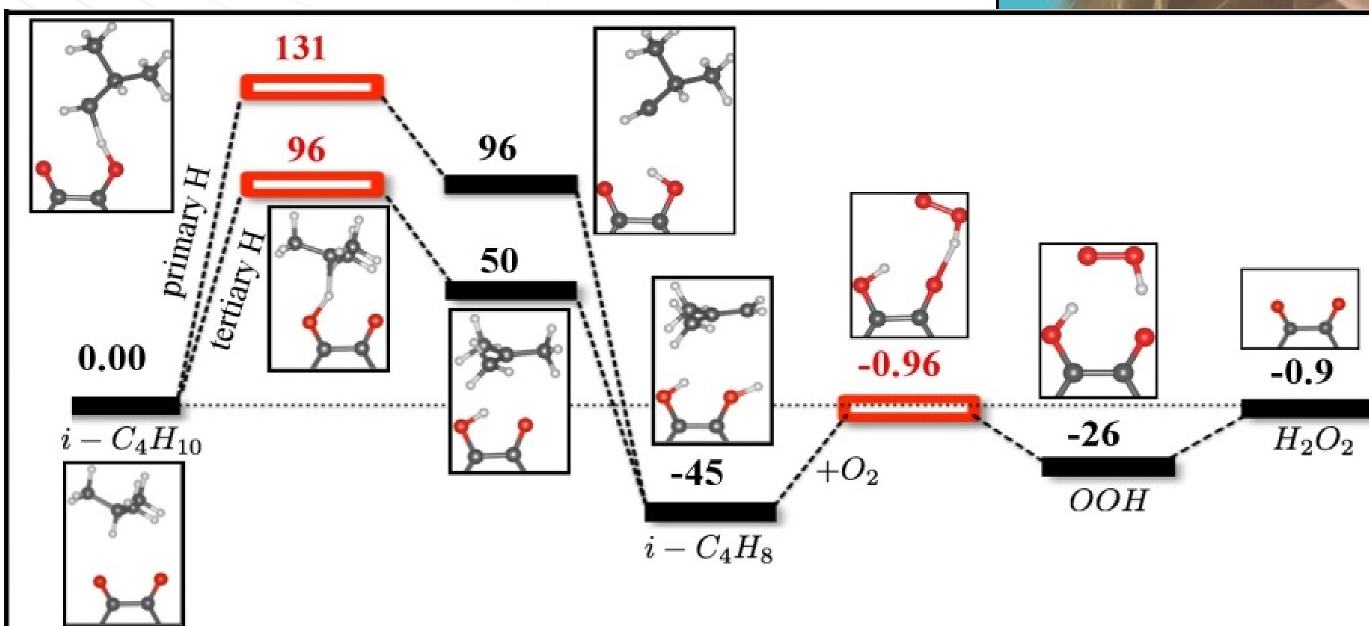
Graphene Catalysis

- Graphene is a pseudo metal
  - Readily accepts and donates electrons
- Bandgap can be tuned with defects and doping
- Low cost





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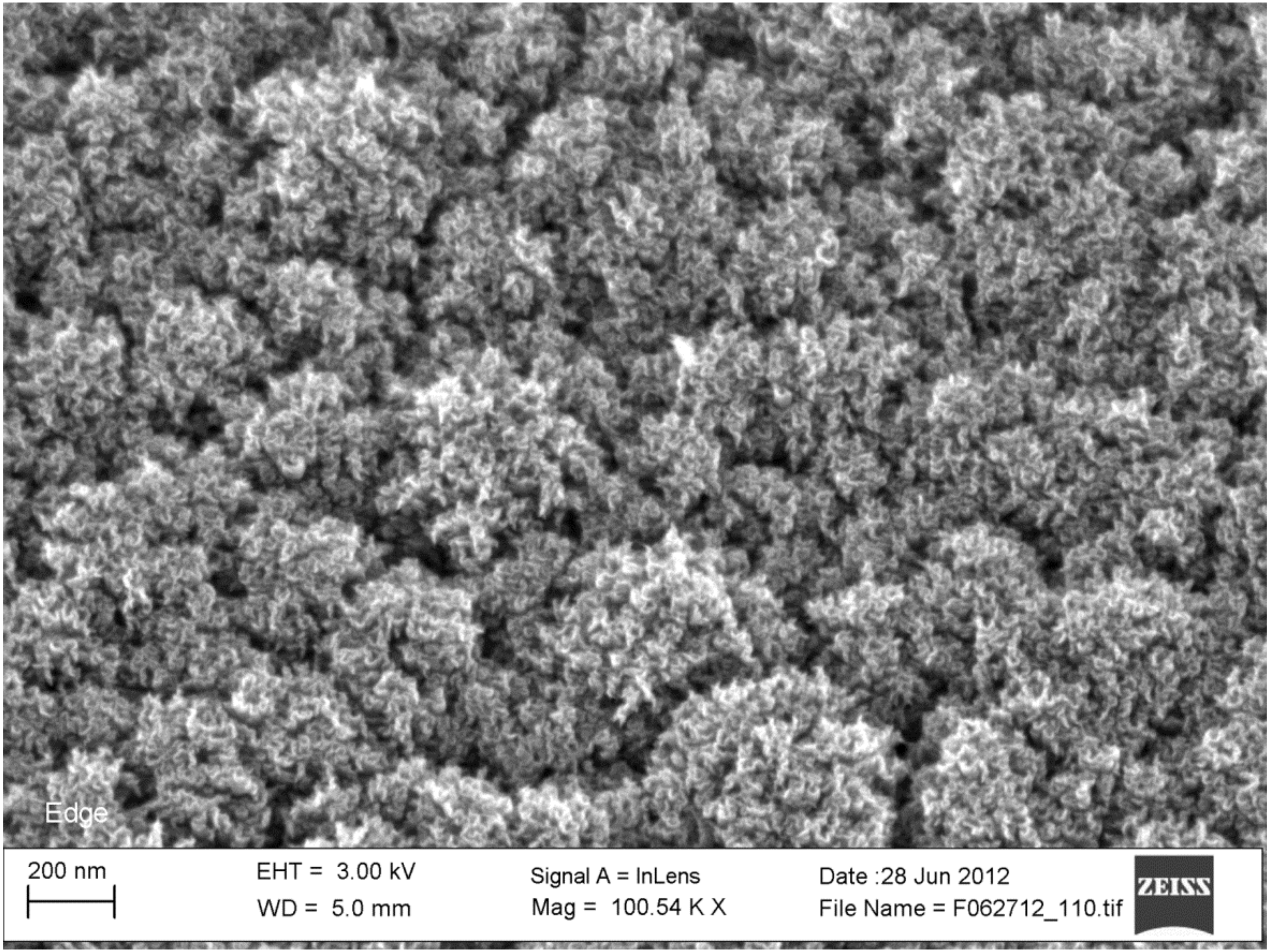
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WD = 5.0 mm
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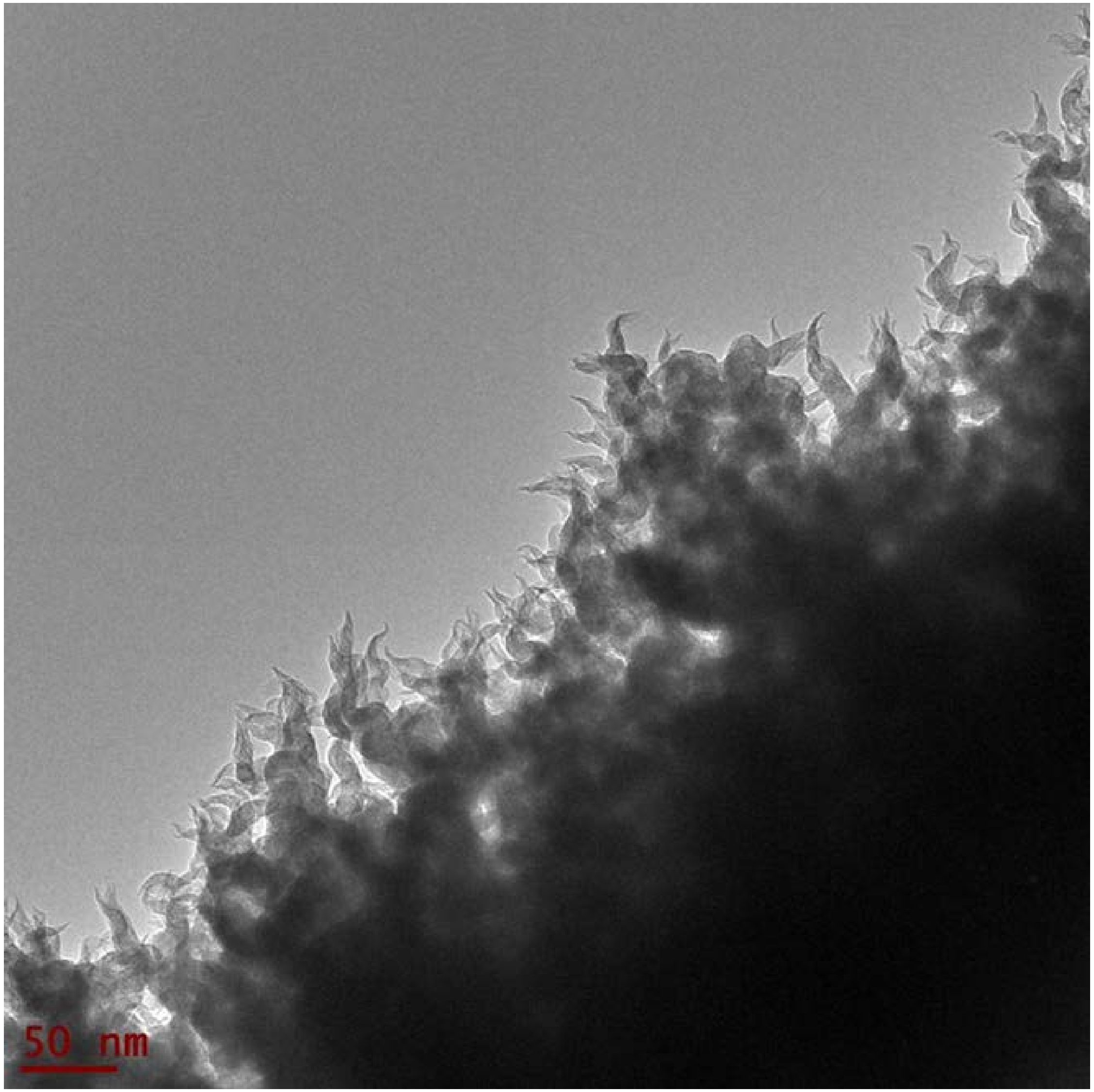
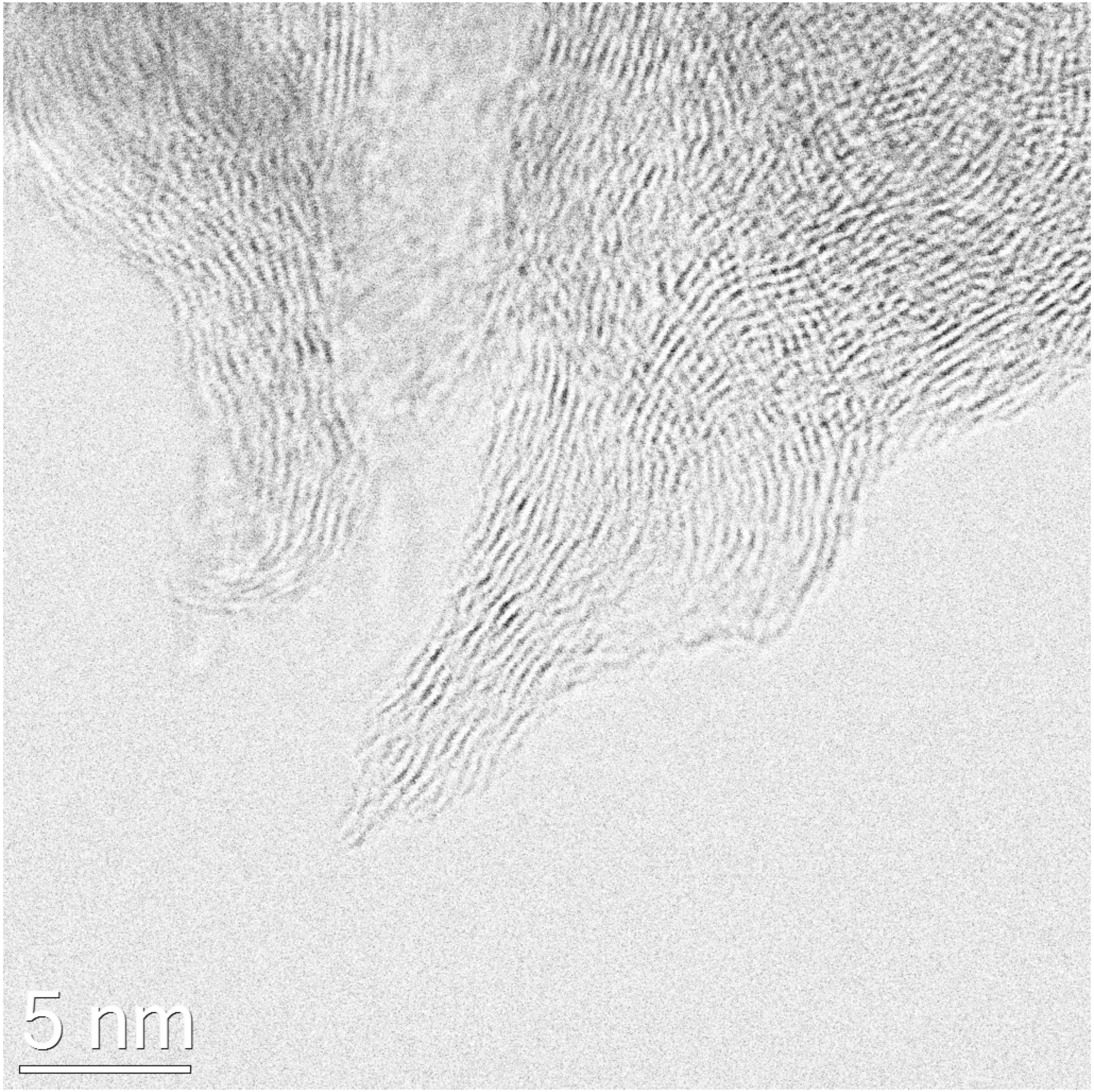
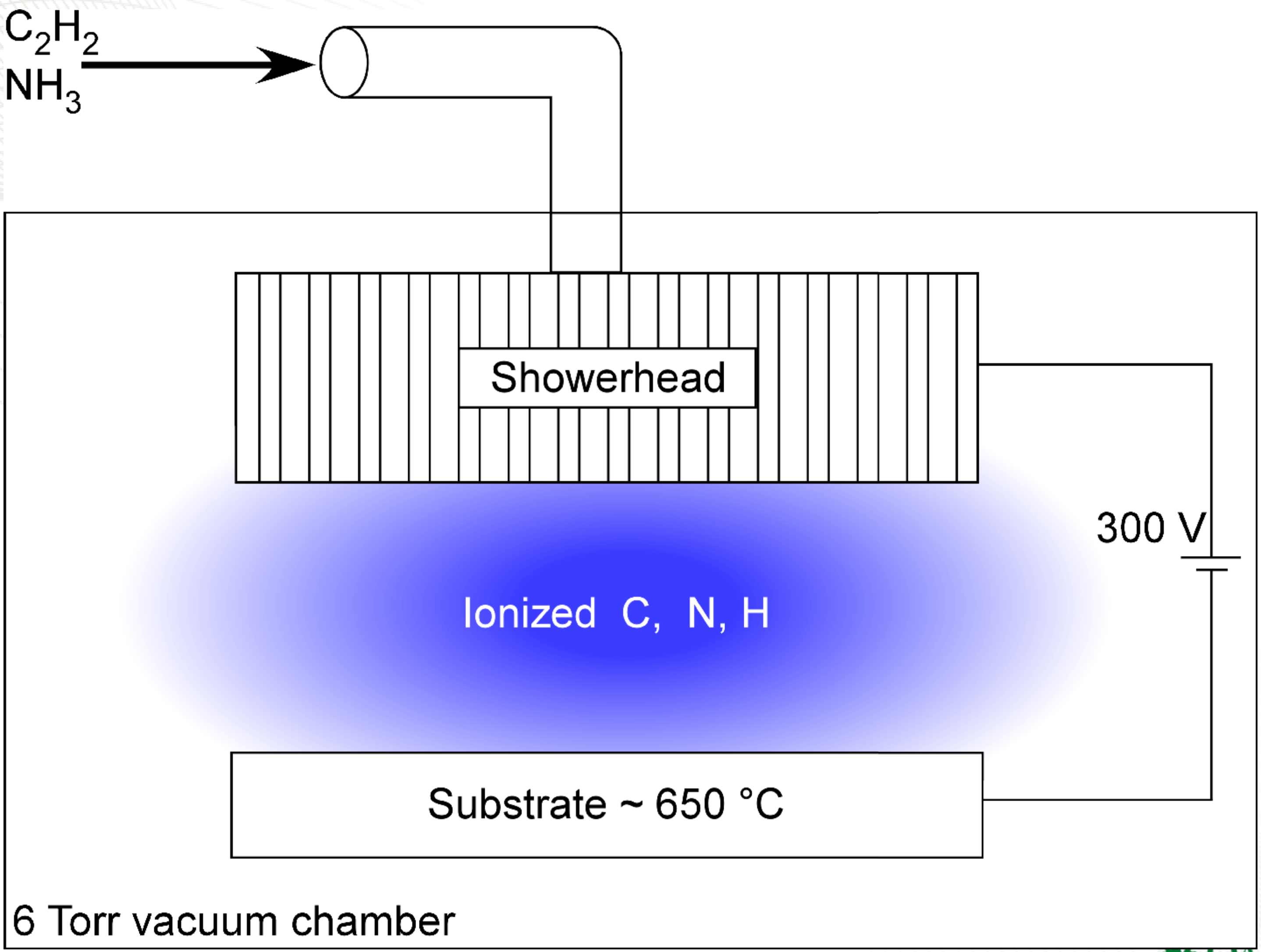
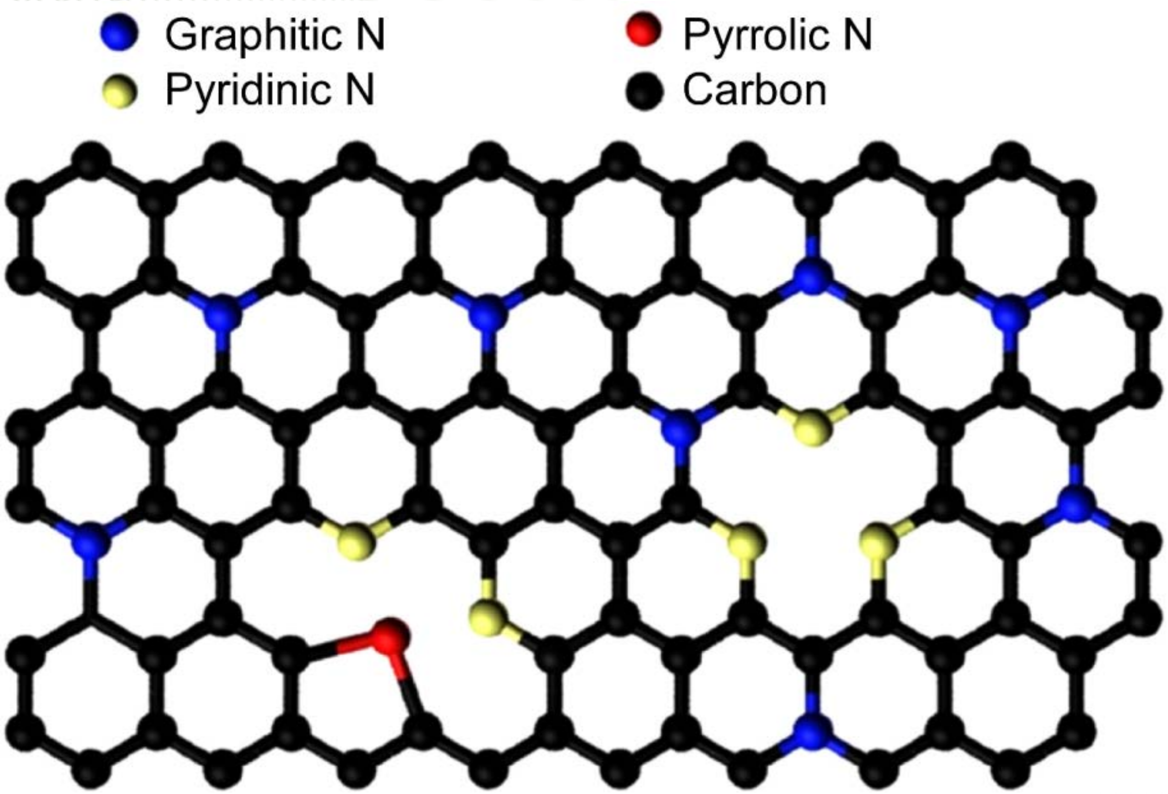

50 nm


5 nm

Plasma-Enhanced Chemical Vapor Deposition (PECVD)



5% Nitrogen Doping



- Pyrolysis elemental analysis: N doping (5.1 ± 0.2 %)
- XPS: N 1s
  - pyridinic (~25%),
  - pyrrolic (~19%),
  - graphitic (~55%).

Cho, Hyunjin, et al. "Catalyst and doping methods for arc graphene." Nanotechnology 25.44 (2014): 445601.

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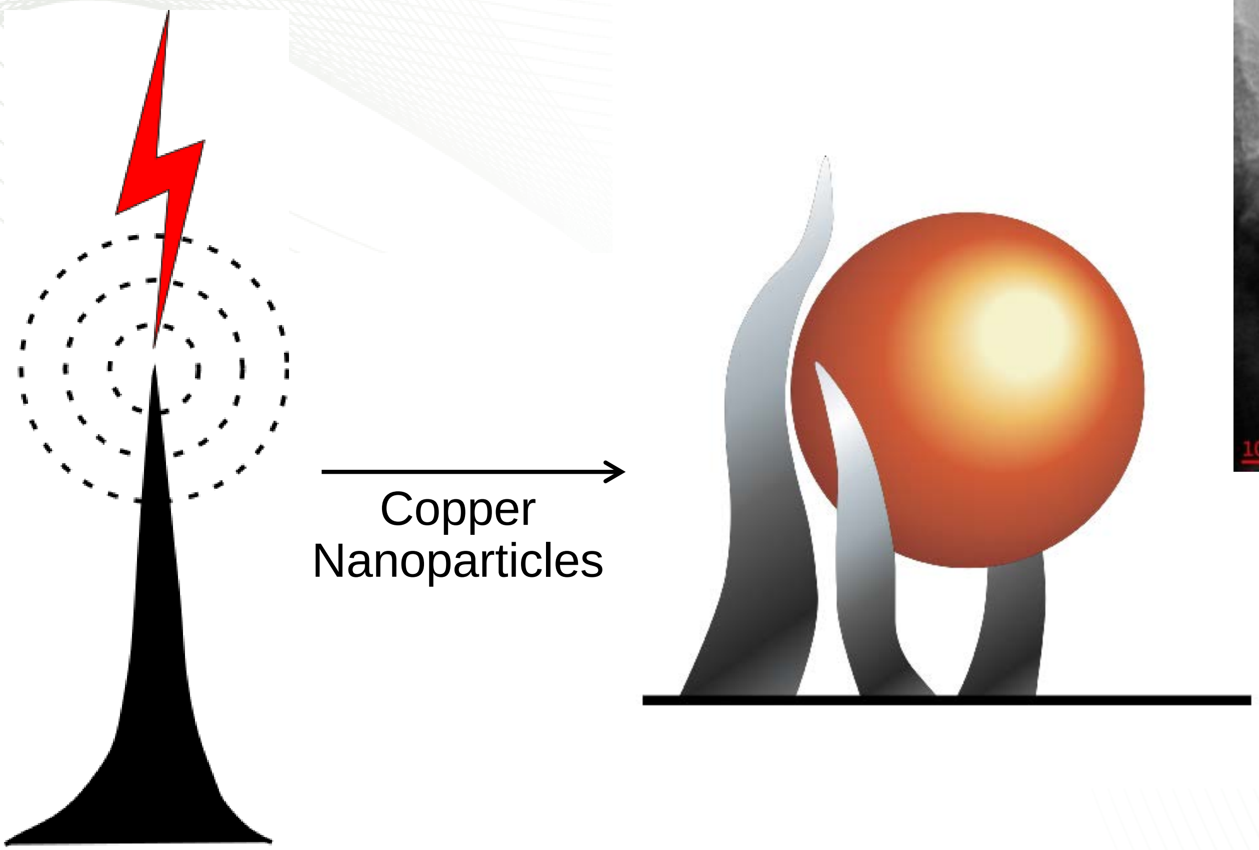
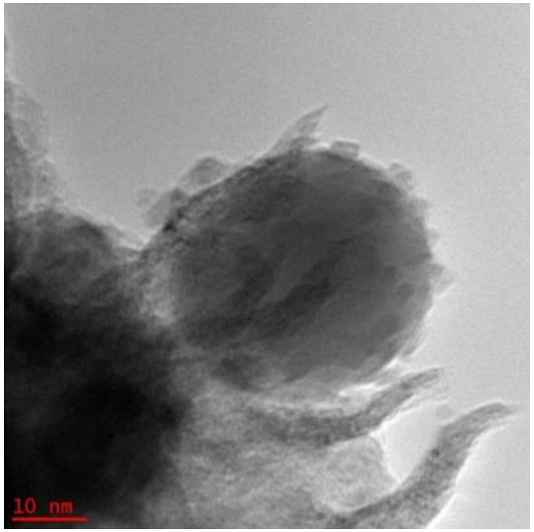
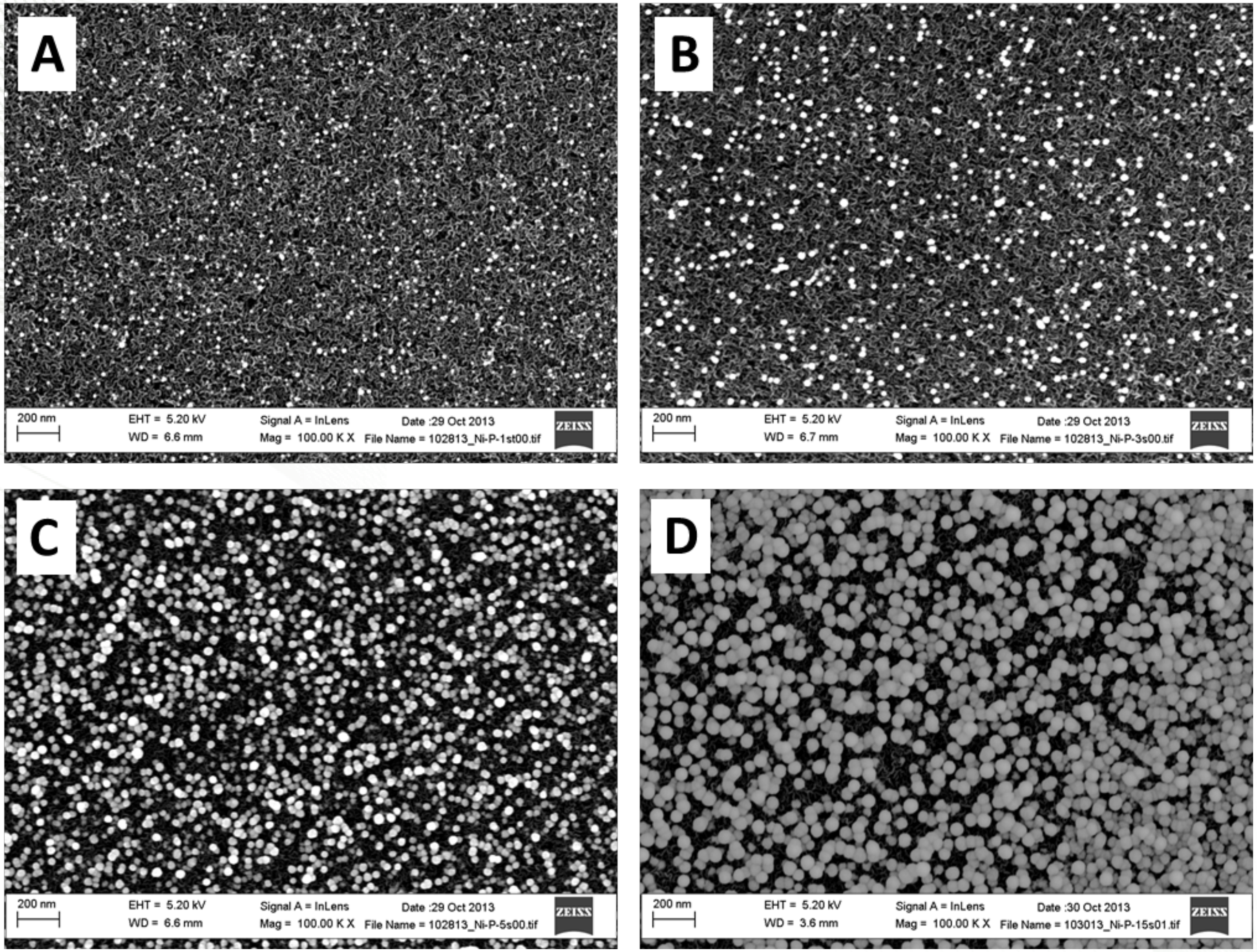
Carbon Nanospikes are Dense and Numerous

- Approximately $1x10^{13}$ spikes per sheet of copy paper
  - o Roughly equivalent to the number of dollars in the national debt
- Each nanospike will concentrate electric field





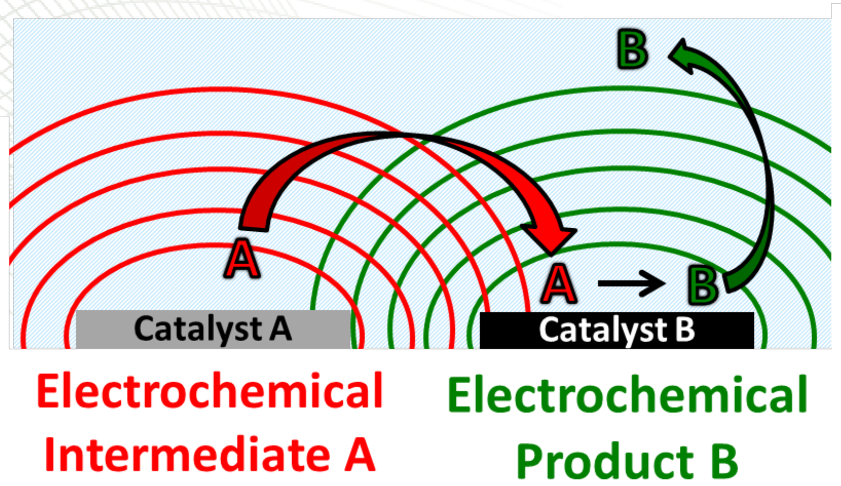
Electronucleation of Particles



SEM images of Ni-P deposited on CNS at – 2 V for (A) 1 s, (B) 3 s, (C) 5 s, and (D) 15 s.

CO_2 Electroreduction

- Motivation: explore sequential electrocatalysis



Can engineered, nanoscale electrocatalysts control the activity and/or selectivity?

Needed a multi-electron test case: CO_2

- Copious literature on copper electrodes for CO_2
  - Nanostructured copper on glassy carbon: CH_4
  - Textured copper film: CO to ethanol
  - Bulk copper plates: mixture of hydrocarbons depending on electrolyte

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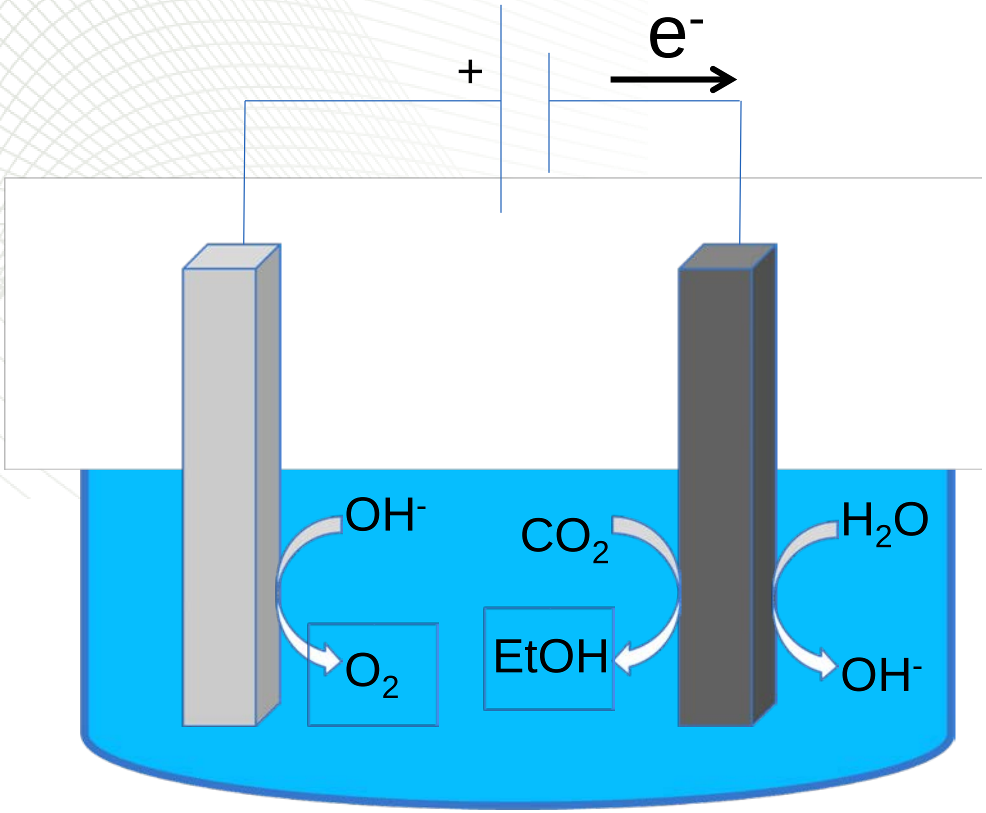
Electrolysis ~ Charging a Battery



CABB Group GmbH

Cathode (catalyst) half-reaction: $9H_2O + 9e^- \rightarrow 9H + 9OH^-$

$2CO_2 + 9H + 3e^- \rightarrow C_2H_5OH + 3OH^-$

Anode half-reaction: $12OH- \rightarrow 3O_2 + 6H_2O + 12e^-$

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Literature Indicates Diverse Product Mix

Table 1. Faradaic efficiencies of products from the electroreduction of CO_2 at a Cu electrode at 5 mA cm^{-2} in various solutions at 19 °C

electrolyte	conc. /mol dm^{-3}	pH[a]	potential /V *vs.*NHE	Faradaic efficiency (%)							
				CH_4	C_2H_4	EtOH	Pr^nOH	CO	$HCOO^-$	H_2	total
$KHCO_3$	0.1	6.8	−1.41	29.4	30.1	6.9	3.0	2.0	9.7	10.9	92.0
KCl	0.1	5.9	−1.44	11.5	47.8	21.9	3.6	2.5	6.6	5.9	99.8
	0.5		−1.39	14.5	38.2	[b]	[b]	3.0	17.9	12.5	
$KClO_4$	0.1	5.9	−1.40	10.2	48.1	15.5	4.2	2.4	8.9	6.7	96.0
K_2SO_4	0.1	5.8	−1.40	12.3	46.0	18.2	4.0	2.1	8.1	8.7	99.4
K_2HPO_4	0.1	6.5	−1.23	17.0	1.8	0.7	tr	1.3	5.3	72.4	98.5
	0.5	7.0	−1.17	6.6	1.0	0.6	0.0	1.0	4.2	83.3	96.7

[a] pH values were measured for bulk solutions after electrolyses. [b] Not analysed.

J. Chem. Soc., Faraday Trans. 1, 1989, **85**(8), 2309–2326

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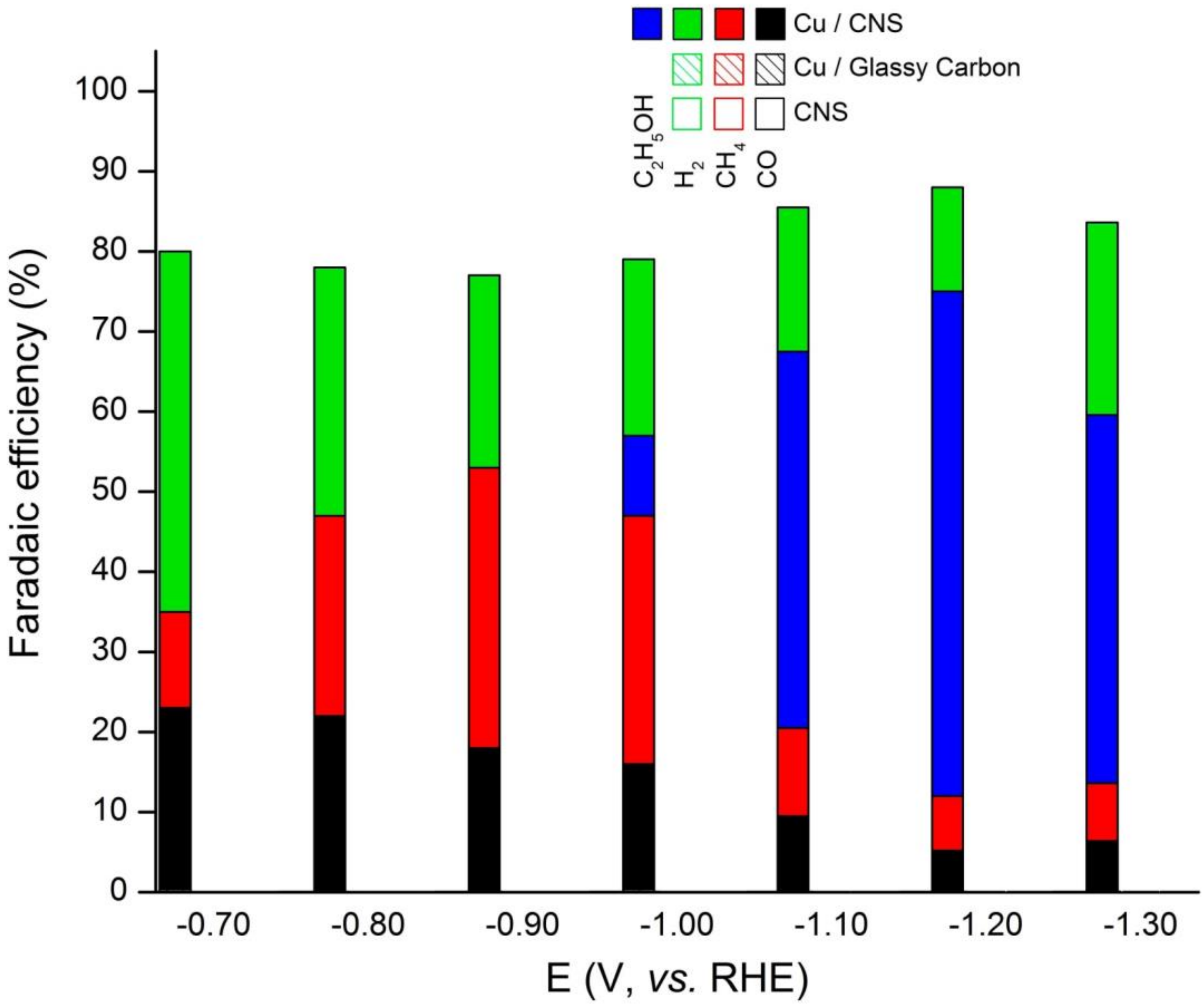
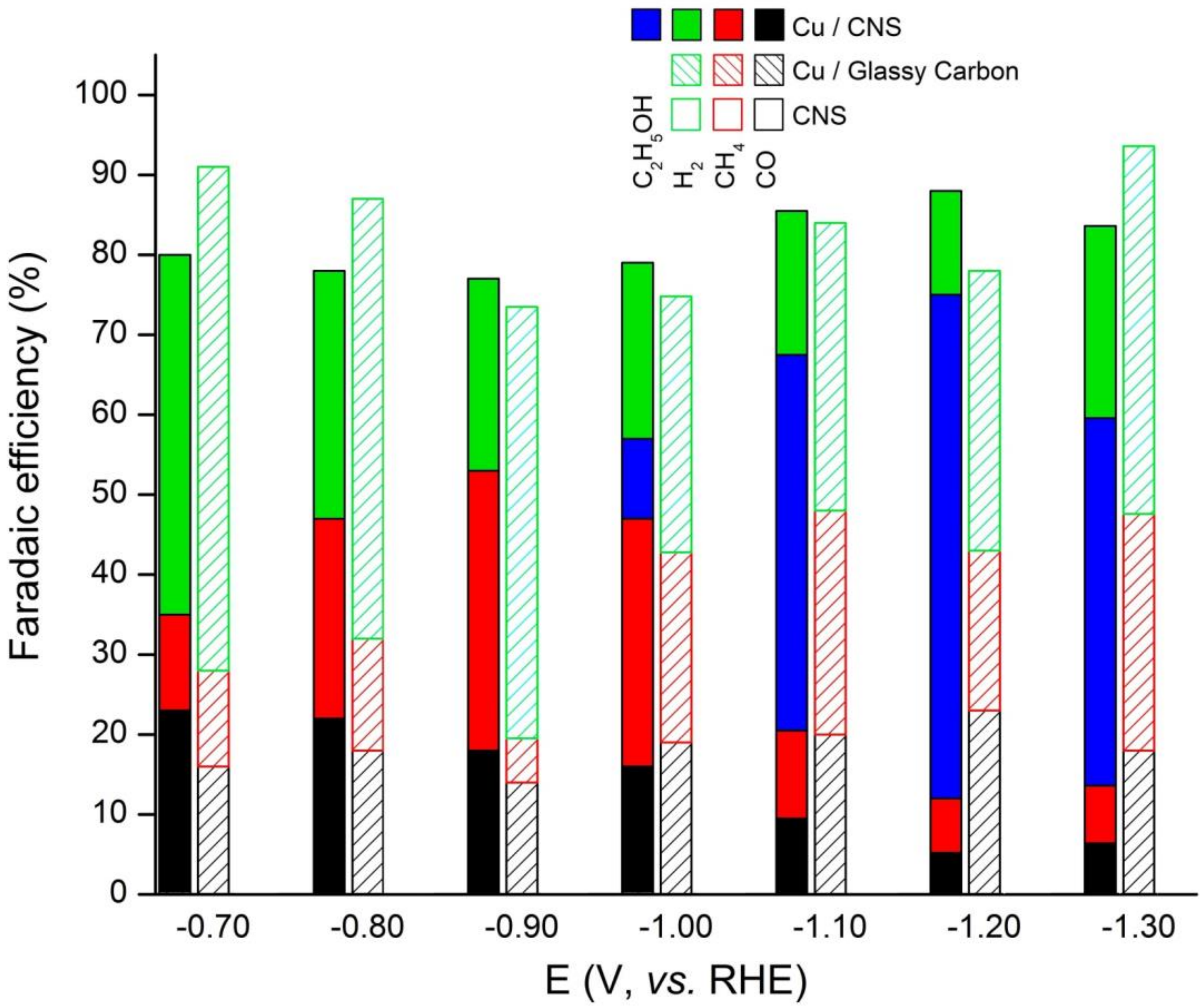
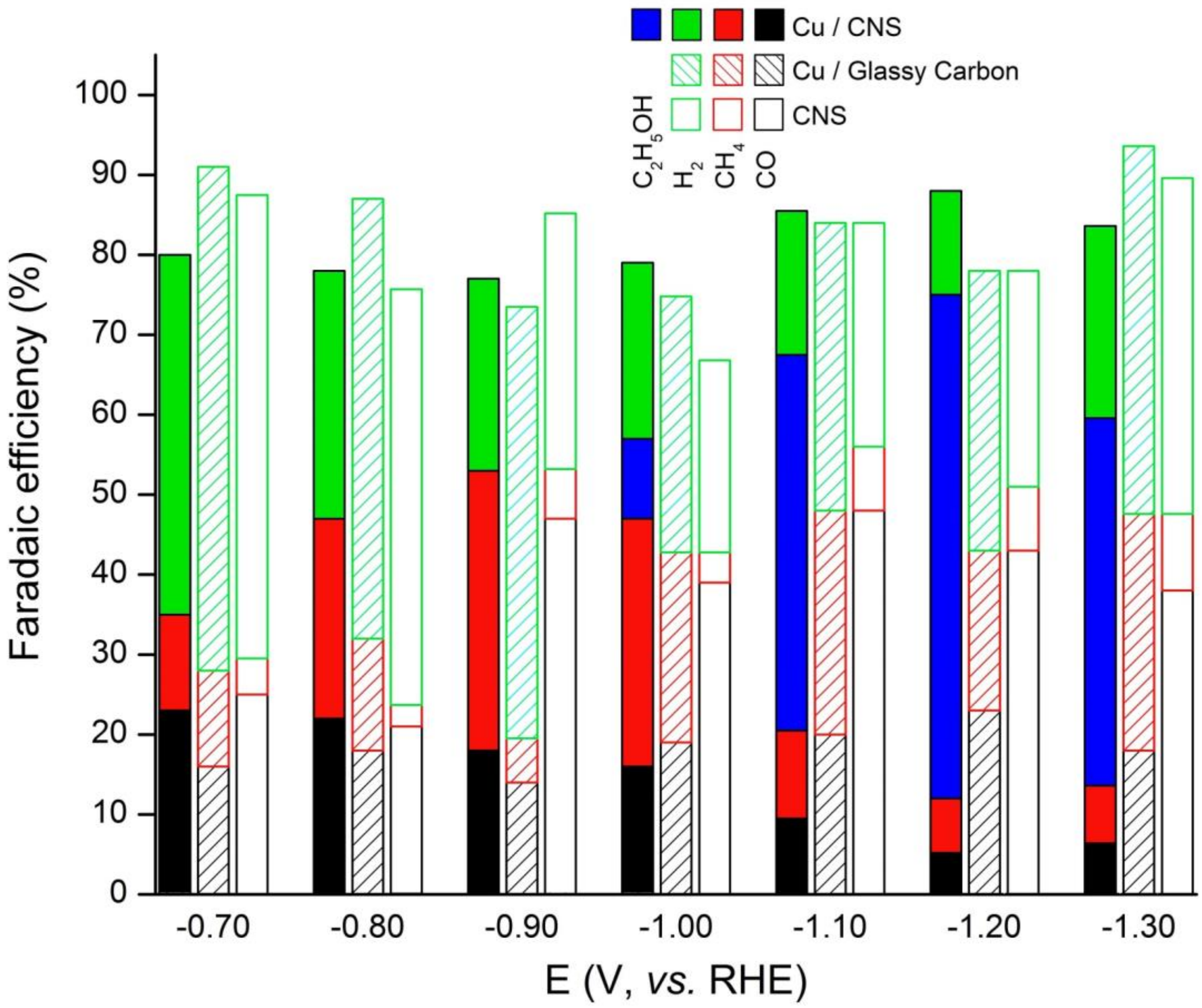
Result: Products from CO_2 Reduction



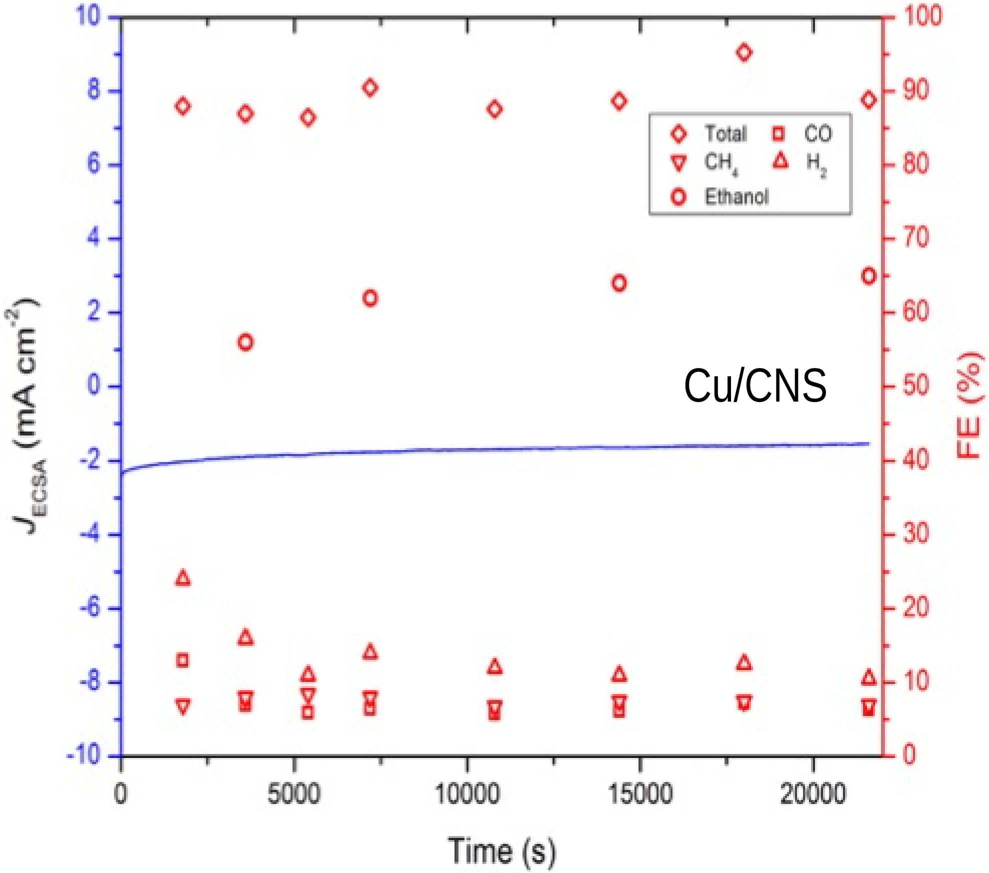
Result: Products from CO_2 Reduction



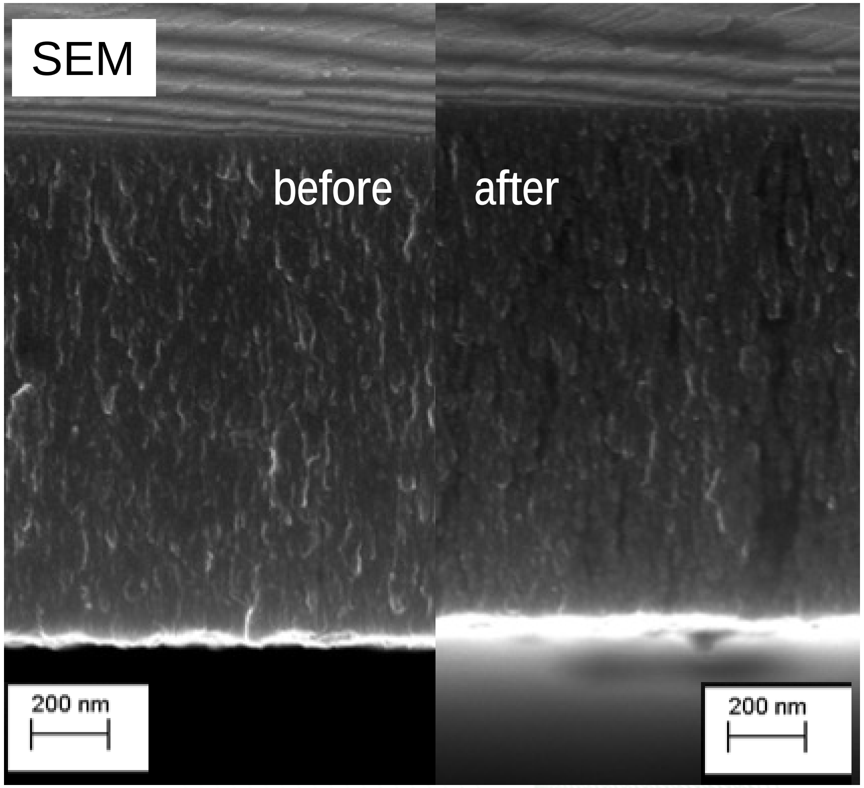
Result: Products from CO_2 Reduction



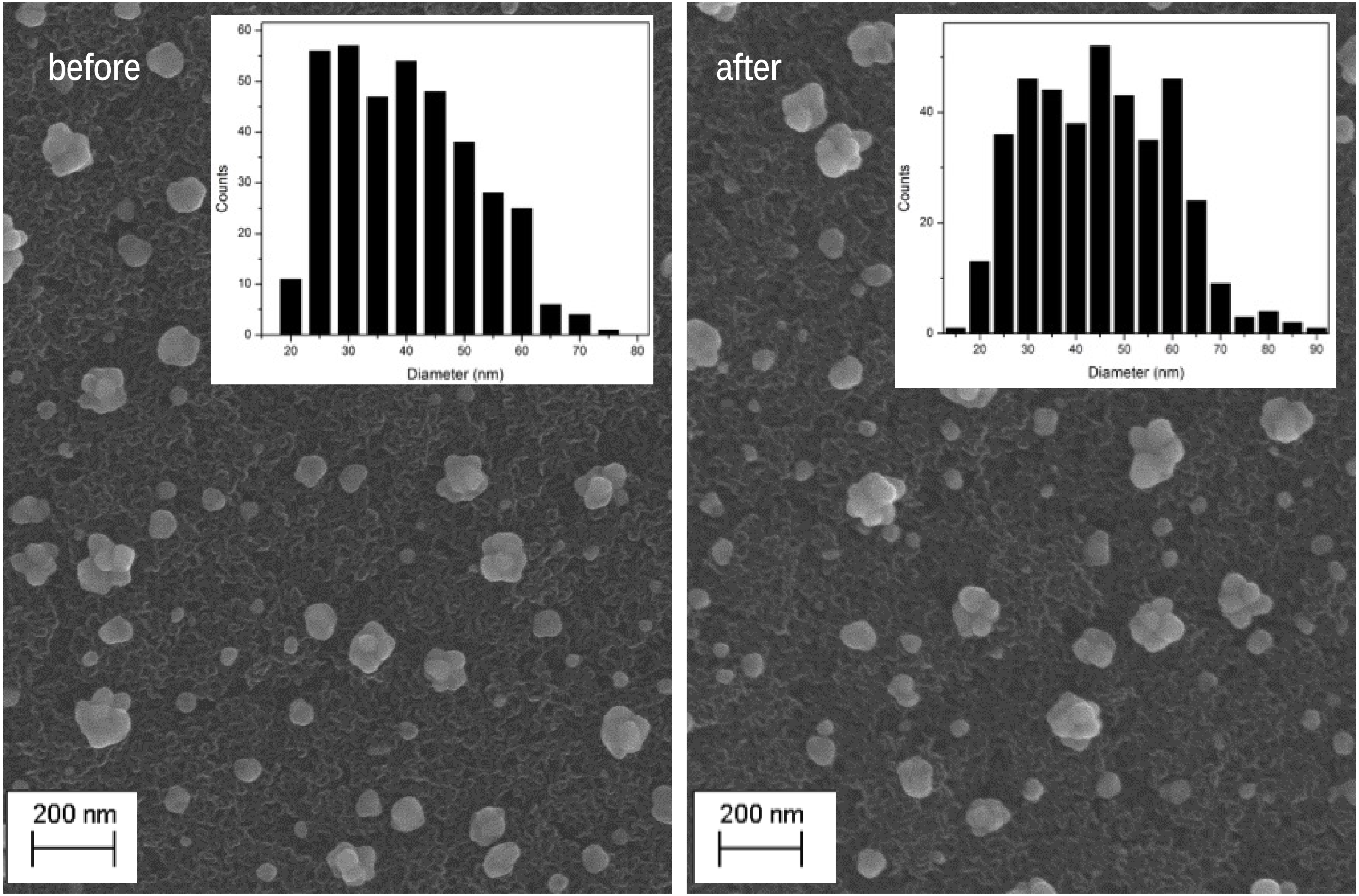
Stability



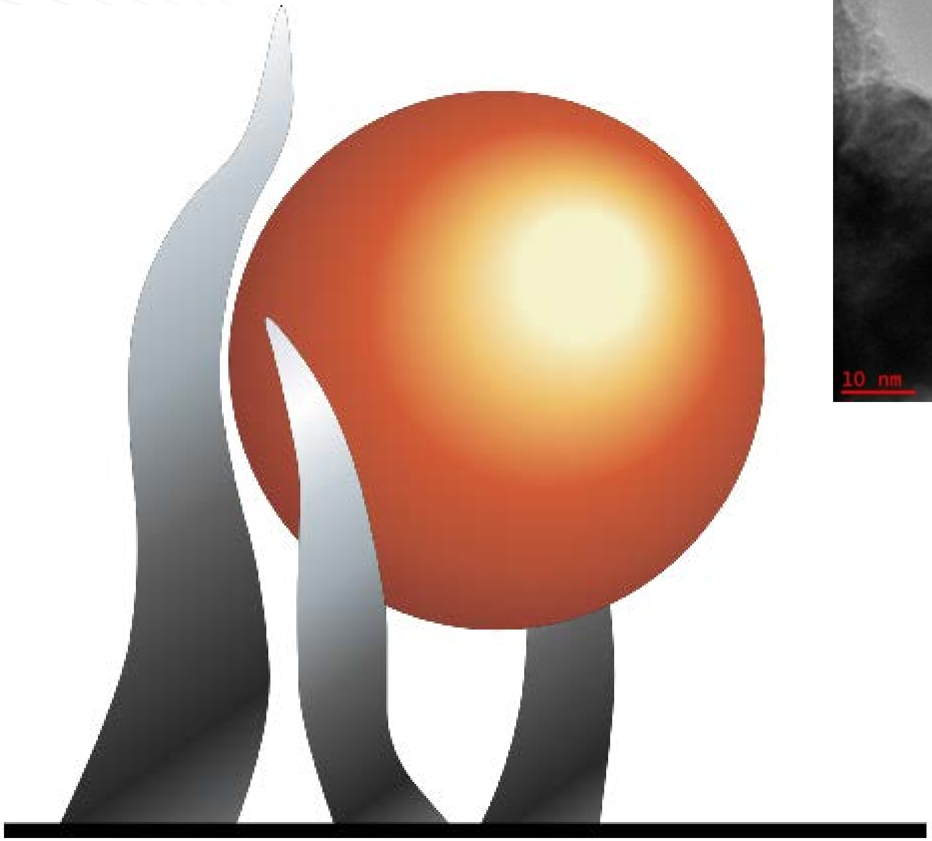
- Stable over a 6-hour experiment.
- Full formation rate for major products achieved in 1 hour.

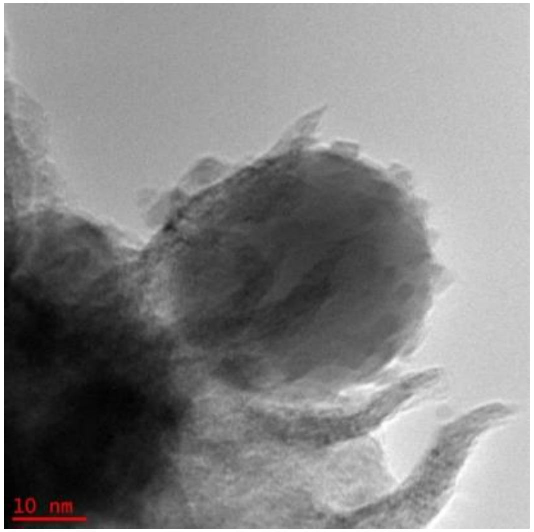


- Side-view SEM images show no change in CNS thickness

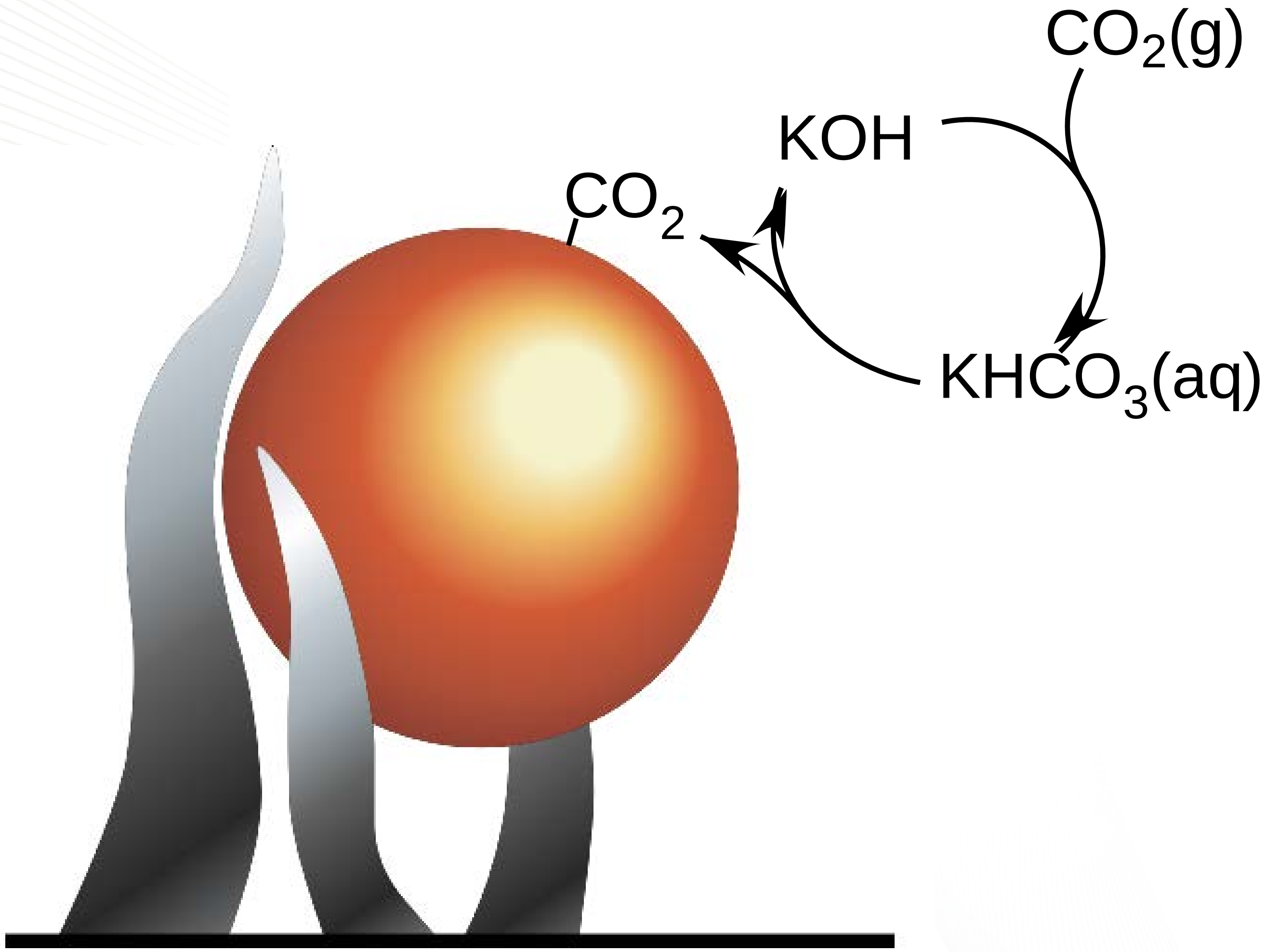

before
Counts
Diameter (nm)
200 nm
after
Counts
Diameter (nm)
200 nm

Why Mostly C2 Products?

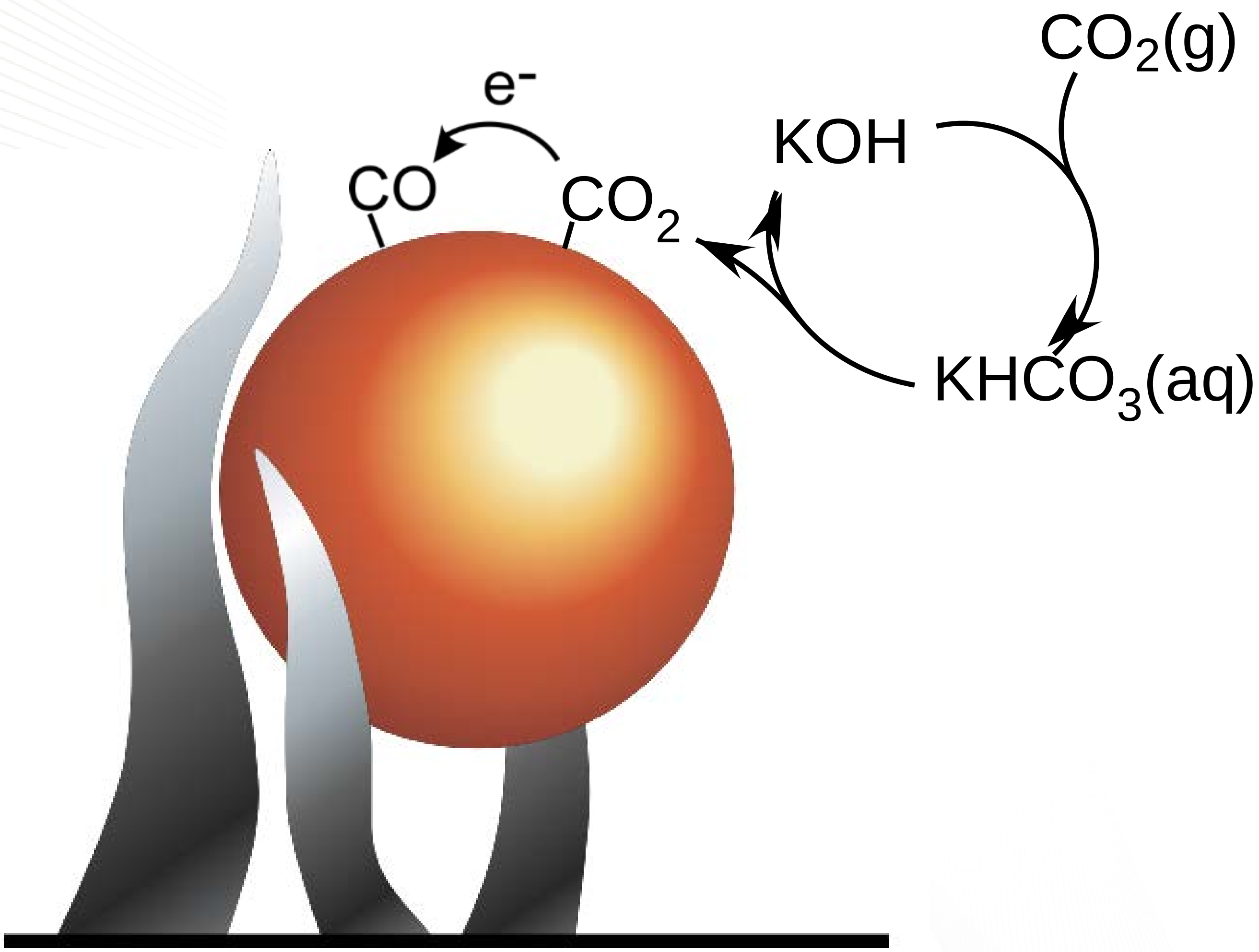




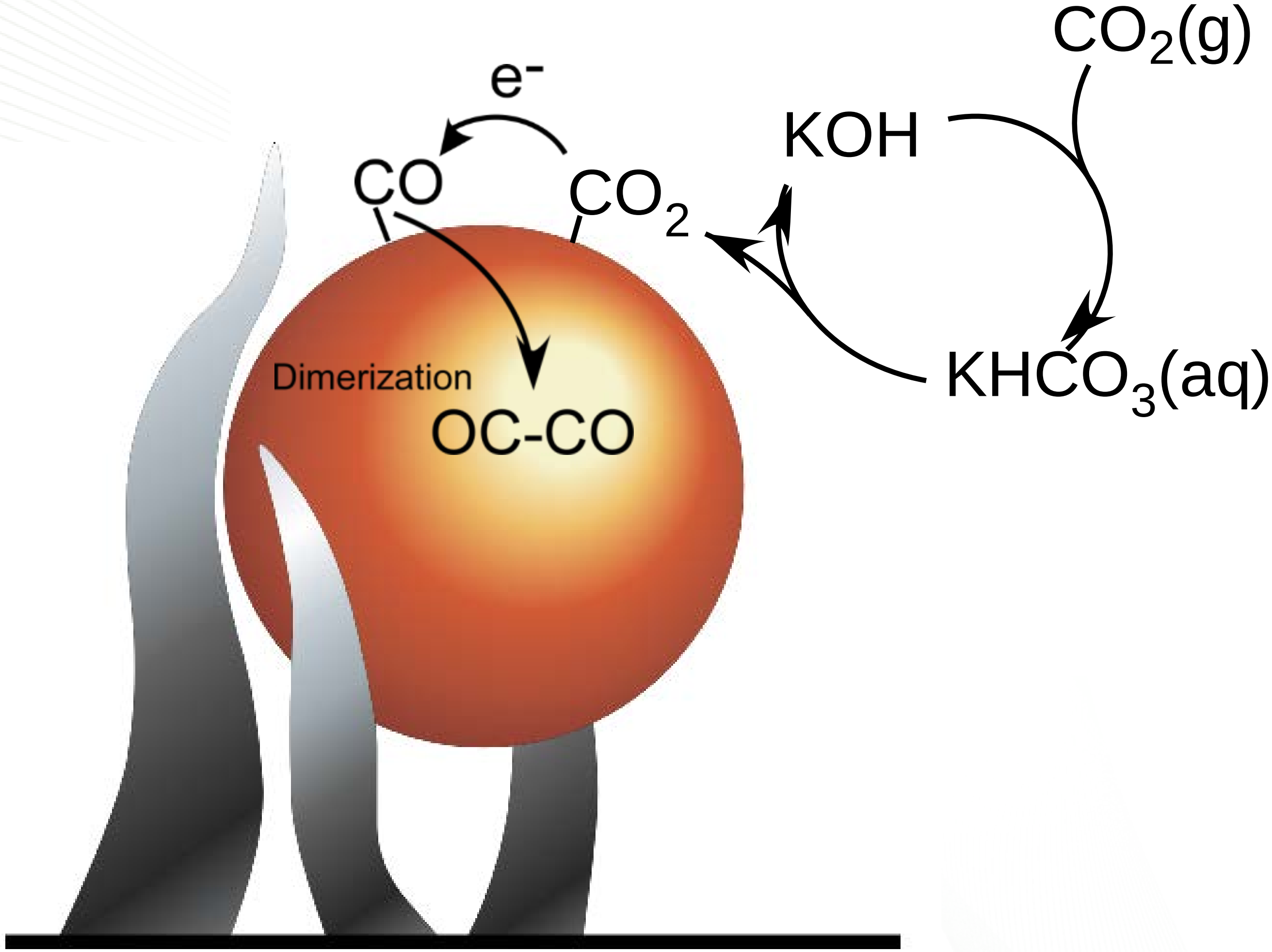
Why?



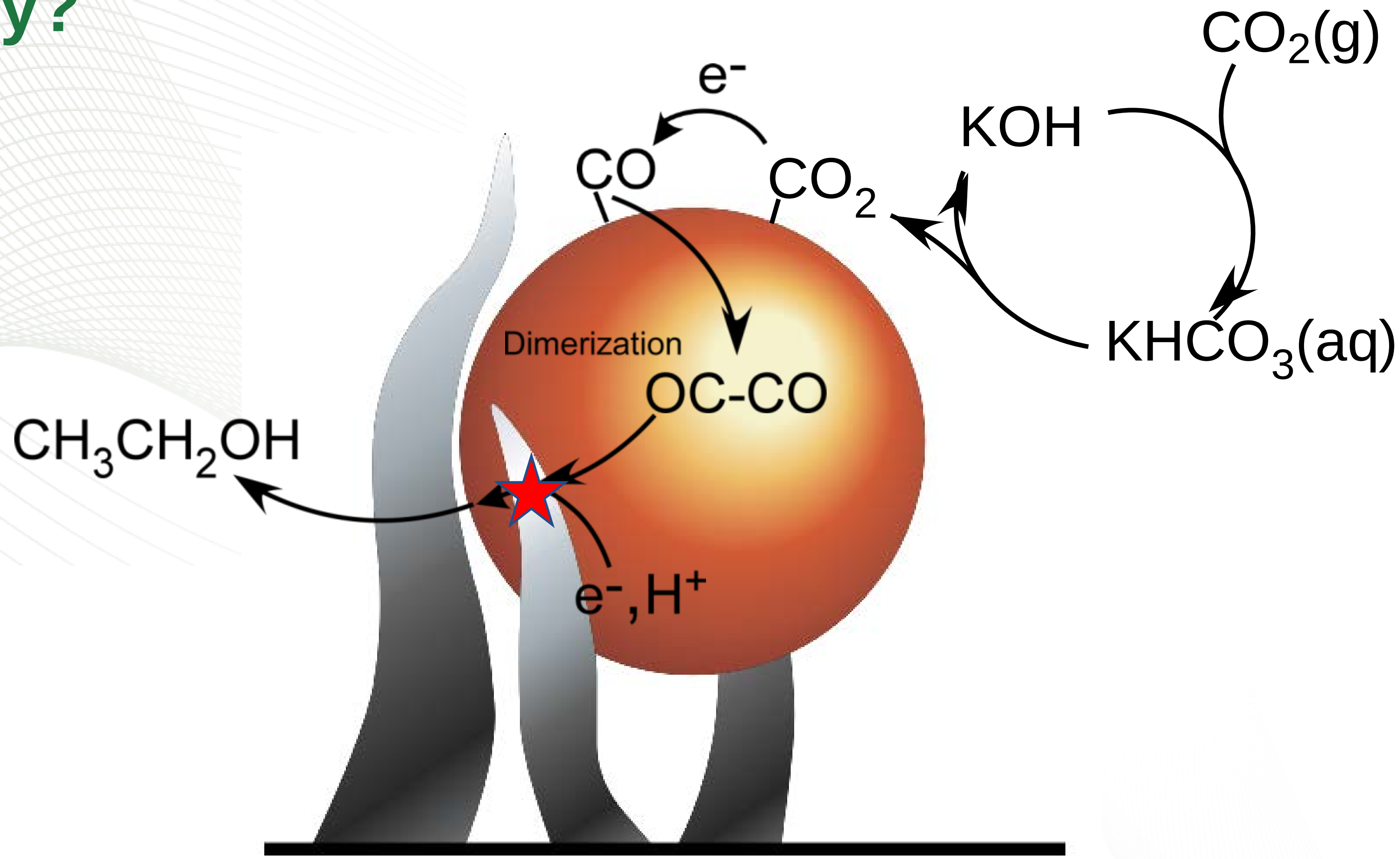
Why?



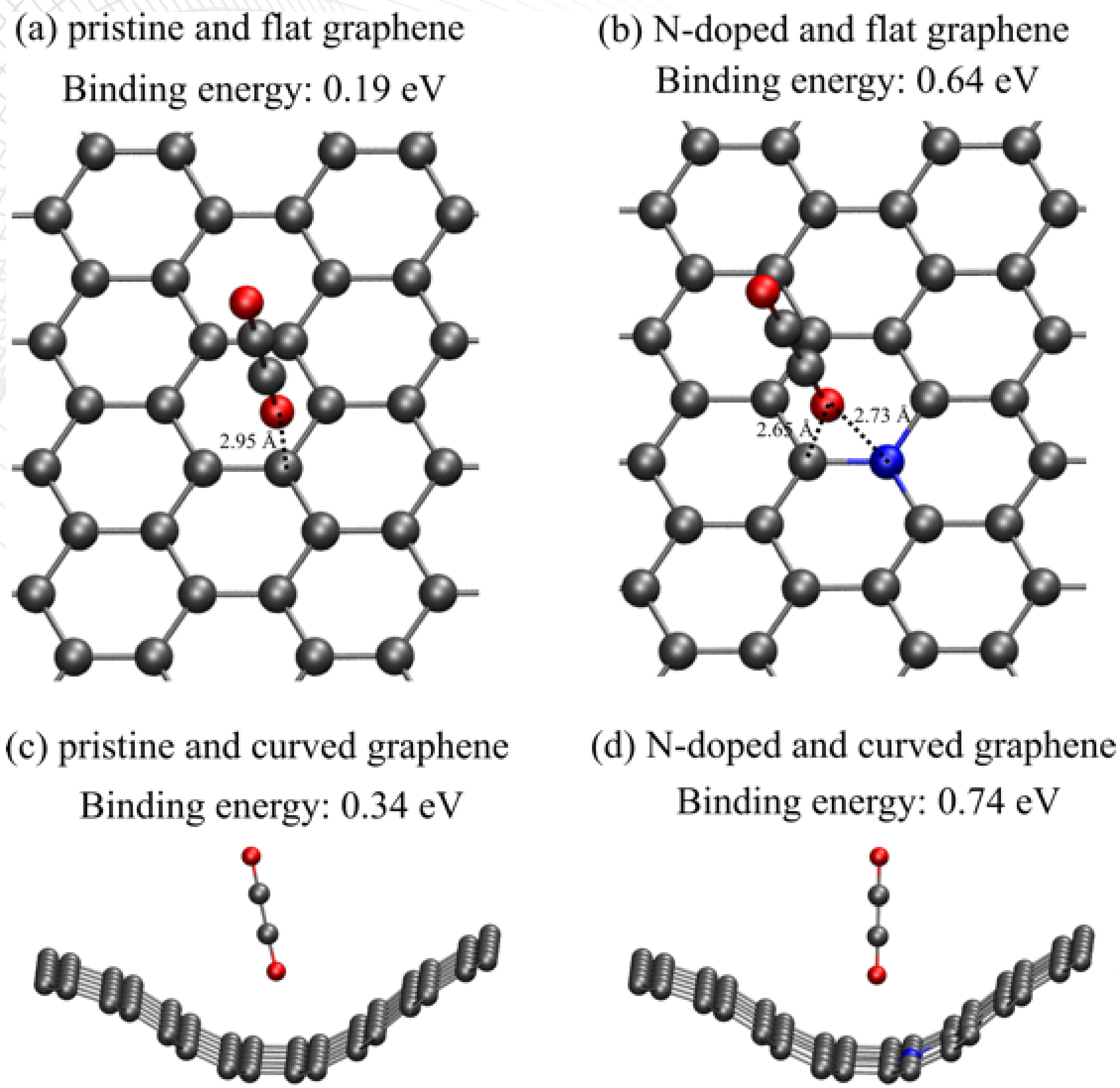
Why?



Why?



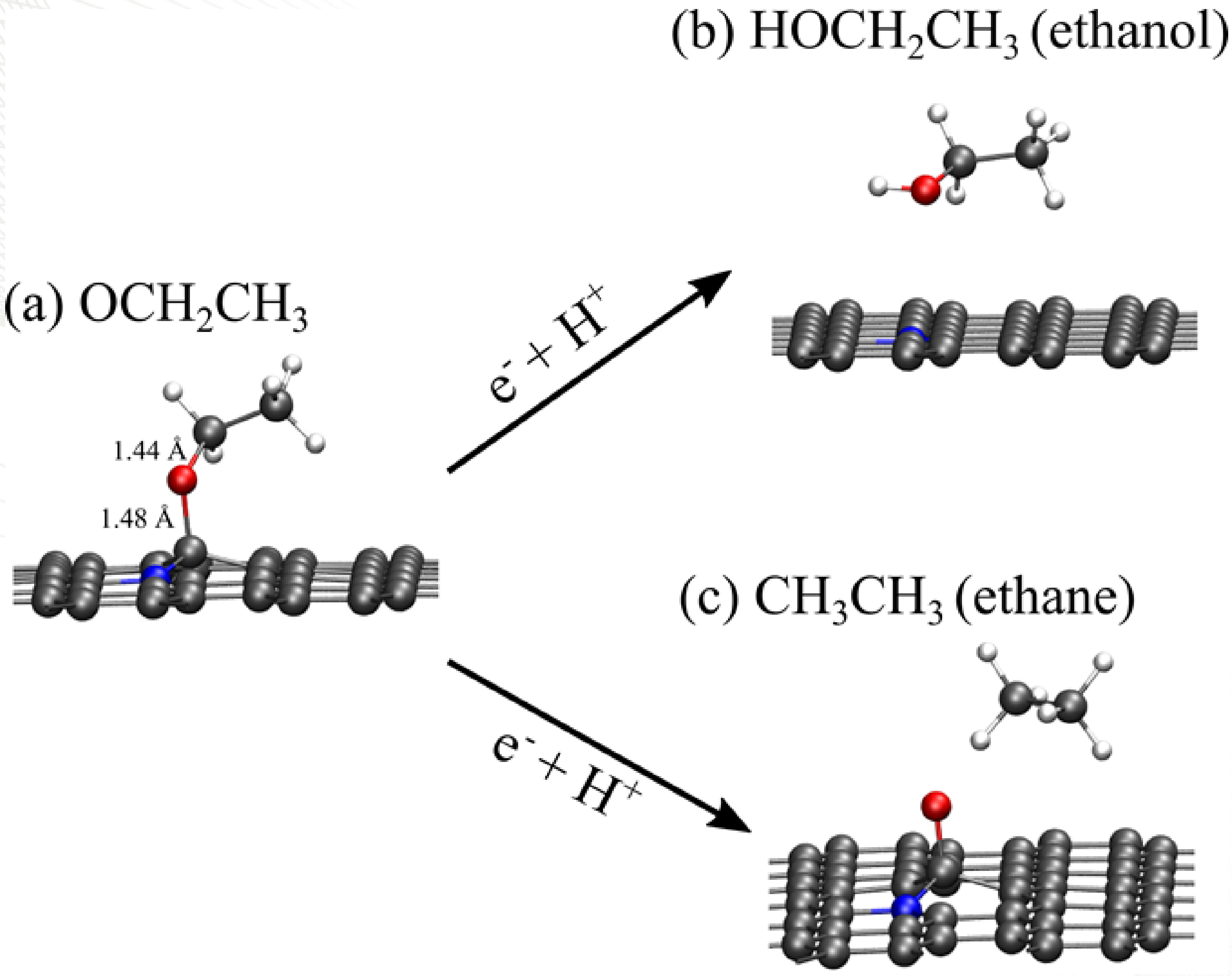
Mechanism



- N dopant: increased binding energy with OCCO.
- Local curvature increase binding energy between OCCO and graphene.

C2 intermediates strongly adsorbed by CNS

DFT of last reduction step favors Ethanol



EtOH cleavage is much more energetically favorable (by 1.59 eV)

Rough Economic Estimate

Consider 1g electrochemical ethanol:

$$\left(\frac{1g}{46g/mol}\right) \times 6.02e^{23} \times \frac{12\mathrm{e}^{-}}{molecule} \div \frac{6.24e^{18}\ \mathrm{e}^{-}}{Coulomb} \times 2.99\mathrm{V} = 75.3\mathrm{kJ\ energy\ in}$$

$$\mathrm{Ethanol\ energy\ density} = 26.4\ \mathrm{kJ/g}$$

$$\mathrm{Energy\ Efficiency} = \frac{26.4\mathrm{kJ}}{75.3\mathrm{kJ}} = 35.1\%$$

$$35.1\% \times 63\%\ \mathrm{Faradaic\ Efficiency} = 22\%\ \mathrm{Total\ Energy\ Efficiency}$$

H_2, CH_4 considered throw-away

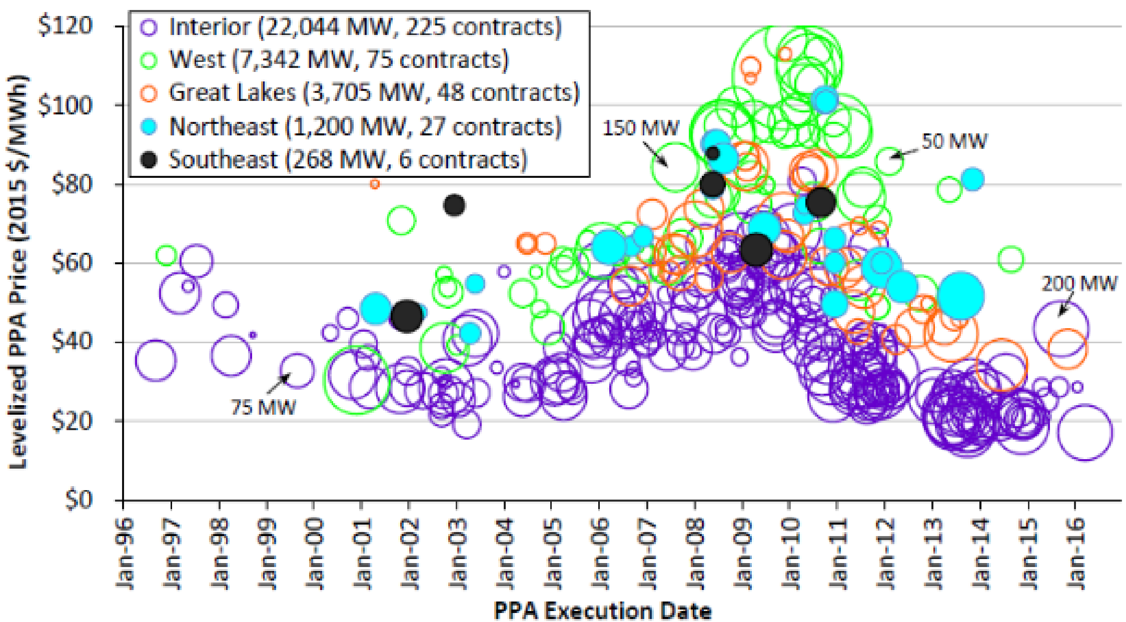
Consider 1 gallon ethanol:

$$78.8\ MJ/gallon = 21.9\ kW \cdot h/gallon$$

$$21.9\ kW \cdot h/gallon \div 22\% = 99.2\ kW \cdot h$$

$$99.2\ kW \cdot h \times \$0.02/kW \cdot h = \$1.98$$ per gallon ethanol for electricity based on laboratory-scale experiments

- Commercial overpotential will be lower due to non-Pt counter electrode
- We have observed single-sample efficiencies closer to 25%



Note: Area of "bubble" is proportional to contract nameplate capacity

Source: Berkeley Lab

Figure 47. Levelized wind PPA prices by PPA execution date and region

American Wind Energy Association, 2016

Cost to Drive

	Leaf		Sentra		Sentra EtOH		Sentra EtOH	
Base Cost Car	$30,680.00		$16,990.00		$16,990.00		$16,990.00	
Energy Efficiency Car	2.94	mile/kwh	33	mpg	33	mpg	33	mpg
Lifetime Miles	150000		150000		150000		150000	
Fuel During Lifetime	51020	kwh	4545	gal	4545		4545	gal
Cost Per Unit Energy	$0.09	/kwh residential	$2.00	gal	$3.00	gal	$4.00	gal
Total Cost Fuel	$4,744.90		$9,090.91		$13,636.36	gal	$18,181.82	
Total Cost Lifetime	$35,424.90		$26,080.91		$30,626.36		$35,171.82	
	Does not include charger installation or tax credits							
	Does not include oil, filters, IC maintenance							

At today's prices, $2/gal margin to achieve zero carbon transportation

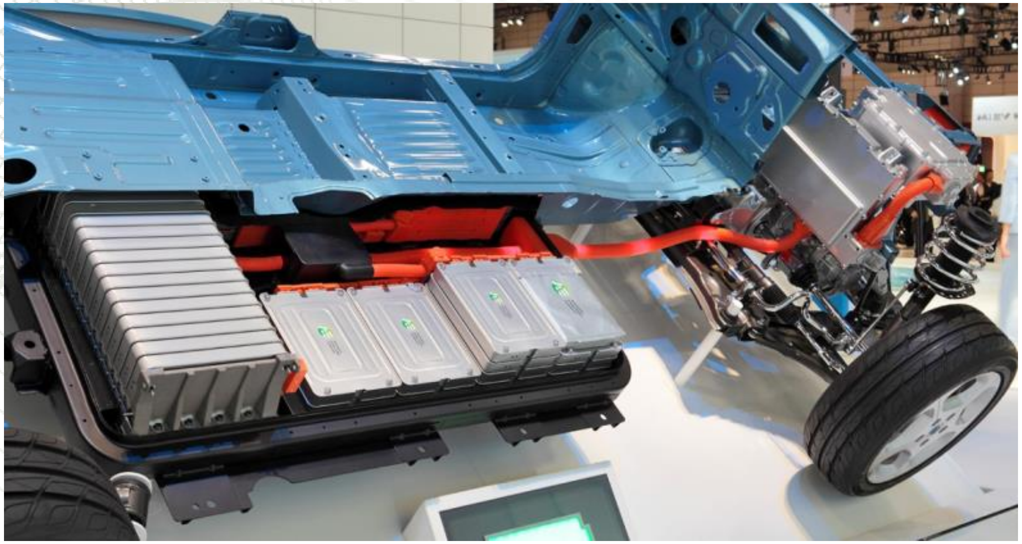
Leaf

https://commons.wikimedia.org/wiki/File:Nissan_Leaf_005.JPG

Sentra

https://commons.wikimedia.org/wiki/File:2015_Nissan_Sentra_S_(6MT),_front_left.jpg

Remove the Capital Cost of the Battery From the Car to the Factory



Portable = small, light, high power density, shape requirements = expensive

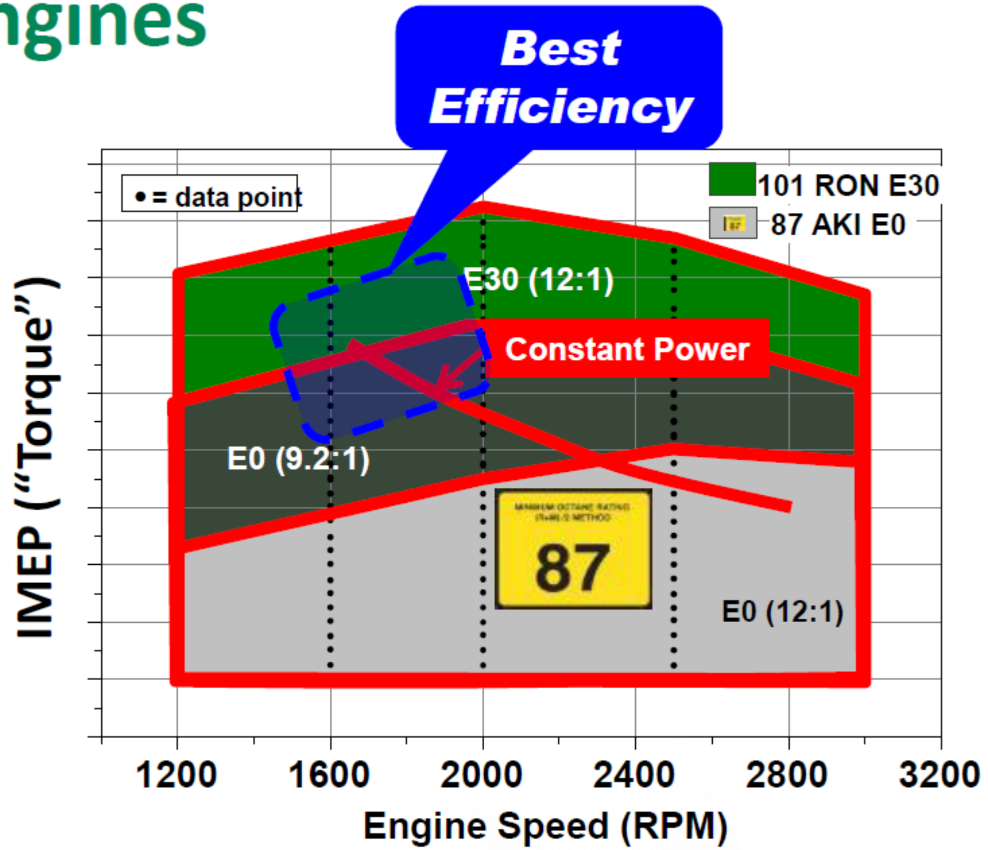
Stationary = large, flexible format, serviceable = cheap(er)

Nissan

Thyssenkrupp

Recent Experiments Highlight Efficiency Benefits of High Octane Fuel for SI engines

- Engines can make more torque and power with higher octane fuel
- Ethanol is very effective at boosting octane number
  - 87 pump octane E0 + 30% Ethanol = 101 RON Fuel
- Increased torque enables downspeeding and downsizing for improved fuel economy
- For future vehicles, engine and system efficiency can balance lower energy density of ethanol blends
- ***Every gallon of ethanol could displace a full gallon of gasoline***



In a high compression research engine, high-octane E30 enables doubling of available torque compared to 87 AKI E0 fuel

- Splitter and Szybist, ORNL

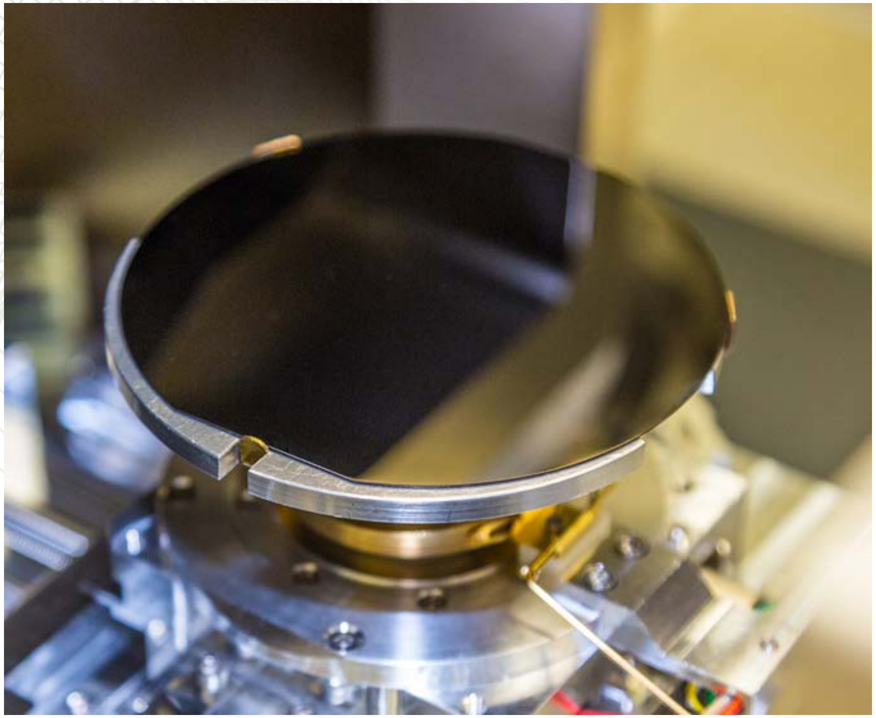
Brian West, ORNL Vehicle Technologies

Oak Ridge National Laboratory

Maturation Work

- Basic science performed under BES Scientific User Facility funding – that work continues
- Recent funding from ORNL Technology Innovation (royalties)
  - Investigate scale up and lifetime of *current catalyst*
  - Project has limited time and scope
- Fossil Energy project is complimentary and important
  - Investigating adaption of catalyst to alternative configurations

Maturation work: adapted chemical vapor deposition to metallic substrates



Original nanospikes grown on silicon wafers

Successfully growing nanospikes on metallic substrates

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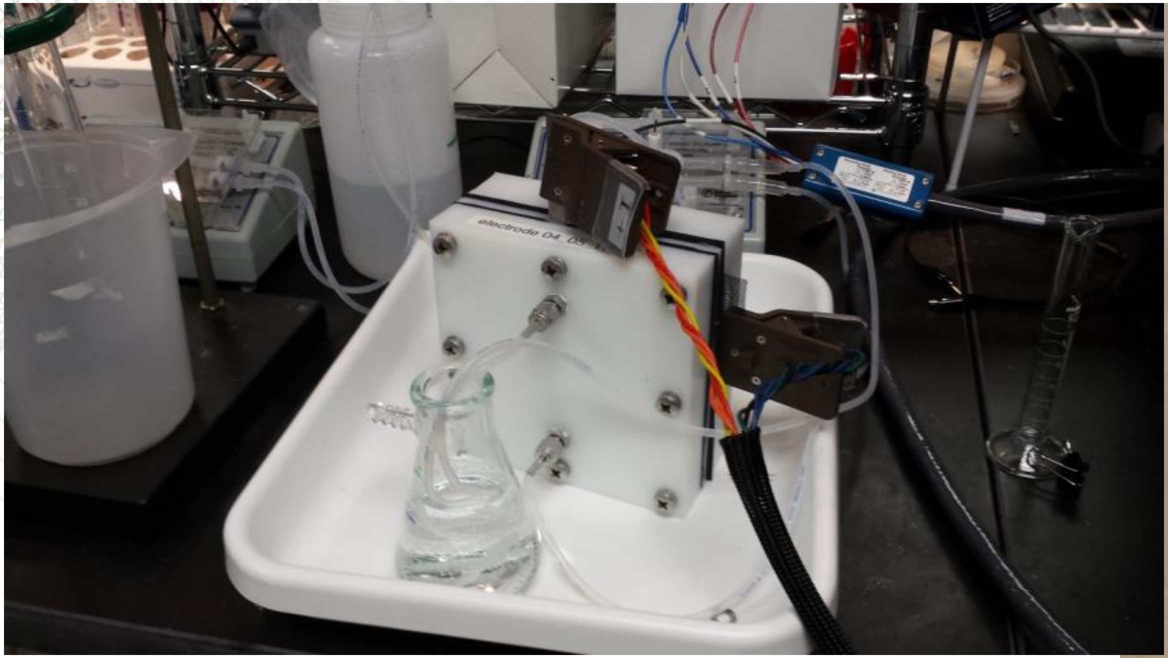
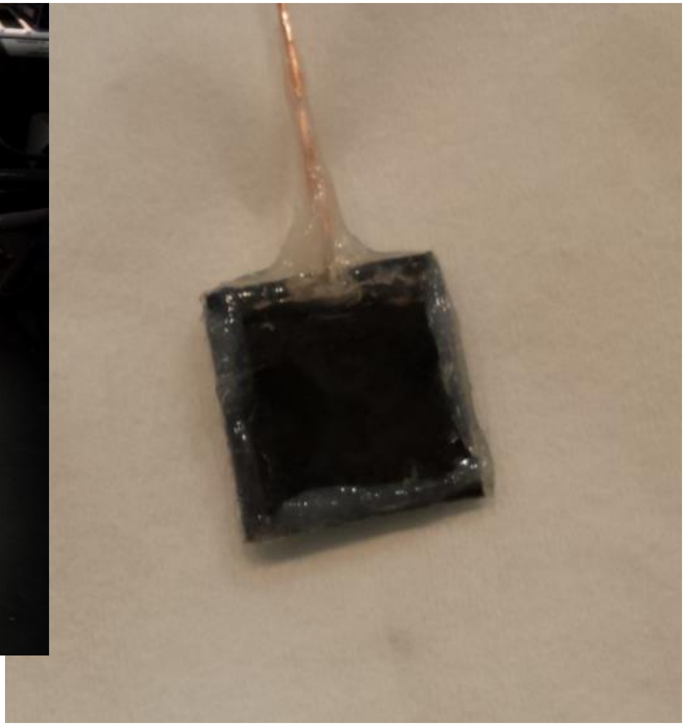
Fabricated large-format electrochemistry cells



Demonstrator electrode = 100 cm^2



Research electrode = 1 cm^2

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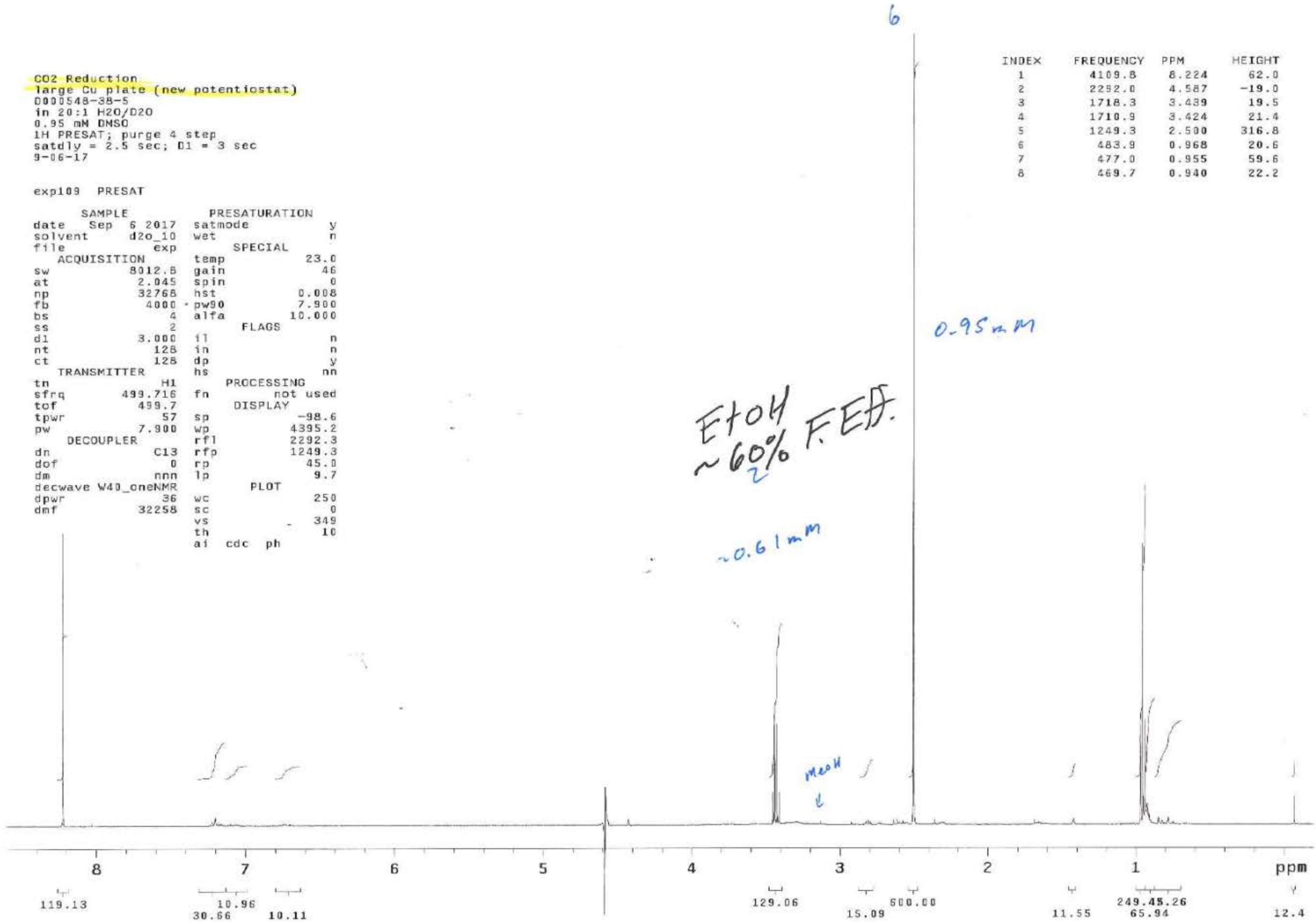
Large Format Results

- Ethanol Produced using a 100 cm^2 electrode
  - (60 mM conc. in 2 h of operation, ~60% F.E.)
- Ethanol Produced using an inexpensive substrate
  - Copper sheet at largest scale (100 cm^2)
  - 316 stainless on intermediate scale (2 cm^2 electrode)



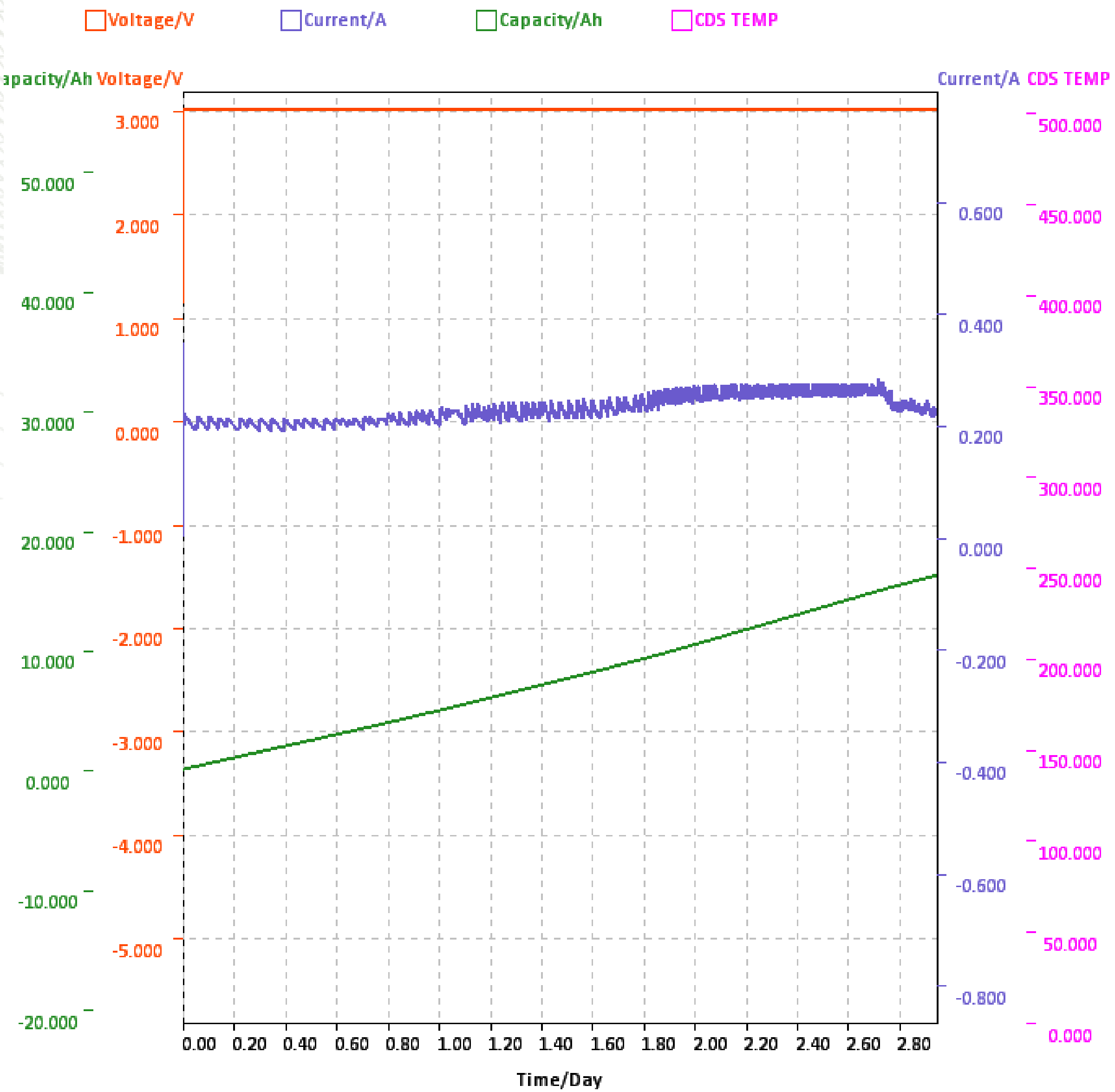
CO2 Reduction
large Cu plate (new potentiostat)
D000548-38-5
in 20:1 H2O/D2O
0.95 mM DMSO
1H PRESAT; purge 4 step
satdly = 2.5 sec; D1 = 3 sec
9-06-17

exp109 PRESAT

```
      SAMPLE                PRESATURATION
date    Sep  6 2017      satmode              y
solvent      d2o_10      wet                  n
file            exp            SPECIAL
    ACQUISITION          temp              23.0
sw           8012.8      gain                46
at            2.045      spin                 0
np            32768      hst              0.008
fb             4000      pw90             7.900
bs                4      alfa            10.000
ss                2             FLAGS
d1            3.000      il                   n
nt              128      in                   n
ct              128      dp                   y
    TRANSMITTER          hs                  nn
tn               H1          PROCESSING
sfrq        499.716      fn            not used
tof           499.7          DISPLAY
tpwr             57      sp               -98.6
pw            7.900      wp              4395.2
     DECOUPLER           rfl             2292.3
dn              C13      rfp             1249.3
dof               0      rp                45.0
dm              nnn      lp                 9.7
decwave W40_oneNMR             PLOT
dpwr             36      wc                 250
dmf           32258      sc                   0
                         vs                 349
                         th                  10
                         ai    cdc   ph
```

INDEX	FREQUENCY	PPM	HEIGHT
1	4109.8	8.224	62.0
2	2292.0	4.587	-19.0
3	1718.3	3.439	19.5
4	1710.9	3.424	21.4
5	1249.3	2.500	316.8
6	483.9	0.968	20.6
7	477.0	0.955	59.6
8	469.7	0.940	22.2

Large format cell for stability



Example: final 3 days of recent run

Others are Working to Commercialize CO_2 Electrochemistry Technologies

- Current Operations
  - OPUS 12; in development
    - Producing formate from CO_2
  - Carbon Recycling International
    - Producing CH_3OH from CO_2 - in production
  - Haldor Topsoe
    - Formate and CO from CO_2 – commercially available
  - Dioxide Materials
    - Formate from CO_2 – close to commercially available
- Previous Operations
  - Liquid Light
    - Formate from CO_2

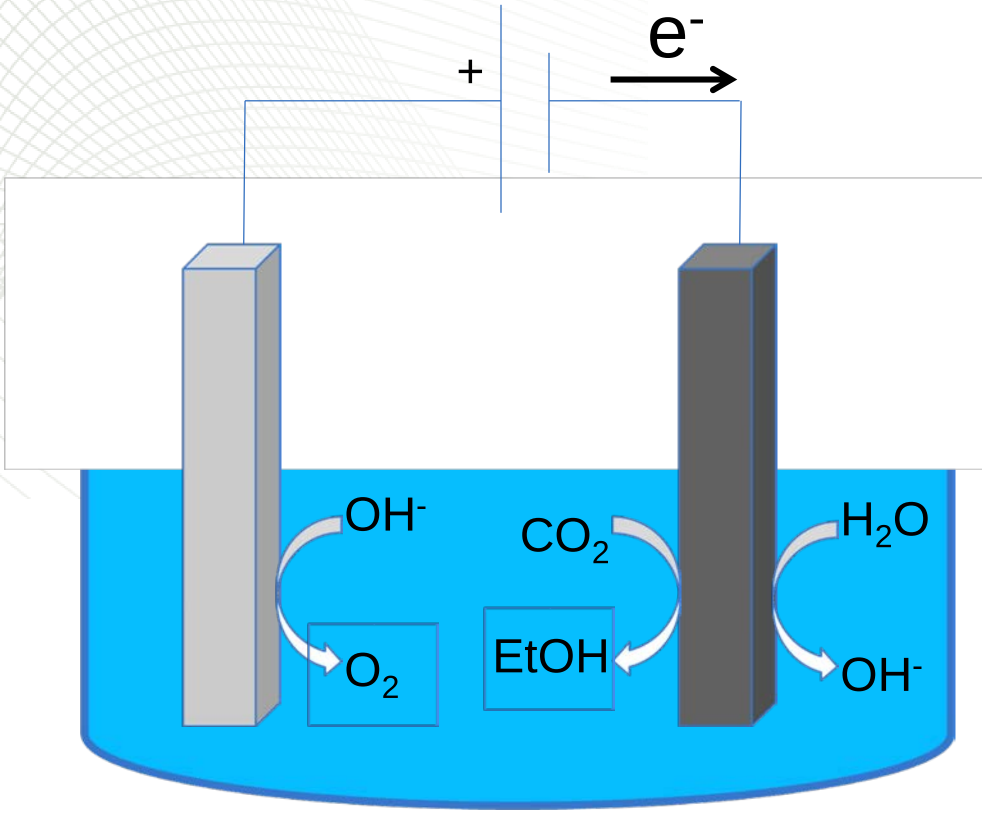
Fossil Energy FWP: FEAA132

- Objectives
  - Maximize the current density. Current density is a measure of activity and determined capital cost.
  - Evaluate and optimize operation within a fossil fuel combustion flue gas
    - Will demonstrate technical feasibility, if possible
    - Will investigate poisoning mechanisms, if they exist
    - Will investigate mitigation or pre-treatment strategies

Obj. 1: Maximizing Current Density

- Current density = electrochemical activity of the catalyst
  - Battery analogue = amps
  - Measure using mA/cm^2, or electrical current per area of the catalyst
    - ARPA-e targets 300 mA/cm^2; we have achieved about ~15 mA/cm^2
    - Our goal is 100 mA/cm^2
  - Directly applicable to capital costs
    - Not competitive in fuel market right now
    - Fine chemicals/beverage market may be accessible soon
- Strategy
  - Adapt catalyst to better electrolytes, different cell and current-collector designs in order to maximize **mass transport**
    - CO_2 solubility
    - Wetting of the catalyst surface
    - Increased geometric surface are using 3D electrodes
    - Attempt implementation of gas-phase mass transport
    - Temperature and pressure

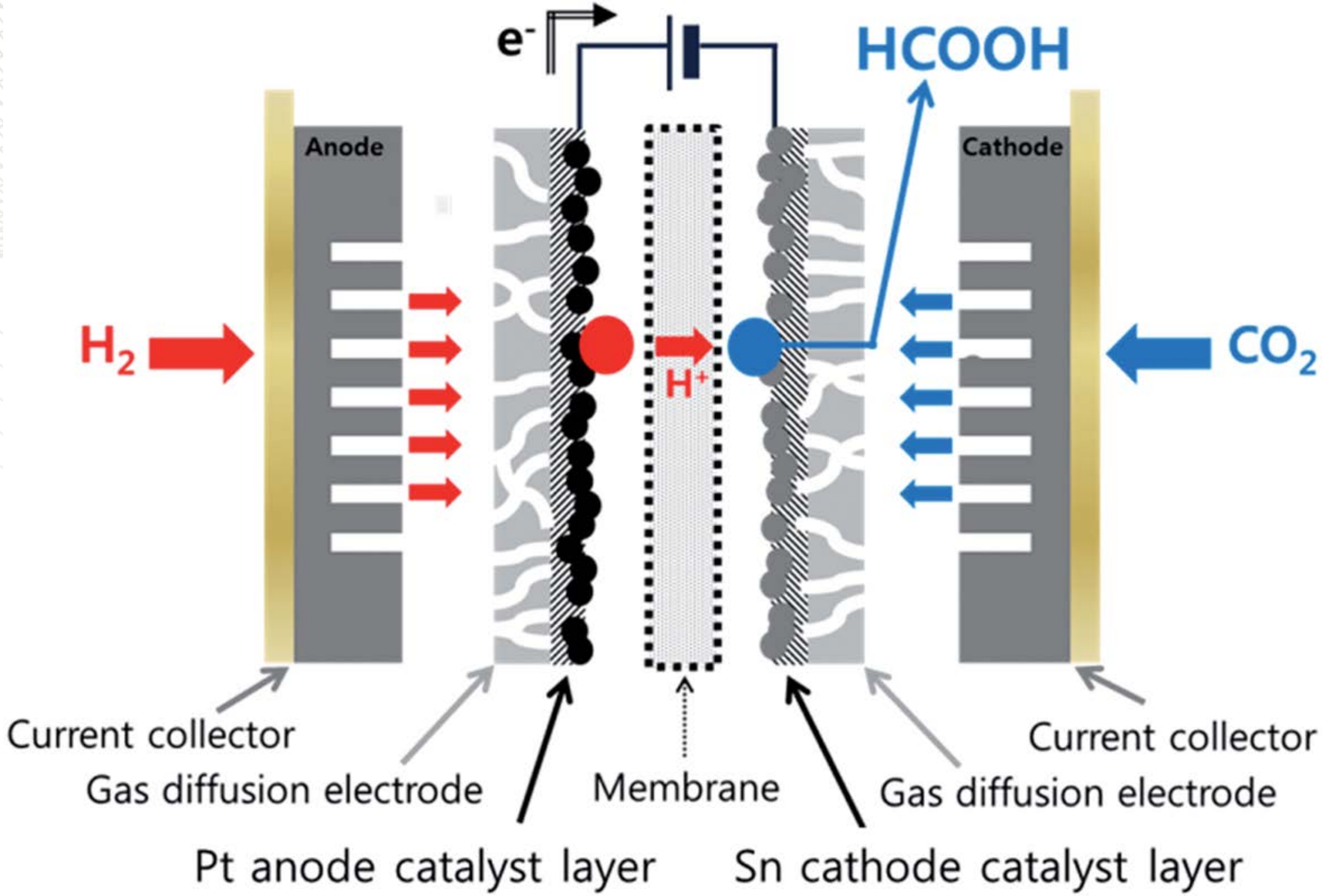
Current Density and Mass Transport



- Mass transport:
  - How quickly reagents can be brought to, and products carried away from, the catalyst surface
  - Is fundamental limitation in electrochemistry
  - Controlled by electrolyte and cell design
  - Influenced by temperature, pressure, concentration

- Today's catalysts commonly operate in $KHCO_3$
- Solubility high, but not as free CO_2
- Rate-limiting step is chemisorption of CO_2 from bicarbonate ion to catalyst surface

Gas-Phase Operation



from [*J. Mater. Chem. A*](), 2015, **3**, 3029-3034

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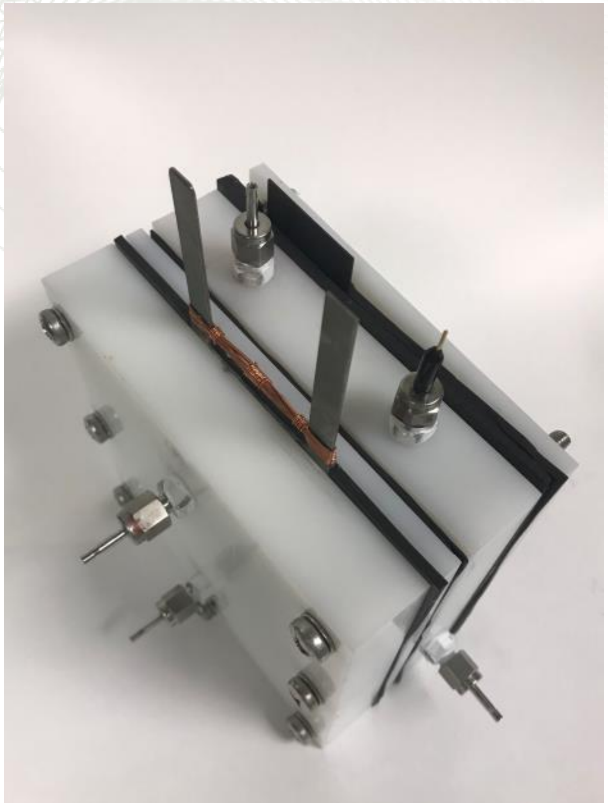
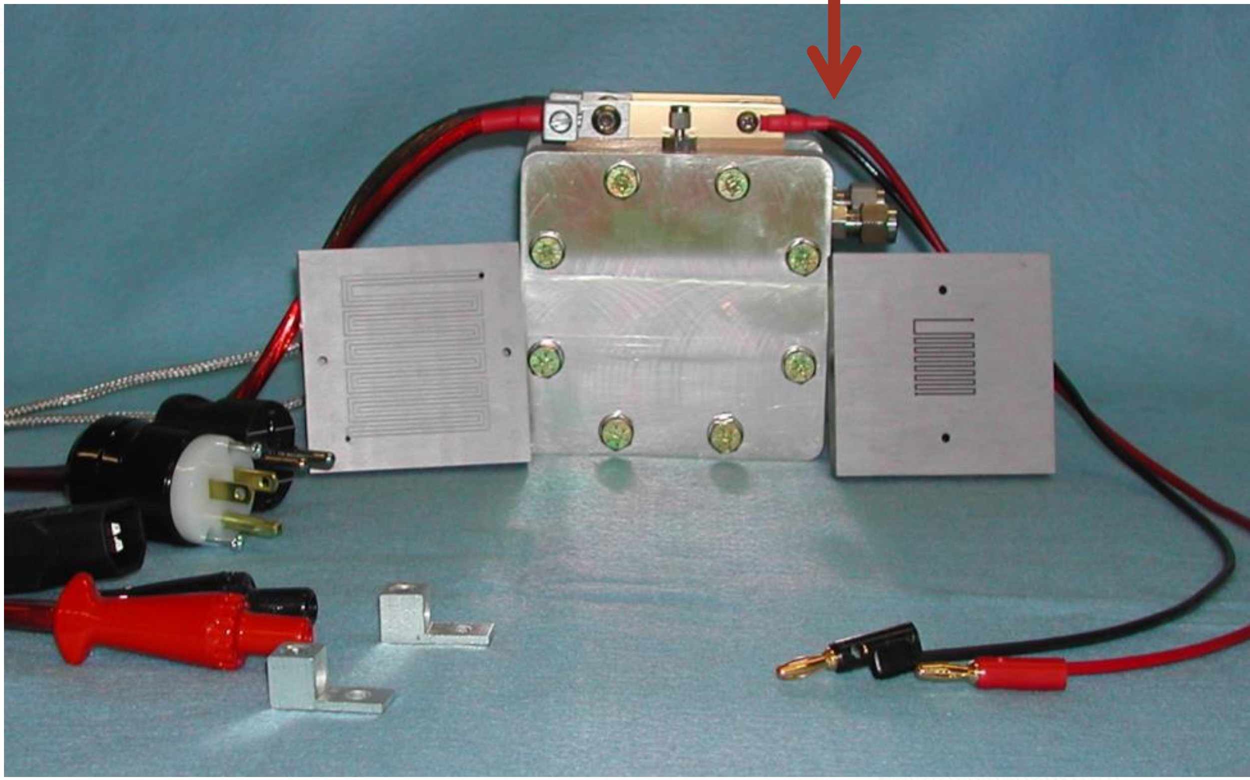
Electrochemical Cell Designs

- In-house cells are not optimized for T and P control
- Limited capability for conversion to gas phase
- Have recently added a commercial research cell





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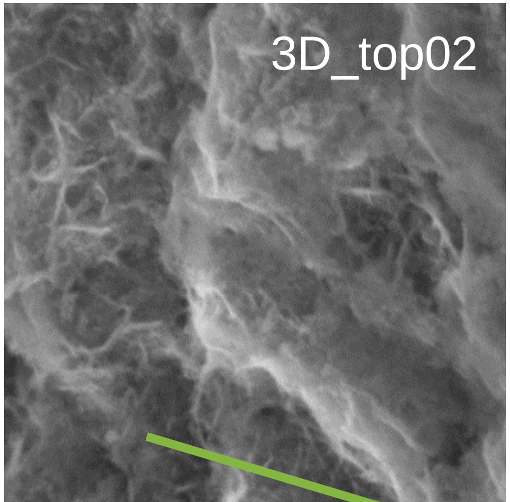
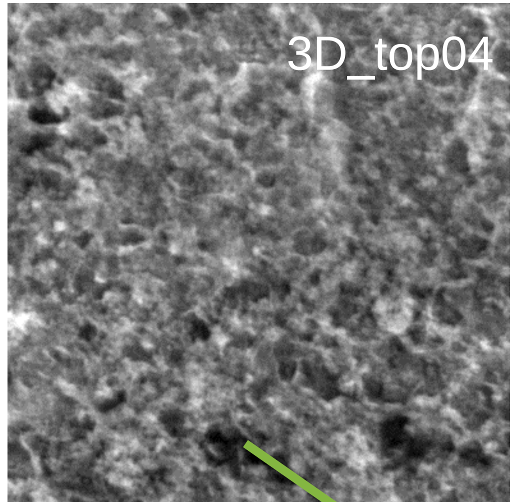
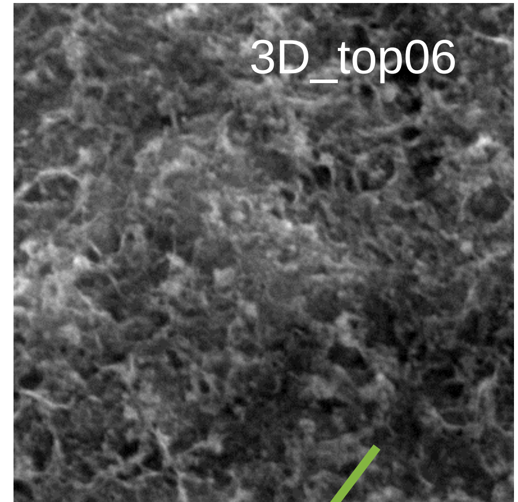
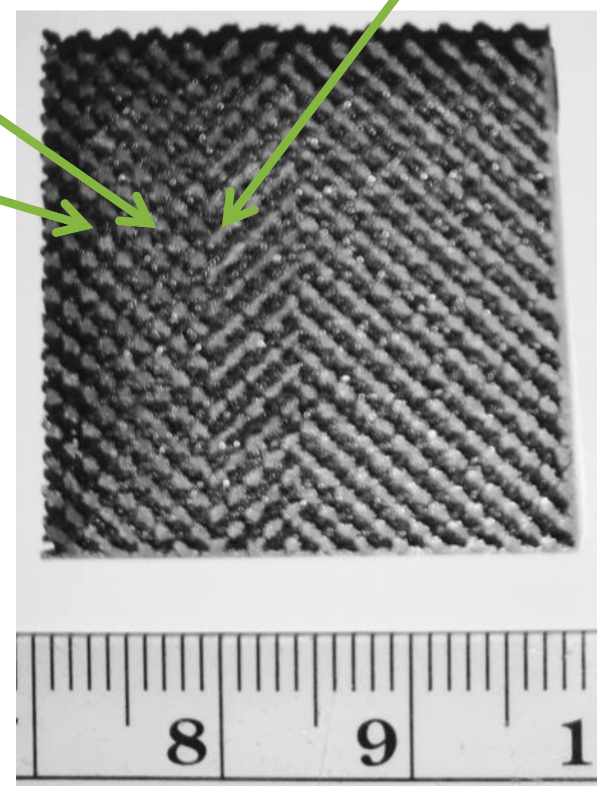
Growth of CNS on a 3D printed mesh









- Enhanced surface area for liquid phase operation
- Potential route to gas phase operation
- CNS were observed ~ 3 mm from the edge;
- A carbon film without clear CNS feature was observed further inside till ~8 mm from the edge.

Other Strategies for Maximizing Current Density

- CNS on carbon cloth – amenable to gas phase and consistent with H_2 fuel cell construction
- Explore alternative electrolytes
  - Requirements are:
    - High CO_2 solubility as a molecule, not ion
    - Wide electrochemical stability window
    - Ability to solubilize salt for electric charge screening
    - Increased wettability (less polar than water)
  - Likely candidates include battery electrolytes
    - Dimethyl carbonate, glymes, acetonitrile

Obj. 2: Test and Optimize Within Flue Gas

- Real world flue gas contains myriad contaminants
- Cost depends on pre-treatment needs
- Must understand impact of contaminants
- Some contaminants (CO, H_2O) may be beneficial to an electrochemical reaction

Table 2
Typical non-nitrogen components of untreated flue gases from Eastern Low Sulfur Coal

Species	Concentration
H_2O	5–7%
O_2	3–4%
CO_2	15–16%
Hg complexes	1 ppb
CO	20 ppm
Various hydrocarbons	10 ppm
HCl	100 ppm
SO_2	800 ppm
SO_3	10 ppm
NO_x	500 ppm

Data from Ref. [37].

C.E. Powell, G.G. Qiao / Journal of Membrane Science 279 (2006) 1–49

Objective 2 Strategy

- Understand reaction parameters
  - Test each contaminant individually, if practical
  - Test interactivity, when data suggest an interaction may exist
- Ultimate goal is to understand the limitations and impacts of feedstock
- Optimization will depend on data

- Will begin around Jan 1, 2018

Project Schedule and Budget

				FY2017	FY2018			
	Start Date	End Date	Cost	4	1	2	3	4
Task 1. Project Management and Planning*	8/15/2017	7/31/2018						
Quarterly report				12/31/17	3/31/28	6/31/18		
Comprehensive Final Report							7/31/18	
Task 2.1 Maximize current density of catalyst for production of ethanol – 3D electrode development	8/15/2017	9/30/2017	$71,000					
Task 2.2. Maximize current density of catalyst for the production of ethanol – 3D electrode, gas phase operation, maximize wettability	10/1/2017	7/31/2018	$49,000					
Milestone: Configure catalyst for gas phase operation					1/31/28		7/31/18	
Milestone: Complete maximization of current density of catalyst								
Task 3. Measure and optimize performance in flue gas	11/1/2018	7/31/2018	$80,000					
Milestone: Test and optimize catalyst against flue gas impurities					3/31/2018			
Milestone: Complete characterization of impurity intolerances							7/31/18	

	Fiscal Year 1				Fiscal Year 2					
	8/15/17 – 9/30/17		10/1/17 – 12/31/17		1/1/18 – 3/31/18		4/1/18 – 6/30/18		7/1/18 – 7/31/18	
	Q1	Total Project	Q2	Total Project	Q3	Total Project	Q4	Total Project	Q5	Total Project
Federal Share	$71,000	$71,000	$33,000	$104,000	$43,000	$147,000	$43,000	$190,000	$10,000	$200,000
Total Planned	$71,000	$71,000	$33,000	$104,000	$43,000	$147,000	$43,000	$190,000	$10,000	$200,000

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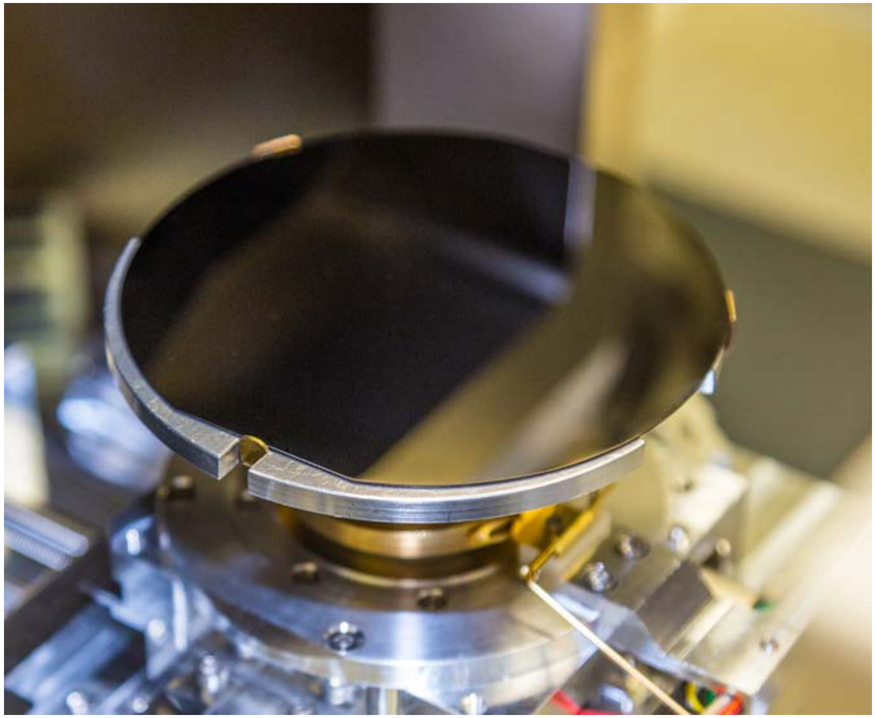
CNS are Idealized Nano-Carbon

- N-doped: raises Fermi level 0.2 V
- Sharp tips
- Easy to grow over large areas, unlike nanotubes
- No binders necessary to create a film
- No catalysts needed for growth
- No purification
- Grows well on most metals: stainless, Ti, Cu
- Physical and chemical behavior similar to other nano-carbons, with major advantages in scale and reproducibility



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Acknowledgement

Dr. Yang Song
Dr. Jingsong Huang
Daniel Johnson
Dr. Zili Wu
Dr. Rui Peng (VA Tech)
Dr. Peter V. Bonnesen
Dale Hensley

Dr. Bobby Sumpter
Dr. Liangbo Liang
Dr. Harry M. Meyer III
Dr. Miaofang Chi
Dr. Cheng Ma
Dr. Dave Cullen
Dr. Andrew Lepore

Oak Ridge National Laboratory

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