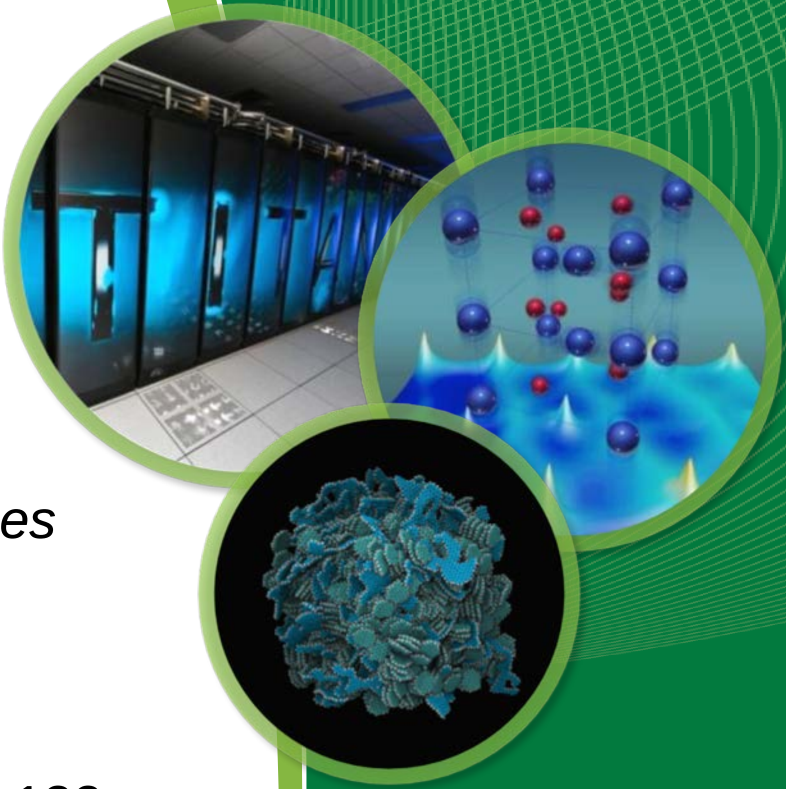
Maximizing Current Density for Electrochemical Conversion of Flue Gas CO_2 to Ethanol



Adam Rondinone

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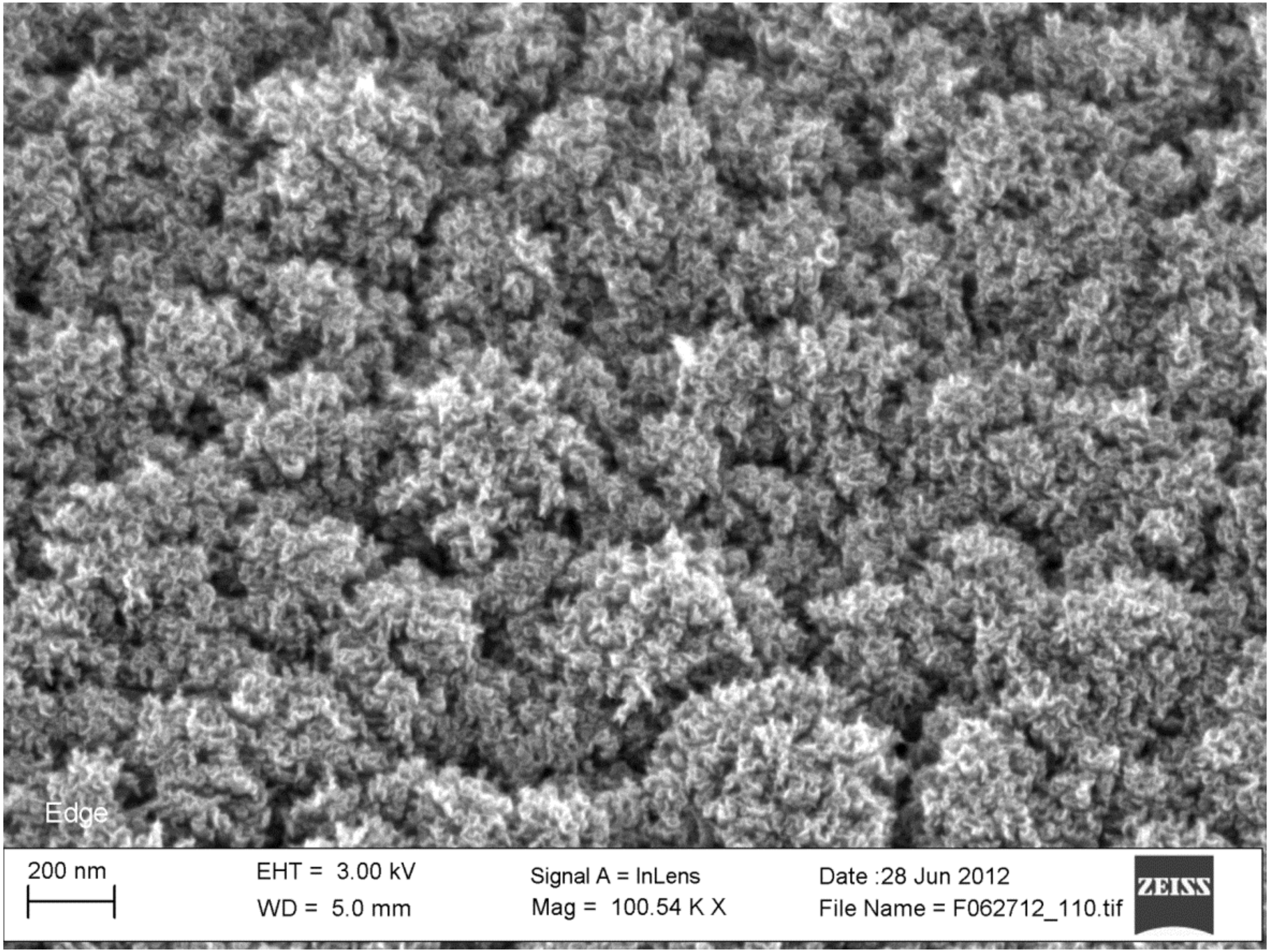
Oak Ridge National Laboratory

NETL/DOE Field Work Proposal #FEAA132

NETL/DOE Project Manager: Sai Gollakota

2018 NETL CO_2 Capture Technology Project Review Meeting

ORNL is managed by UT-Battelle
for the US Department of Energy


Edge
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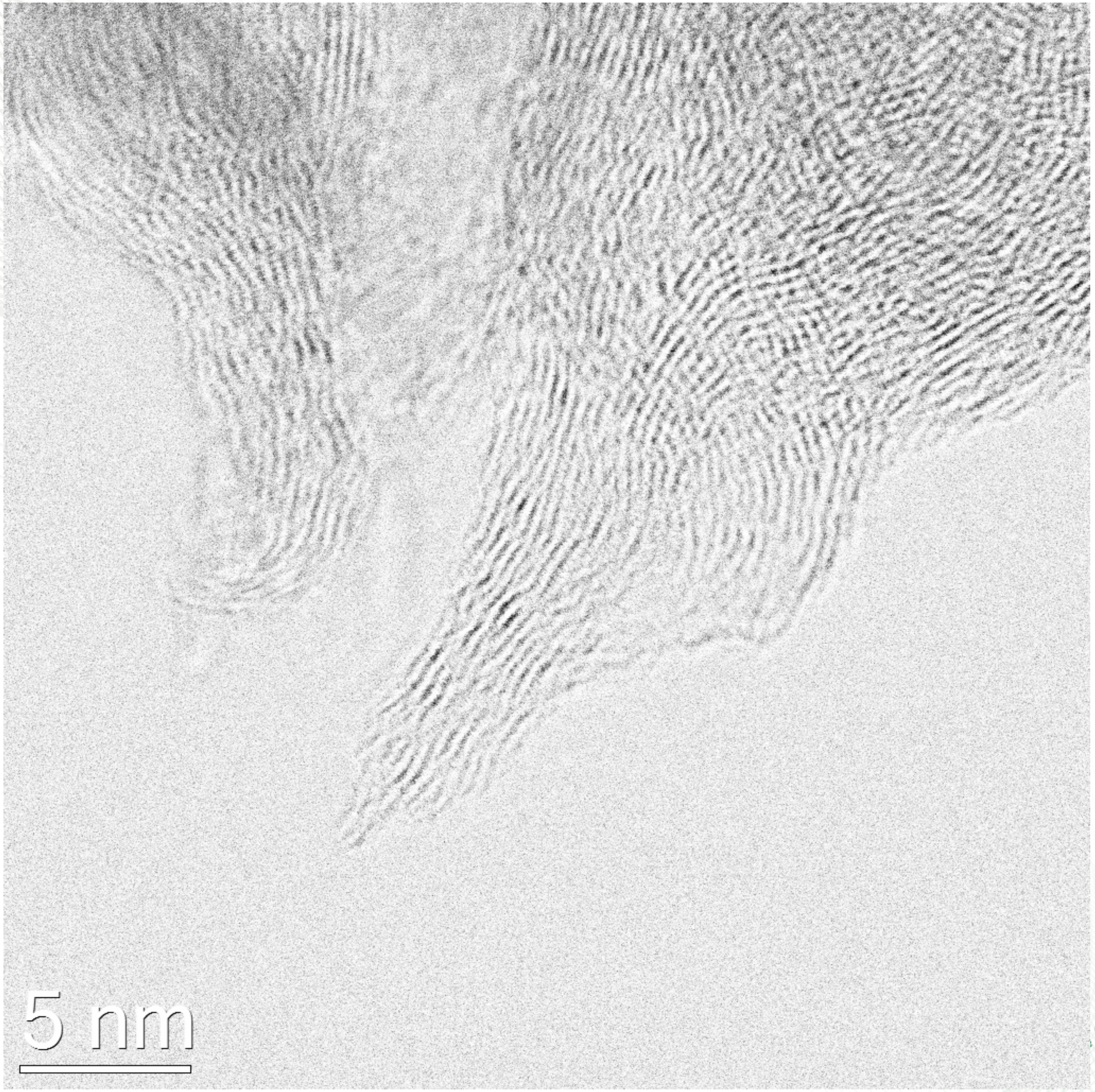
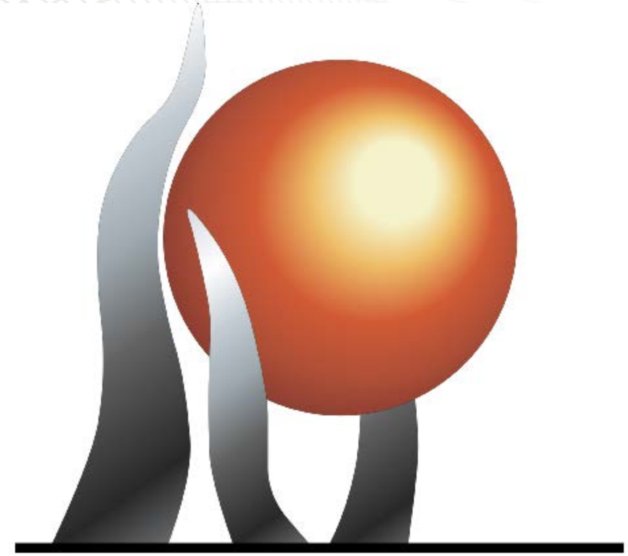
EHT = 3.00 kV
WD = 5.0 mm
Signal A = InLens
Mag = 100.54 K X
Date :28 Jun 2012
File Name = F062712_110.tif

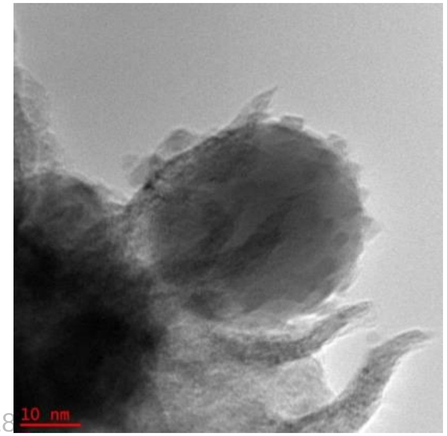
Carbon Nanospikes

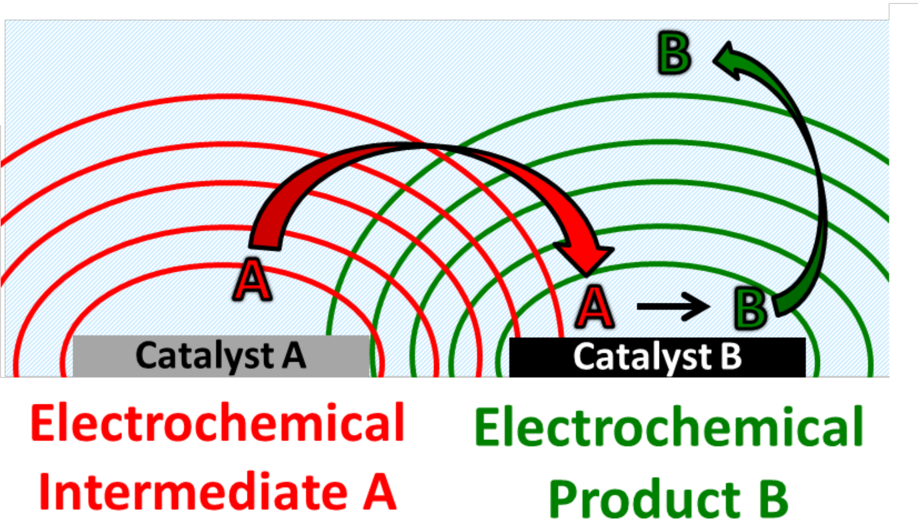


Paired with Nanoparticle Co-Catalyst

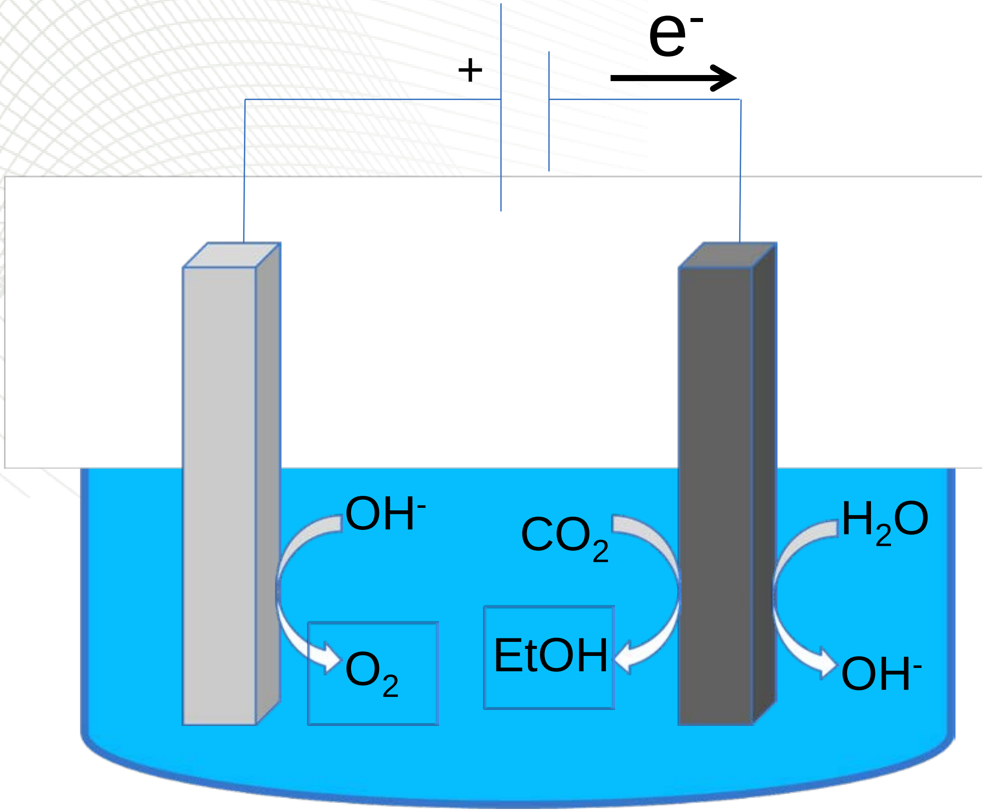
- Approximately 1×10^{14} spikes per m^2
- Tandem catalyst for electrochemical synthesis







Electrosynthesis ~ Charging a Battery



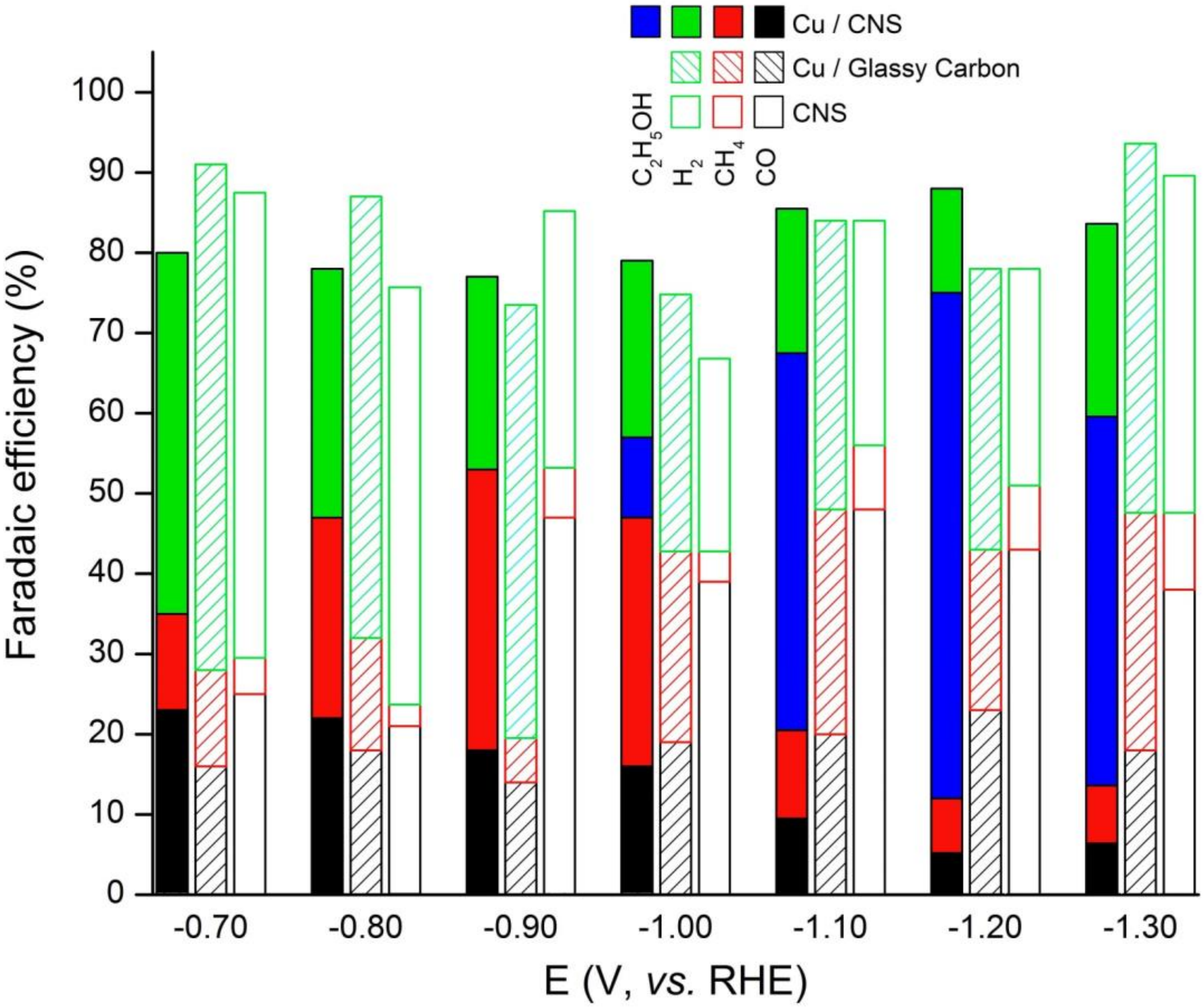
CABB Group GmbH

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

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

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

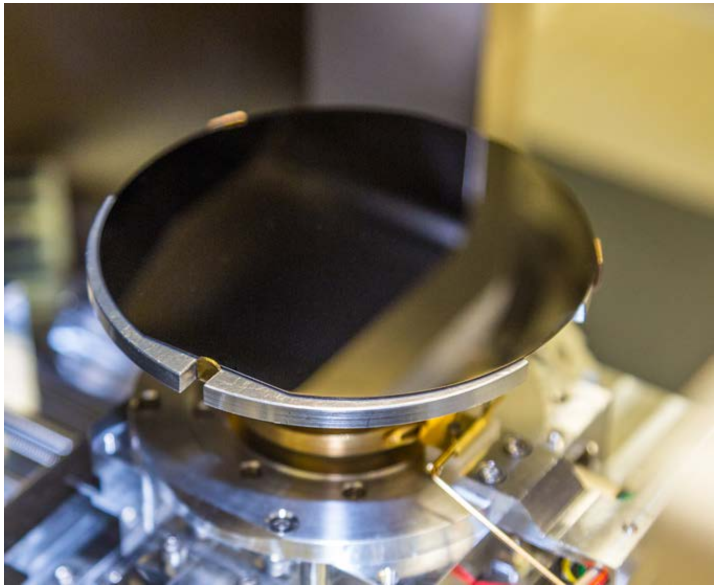
Products from CO_2 Reduction



Song, Y., et al, *High-Selectivity Electrochemical Conversion of CO_2 to Ethanol using a Copper Nanoparticle/N-Doped Graphene Electrode*. ChemistrySelect, 2016. **1**(19): p. 6055-6061.

Fossil Energy FWP: FEAA132

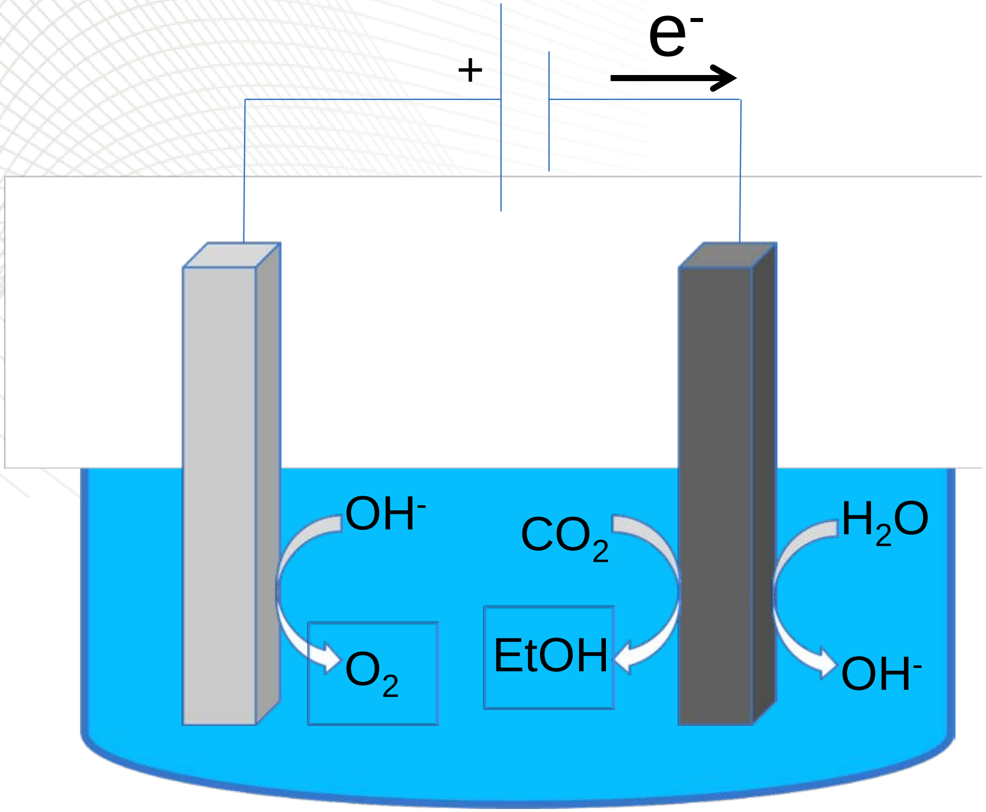
- Budget $200k
- Timeline: 1 year
- Objectives
  - Raise the current density
    - Alternative electrode structure, non-planar configurations
  - Evaluate and optimize operation within a fossil fuel combustion flue gas
    - Will demonstrate technical feasibility, if possible
    - Will investigate poisoning mechanisms, if they exist



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
  - Originally around 2 mA/cm^2
- Strategy
  - Adapt catalyst to better electrolytes, different cell and current-collector designs in order to maximize mass transport
    - Attempt implementation of gas-phase mass transport
    - CO_2 solubility
    - Wetting of the catalyst surface
    - Increased geometric surface are using 3D electrodes
    - Temperature and pressure

Current Density and Mass Transport



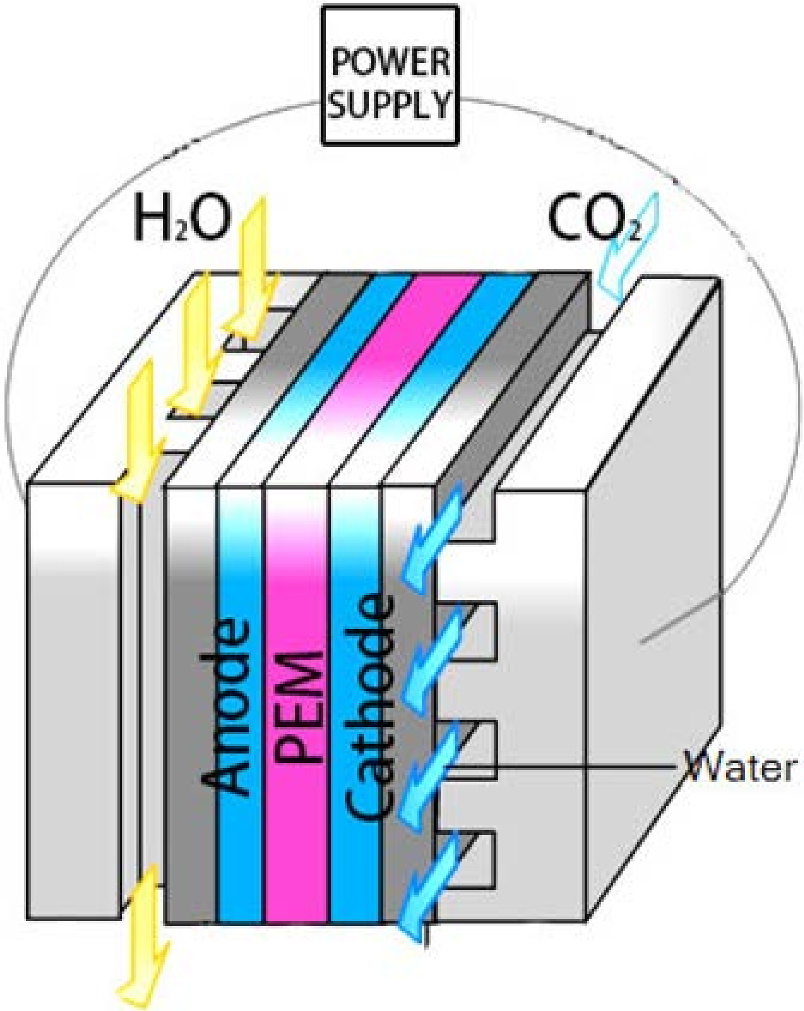
- Mass transport:
  - How quickly reagents can be brought to, and products carried away from, the catalyst surface
  - Is fundamental limitation in electrochemistry
  - Controlled by electrolyte and cell design
  - Influenced by temperature, pressure, concentration

- 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

Vapor Phase Operation

Vapor or gas phase operation is a significant pathway towards increased current density

At start of this project we were not sure that our mechanism was compatible



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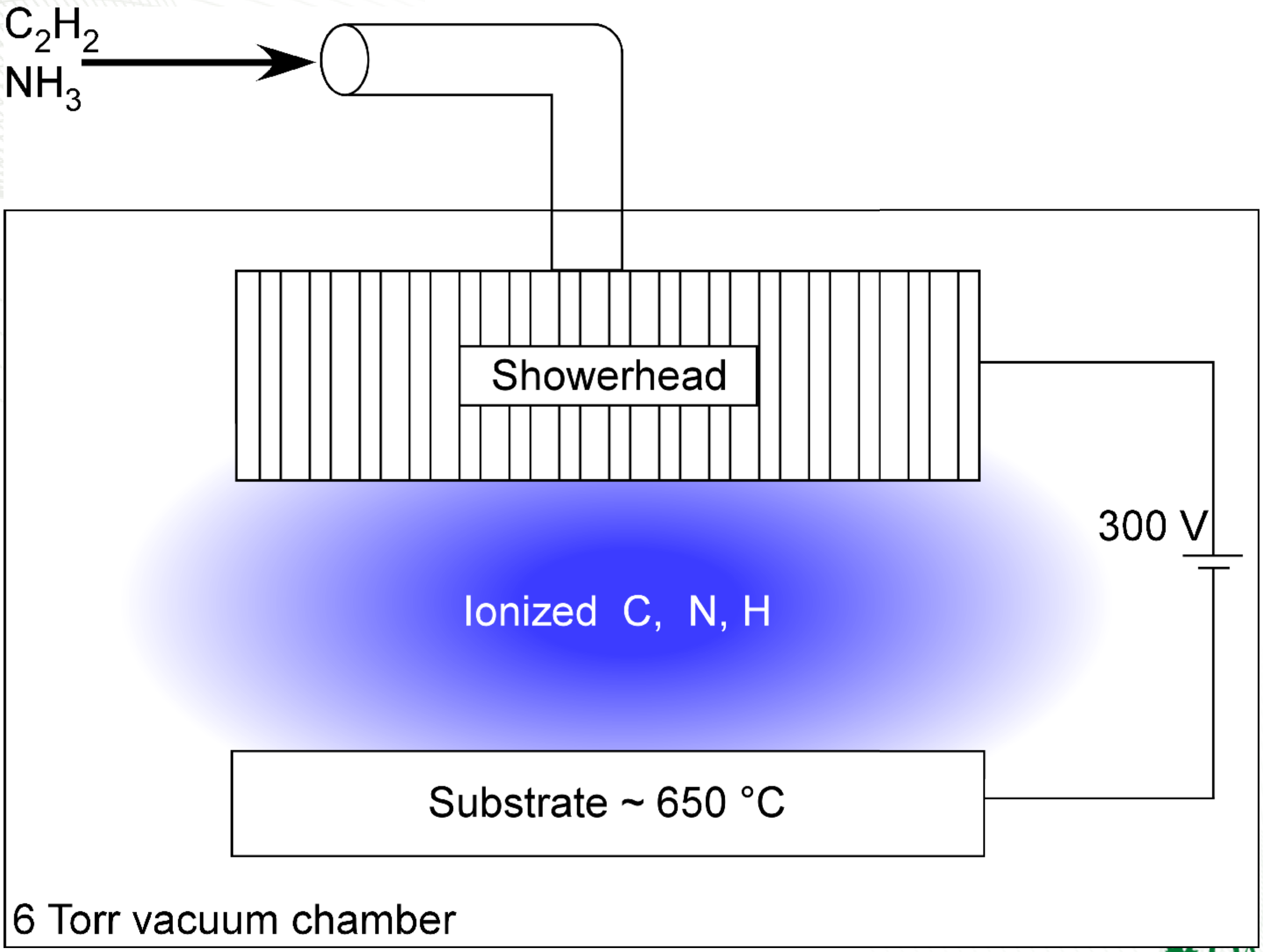
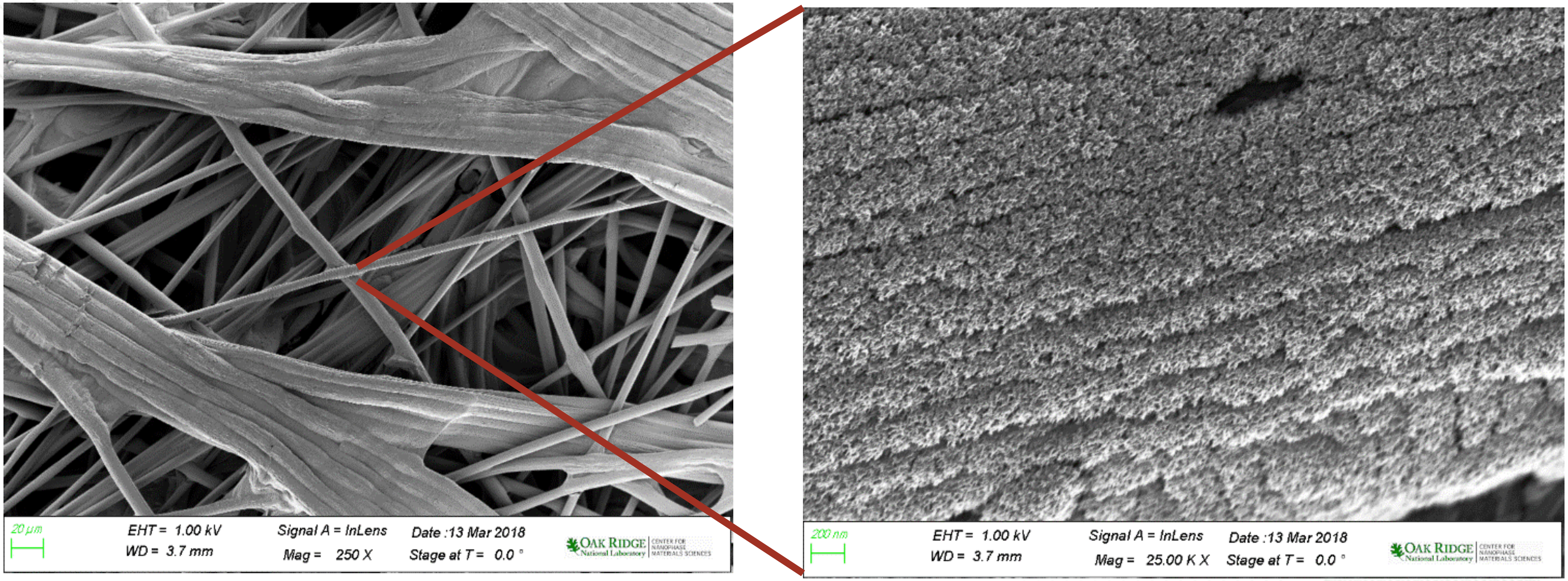
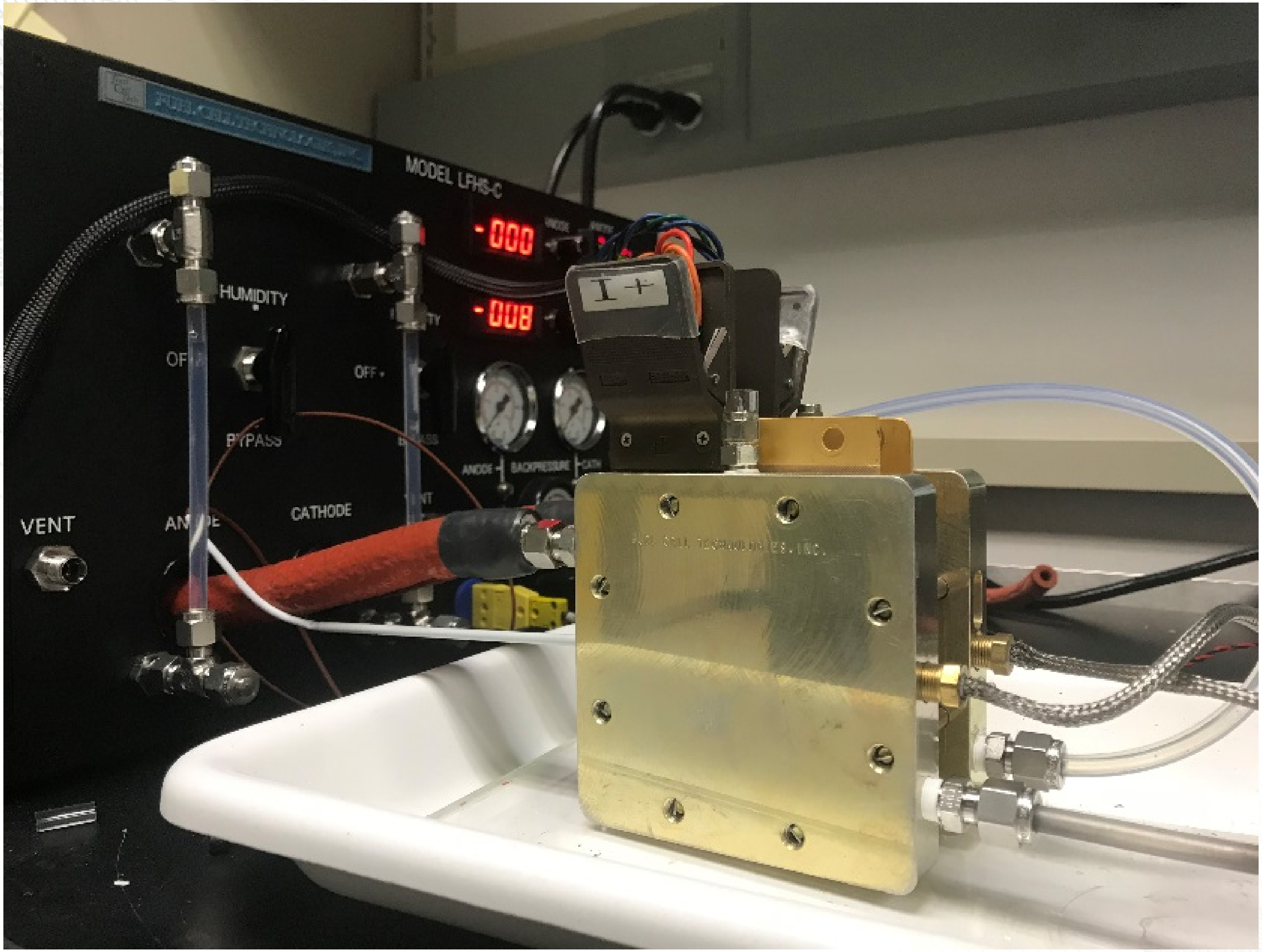
Plasma-Enhanced Chemical Vapor Deposition (PECVD)



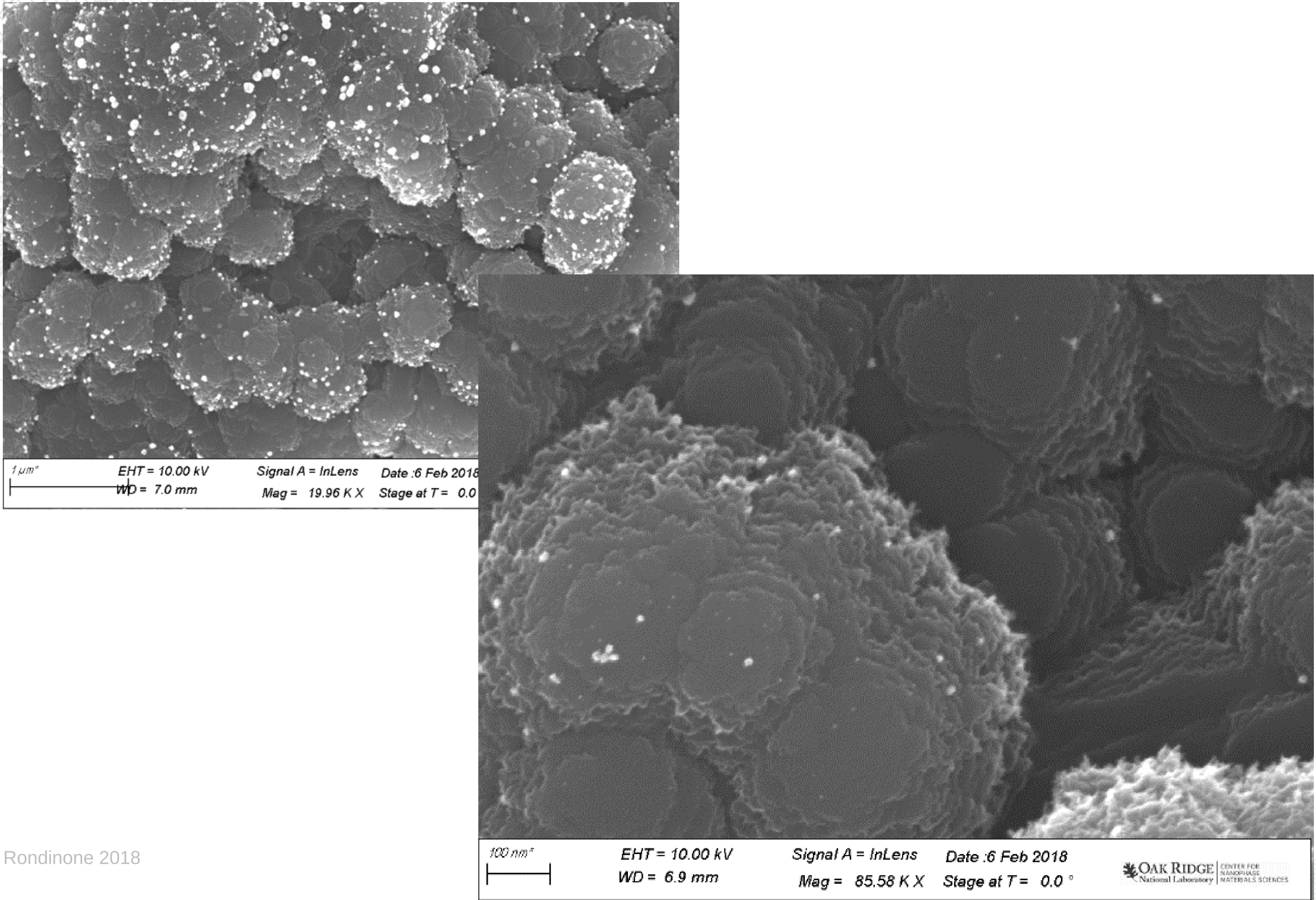
Gaseous Diffusion Layer

- Stability on graphite means that carbon cloth can also be used
- Forms a gas diffusion electrode (GDE)
- Coating depth is limited due to plasma deposition process
- Appears to coat several microns into the carbon cloth, which appears to be sufficient

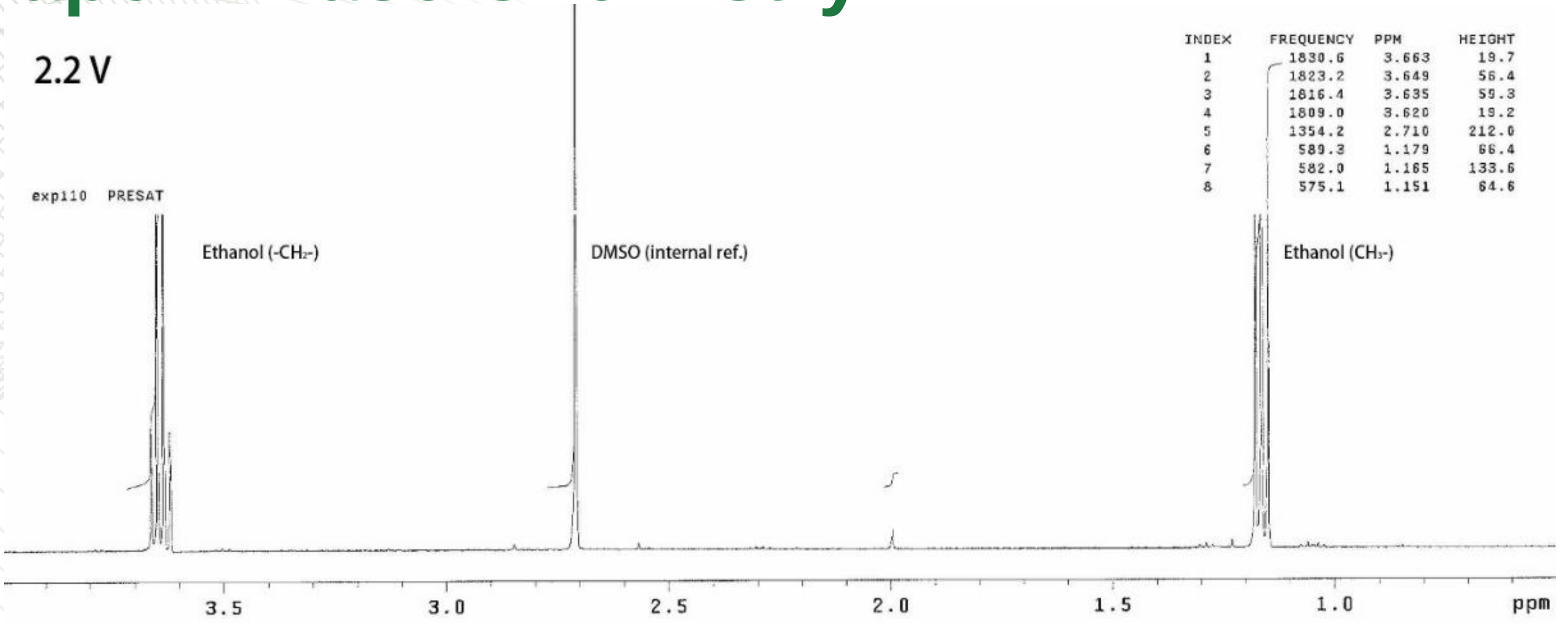



MODEL LFHS-C
-000
-008
HUMIDITY
OFF
BYPASS
VENT
ANODE
CATHODE
BACKPRESSURE
I+

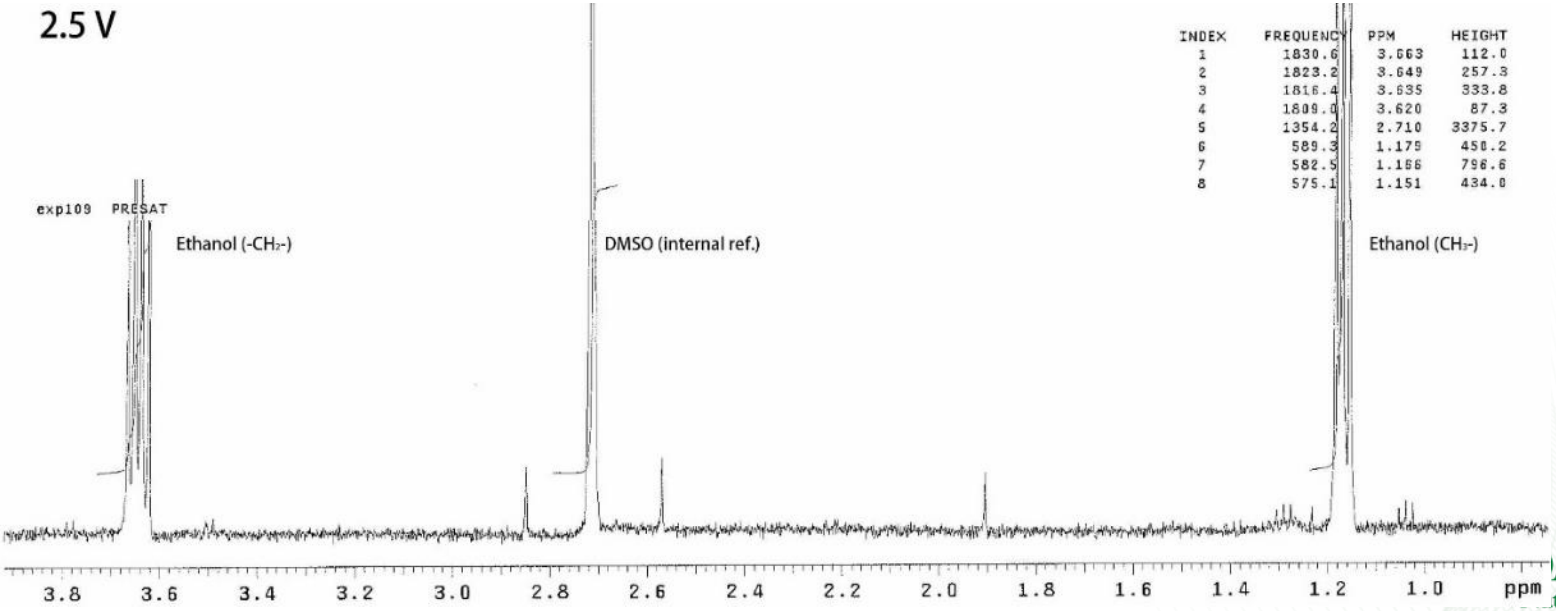
Gas Diffusion Durability



Vapor Phase Chemistry



```
INDEX   FREQUENCY   PPM     HEIGHT
  1      1830.6    3.663     19.7
  2      1823.2    3.649     56.4
  3      1816.4    3.635     59.3
  4      1809.0    3.620     19.2
  5      1354.2    2.710    212.0
  6       589.3    1.179     66.4
  7       582.0    1.165    133.6
  8       575.1    1.151     64.6
```



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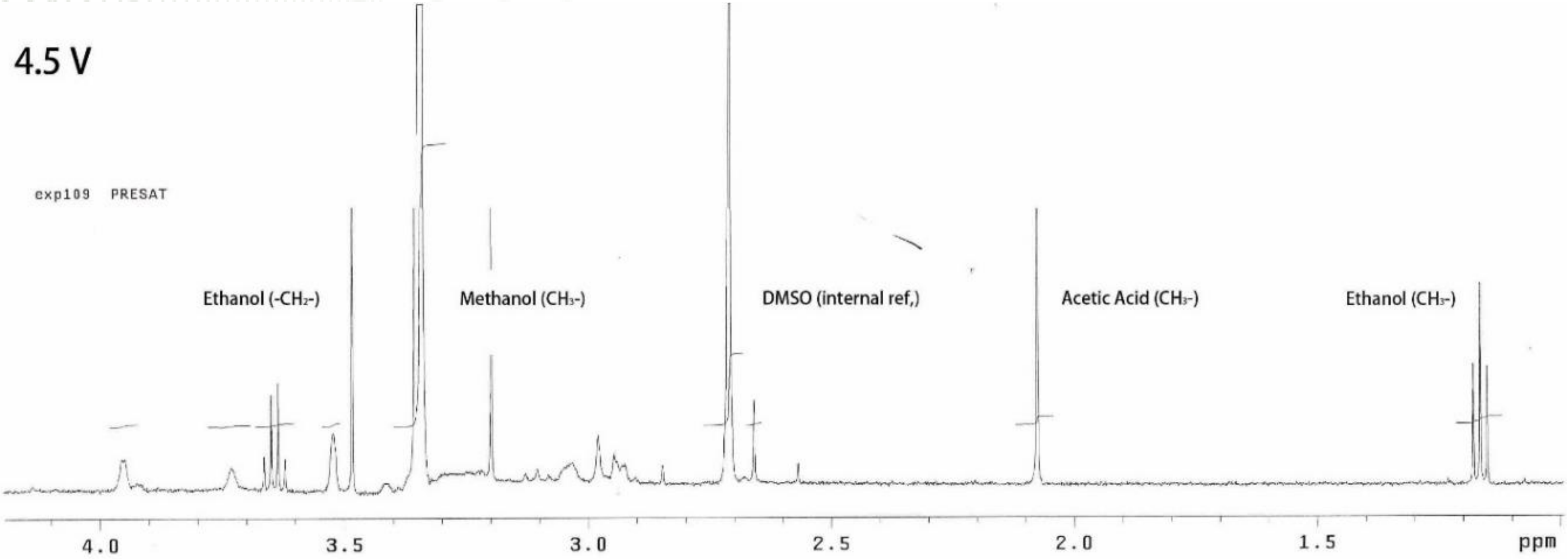
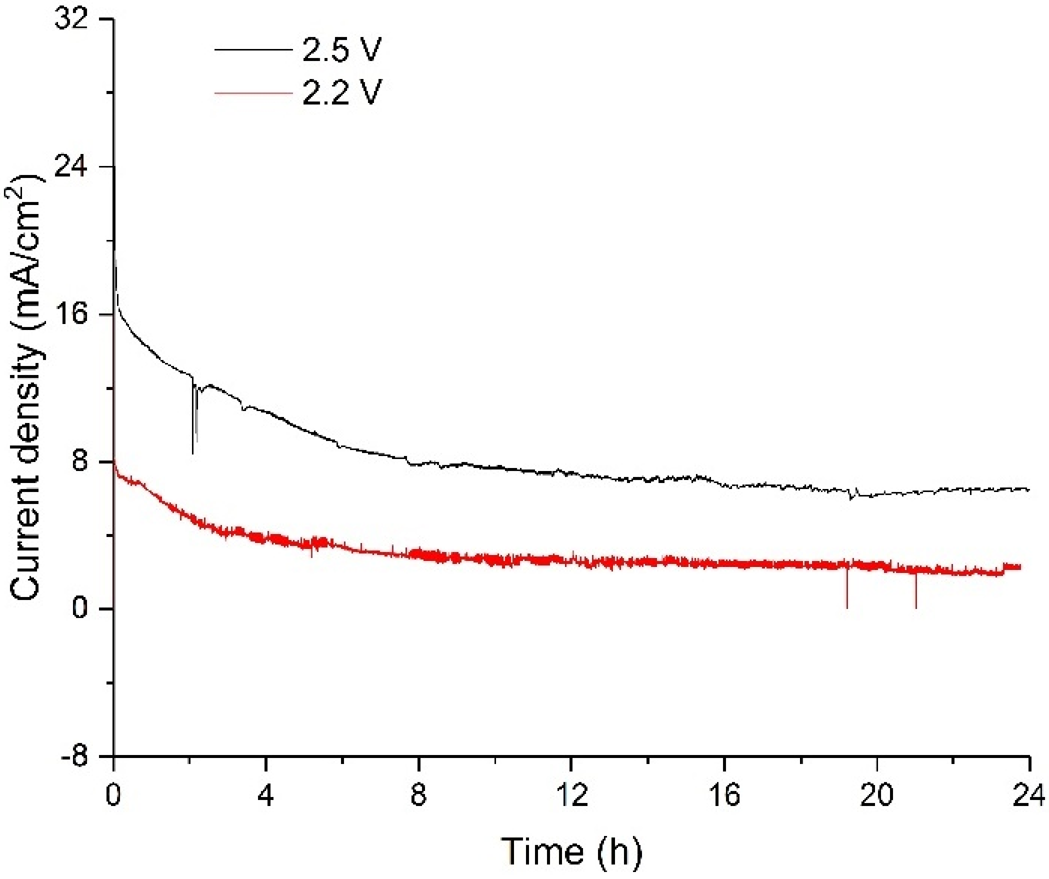
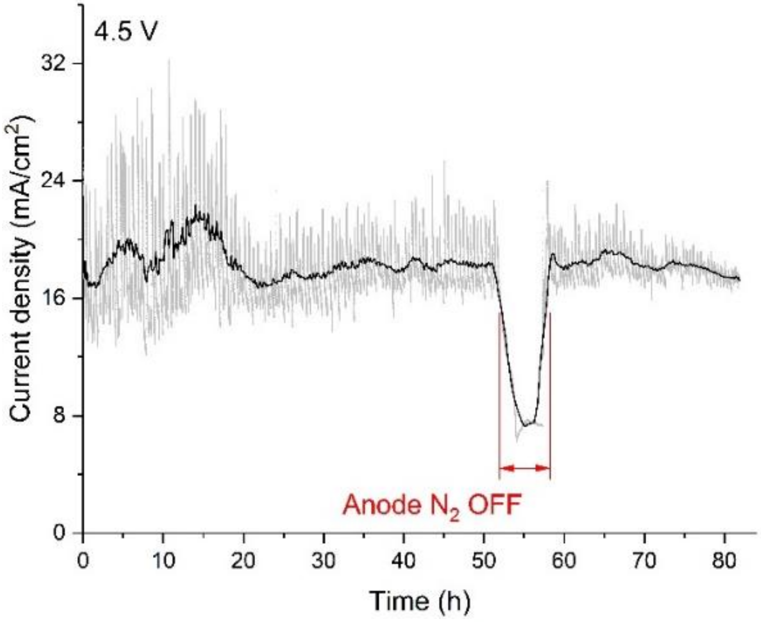
  2      1823.2    3.649    257.3
  3      1816.4    3.635    333.8
  4      1809.0    3.620     87.3
  5      1354.2    2.710   3375.7
  6       589.3    1.179    450.2
  7       582.5    1.166    796.6
  8       575.1    1.151    434.0
```

4.5 V


exp109 PRESAT
Ethanol (-CH₂-)
Methanol (CH₃-)
DMSO (internal ref,)
Acetic Acid (CH₃-)
Ethanol (CH₃-)
4.0
3.5
3.0
2.5
2.0
1.5
ppm

Vapor Phase Stability with Time





What this means for Current Density

- Current density is higher than in water electrolyte, but still too low for practical application
- There are a large number of variables that must be optimized and we have not yet had the time to do so
  - Temperature of cell (1)
  - Humidity and flow rate for each compartment (4)
  - Backpressure for each compartment (2)
    - 7 variables just for physical conditions
- Hydration control is a major issue that is largely unresolved
  - Sargent recently published vapor phase cell with KOH electrolyte between Teflon-soaked GDE and membrane

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

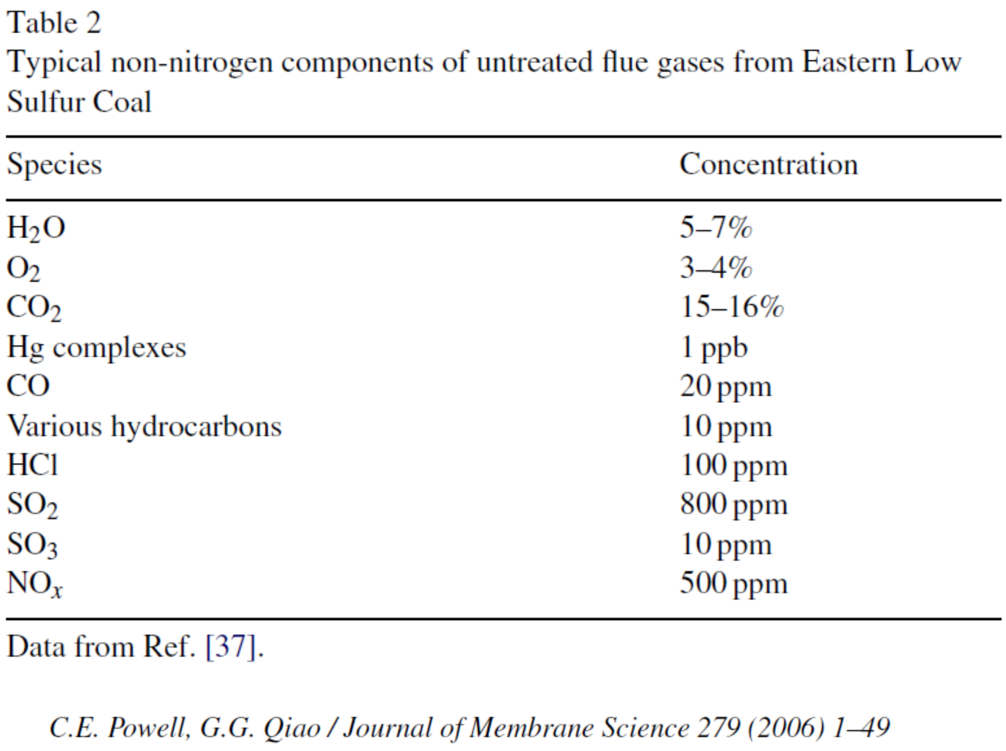


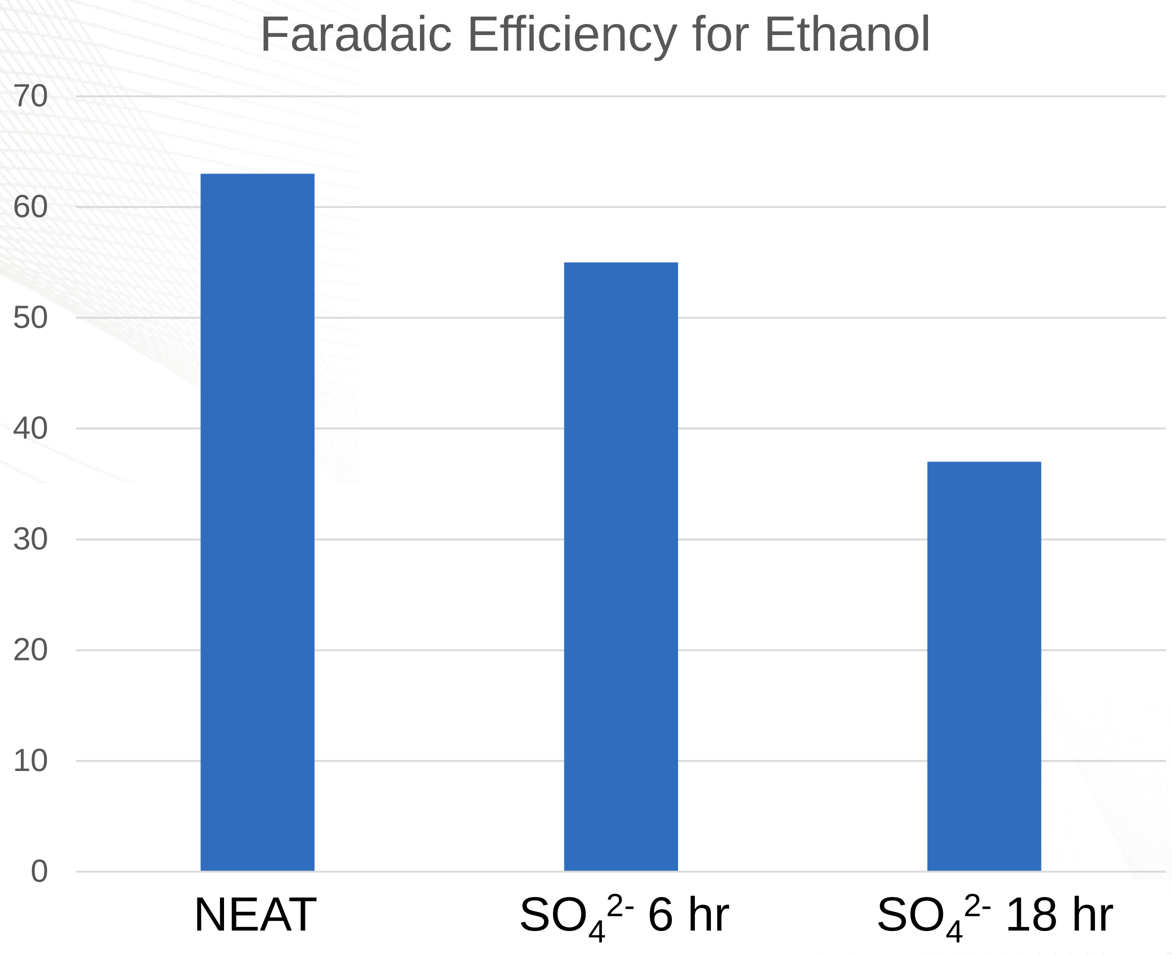
Table 2
Typical non-nitrogen components of untreated flue gases from Eastern Low Sulfur Coal

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

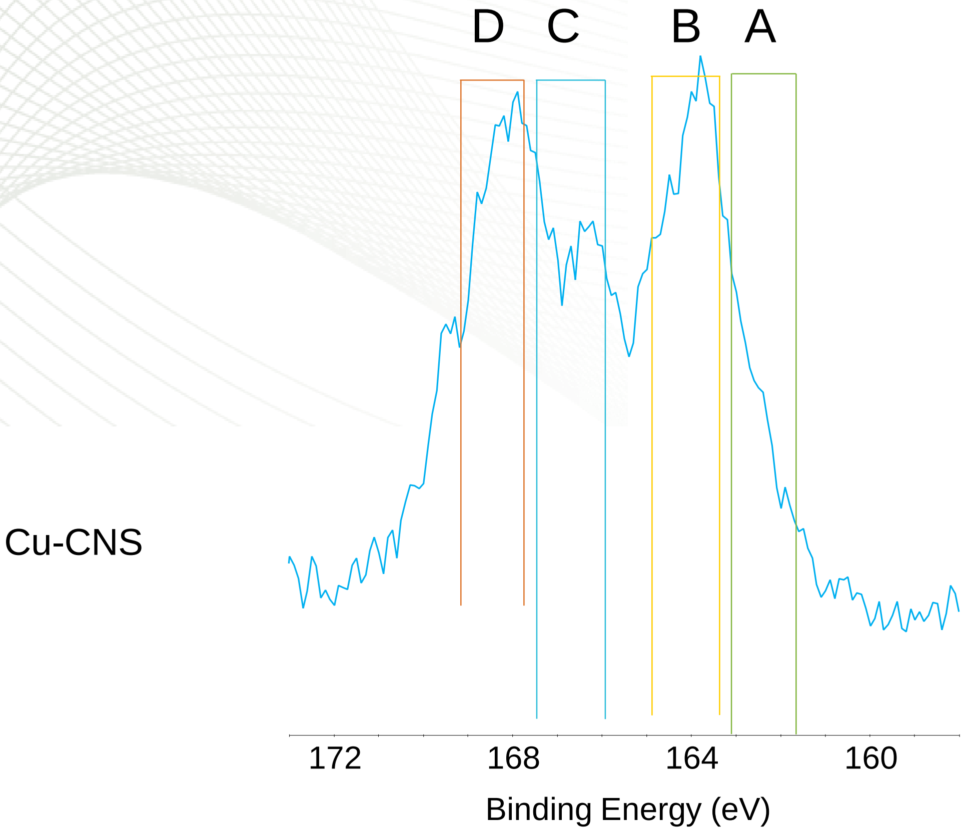
Data from Ref. [37].

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

Effect of Sulfur



XPS Analysis of S-Contaminated Electrode



(A) B.E. = 162.0 eV
- metal sulfide, likely Cu-sulfide
- could be elemental S

(B) B.E. = 163.4 to 163.6 eV
- metal sulfide, likely Cu-sulfide

(C) B.E. = 165.8 eV to 166.4 eV
- SO_3^- or SO_2^-

(D) B.E. = 168.0 eV
- sulfate, SO_4^-

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National Laboratory

Sulfate Mechanism

$$SO_4^{2-} + 4H_2O + 8e^- \rightarrow 8OH^- + S^{2-}$$

$$Cu + S^{2-} \rightarrow CuS + 2e^-$$

- Copper sulfide or mixtures of sulfate/sulfide are found on the nanospike surface
- Reaction is inhibited
- Uptake of sulfur is slow and could be mitigated by periodic refreshing of the nanoparticles

NO_x Contamination Tolerance

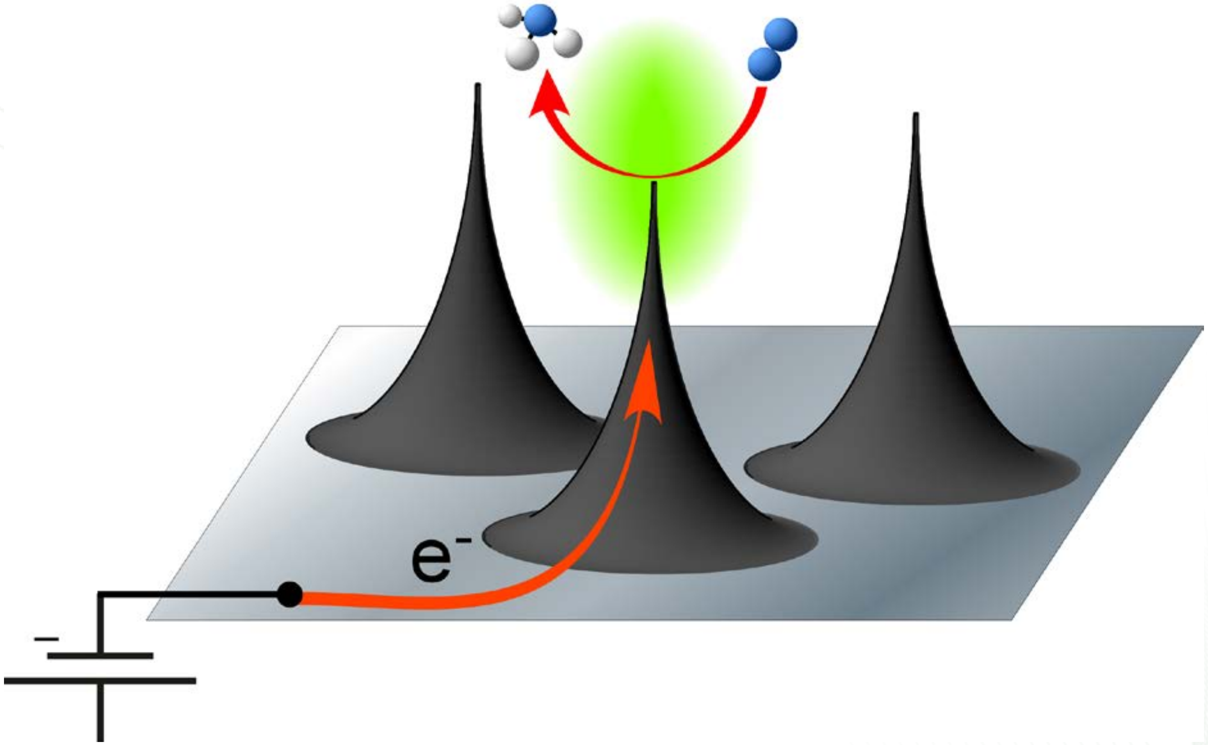
- Nitrogen in all forms appears to poison the reaction
- NO gas is a complete inhibitor
- NO_3^- is a complete inhibitor
- N_2 also fouls the reaction
  - Exposure of the cell to air during the reaction does not appear to be a problem due to low N_2 solubility
  - Introducing N_2 to the electrolyte with CO_2 fouls the reaction – it proceeds but not to ethanol
  - There are exceptions to this

Recently Discovered N_2 Reactivity

Can we use electricity instead of T and P?

$$3H_2O + 2N_2 \xrightarrow{e^-} 3/2O_2 + 2NH_3$$

A high electric field can destabilize N_2



Song, Y. et al, *A physical catalyst for the electrolysis of nitrogen to ammonia. Science Advances, 2018.* ***4(4).***

Expect that Most Forms of N go to NH_3

$NO \rightarrow NH_3$

$NO_2 \rightarrow NH_3$

N_2O ?

$N_2 \rightarrow NH_3$

$NO_3^{2-} \rightarrow NH_3$

NH_3 in bicarbonate likely exists as NH_4^+

Ammonium passivates Cu electrodes

A. Lalitha et al. / Electrochimica Acta 51 (2005) 47–55

Summary

- Have demonstrated that vapor phase operation is possible, but current density is still low
  - Can fabricate gas diffusion electrode using our nanospike catalyst
  - Electrode is stable
  - Reaction mechanism intact
  - Unresolved issues with hydration and separator membrane
- Have investigated the impact of coal combustion contaminants, primarily S and N species
  - Poisoning understood to occur at Cu nanoparticle
  - Sulfur somewhat tolerated
  - Nitrogen generally not tolerated
  - Mitigation possible through in-situ regeneration of Cu particles
  - All copper based catalysts could be subject to this poisoning effect

Acknowledgement

Acknowledgment: This material is based upon work supported by the Department of Energy under Field Work Proposal: #FEAA132.