Electrochemical Pathway for Sustainable Manufacturing (EPSuM)

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Webinar
National Academies' Government-University-Industry Research Roundtable (GUIRR) & University-Industry Demonstration Partnership (UIDP)
October 22nd, 2014

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Agenda

- Electrochemical Science and Technology (Gerri Botte, Ohio University)
  - Overview and applications
  - NIST/EPSuM program
- Case Studies
  - Advanced Conversion (Botte)
  - Advanced Materials (graphene synthesis, Botte)
  - Fertilizer Production (Botte)
  - Water Remediation (Kent Shields, E3 Clean Technologies)
  - Emissions Control (Shields)
- EPSuM Roadmap Process (Gary Walzer, PolymerOhio)

Electrochemical Science and Technology

Electrochemistry and Electrochemical Engineering

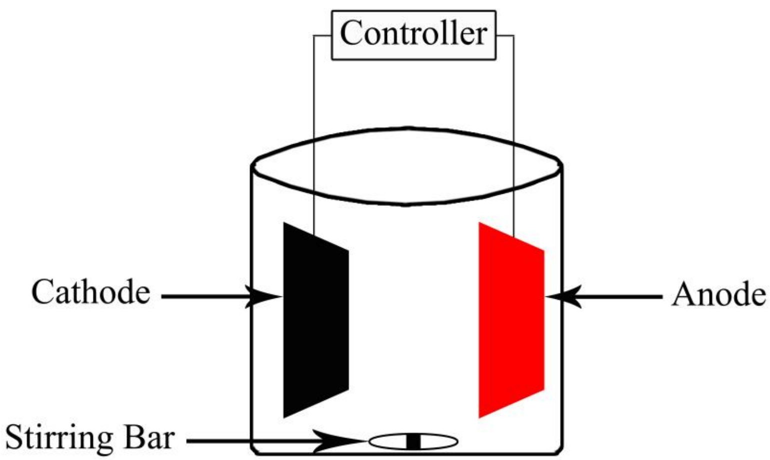
- Electrochemistry
  - Branch of chemistry concerned with the interrelation of electrical and chemical effects
- Deals with
  - The study of chemical changes caused by the passage of a current
  - The production of electrical energy by chemical reactions

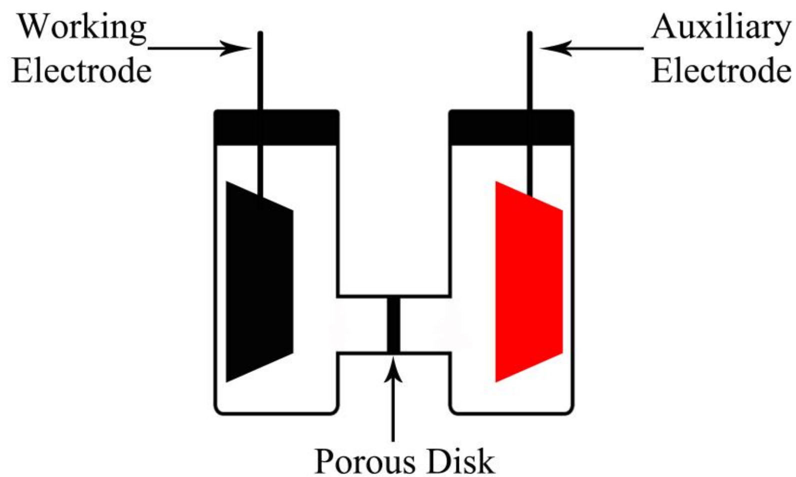
- Electrochemical Engineering
  - The use of chemical engineering fundamental principles for the study and analysis of electrochemical systems
- Deals with
  - Rational design of electrochemical processes and devices
  - Implements: thermodynamics, transport phenomena, kinetics, mathematical modeling

Electrochemical Processes

Fundamentals

- The Electrochemical Cell
  - Anode (Oxidation) $A \longrightarrow A^{+} + e^{-}$
  - Cathode (Reduction) $B + e^{-} \longrightarrow B^{-}$
  - Electrolyte
  - Divided or Undivided Reactor



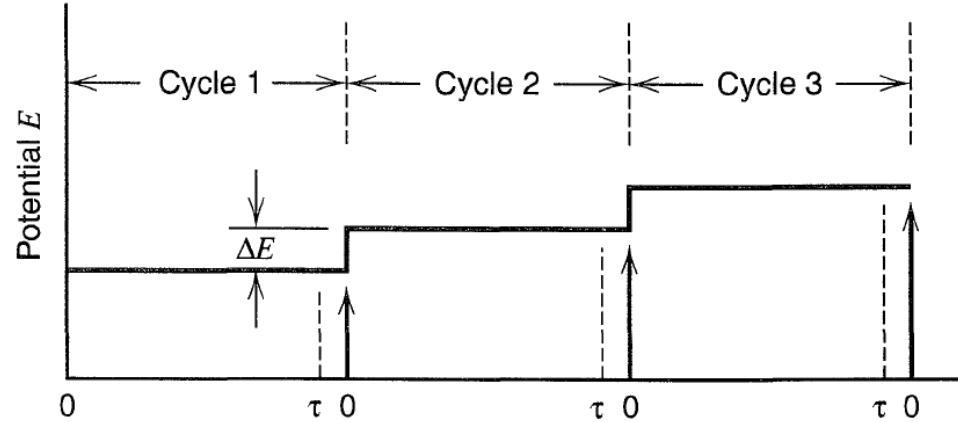


G.G. Botte, **D.A. Daramola** and M. Muthuvel, In *Comprehensive Organic Synthesis II*, G.A., Molander; P. Knochel, Eds., (2014)

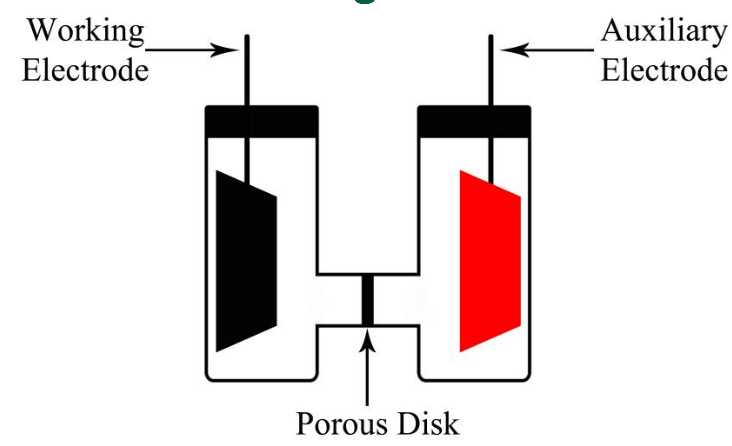
Electrochemical Processes

Advantages when compared to chemical processes

- Simple to control
- Minimization of separation and operation costs
- Operation at mild temperatures and pressure
- Higher product selectivity and purity
- Lower number of reaction steps
- Inexpensive starting materials
- Less polluting chemicals or byproduct
- Lower consumption of energy (easy integration with renewable energy)



Voltage Control



Product Separation

Electrochemical Processes

Criticisms for their adoption

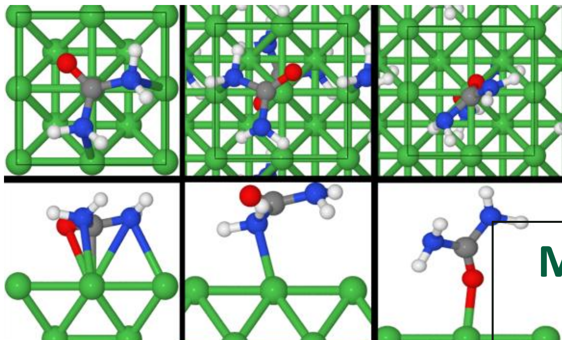
- Lag in the education in electrochemistry and electrochemical engineering
- Lack of suitable resources for cell construction
- Capital cost involved in electrodes and cells

Significant progress occur in the past 40 years

- Materials science and nanotechnology
- In-situ spectroscopy and microscopy
- Multiscale modeling

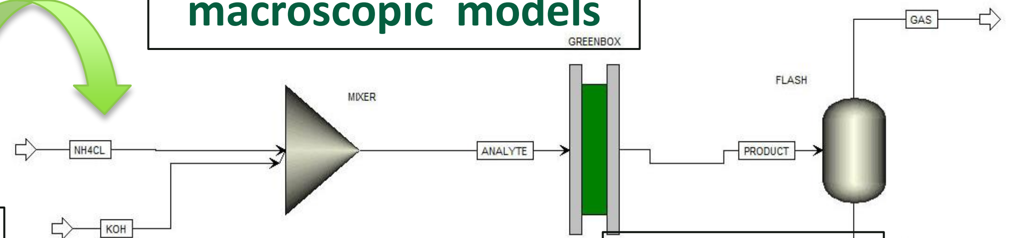
Examples of Advances in Electrochemical Science and Technology

- Multi-scale Modeling



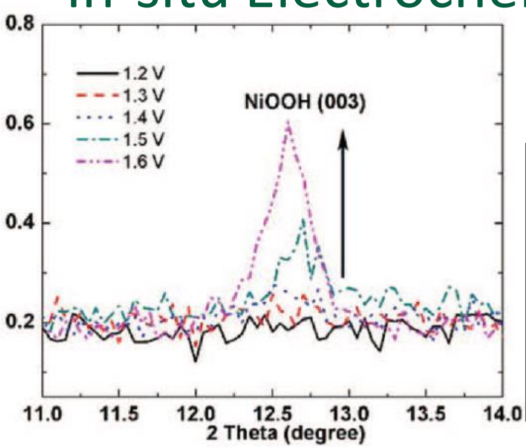
Molecular scale

Microscopic and macroscopic models

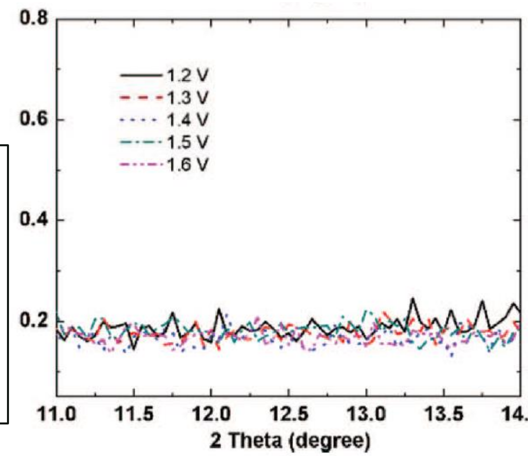


Unit Operations

- In-situ Electrochemistry



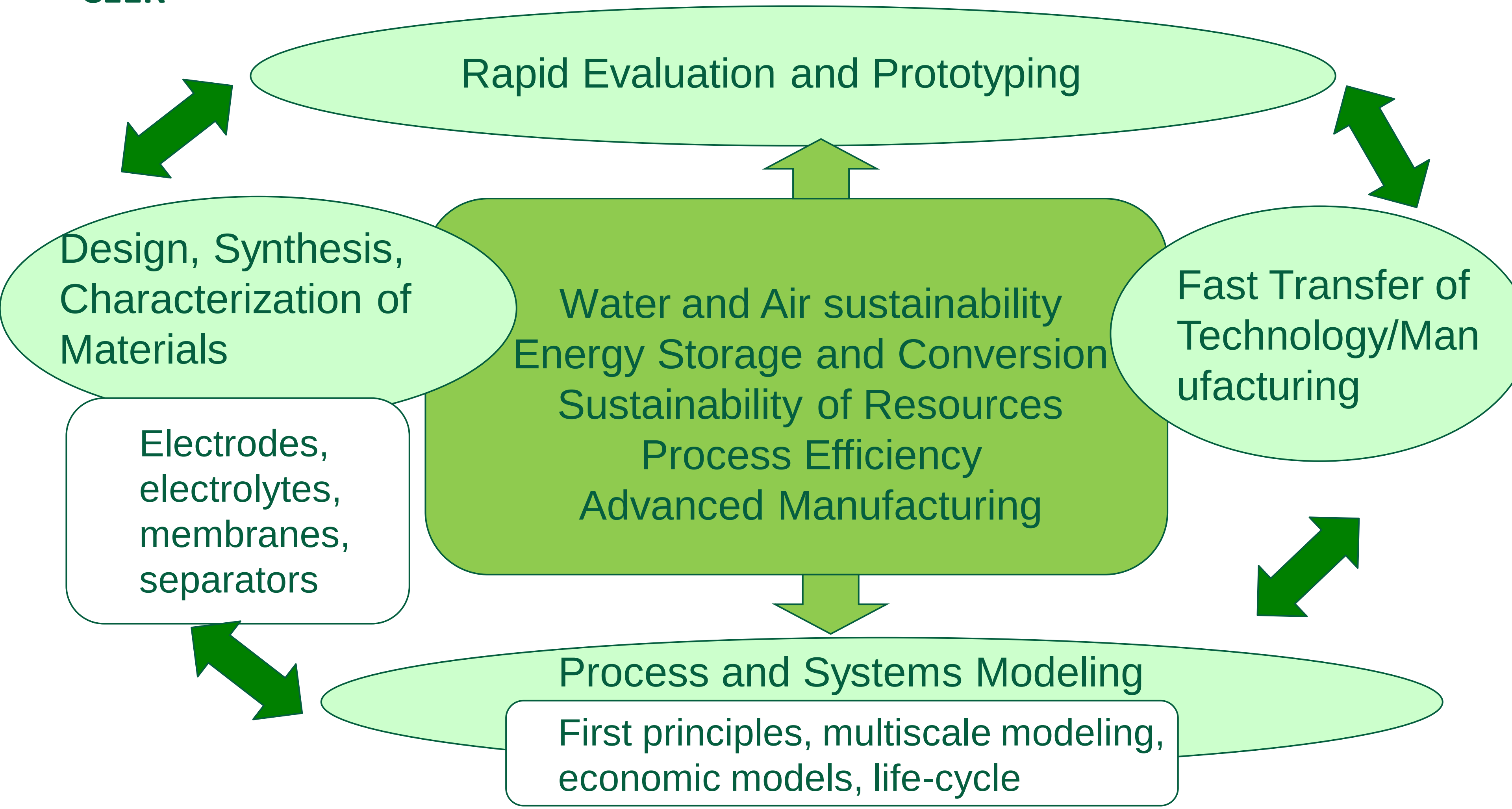
X-ray Spectra in the presence of 5M KOH



X-ray Spectra in the presence of 5M KOH and 1M Urea

Current Approach to Electrochemical Science and Technology

CEER



Planned Consortium: Electrochemical Pathway for Sustainable Manufacture (EPSuM)

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

CEProTECH

ECS

OH!Polymer
PolymerOhio, Inc.

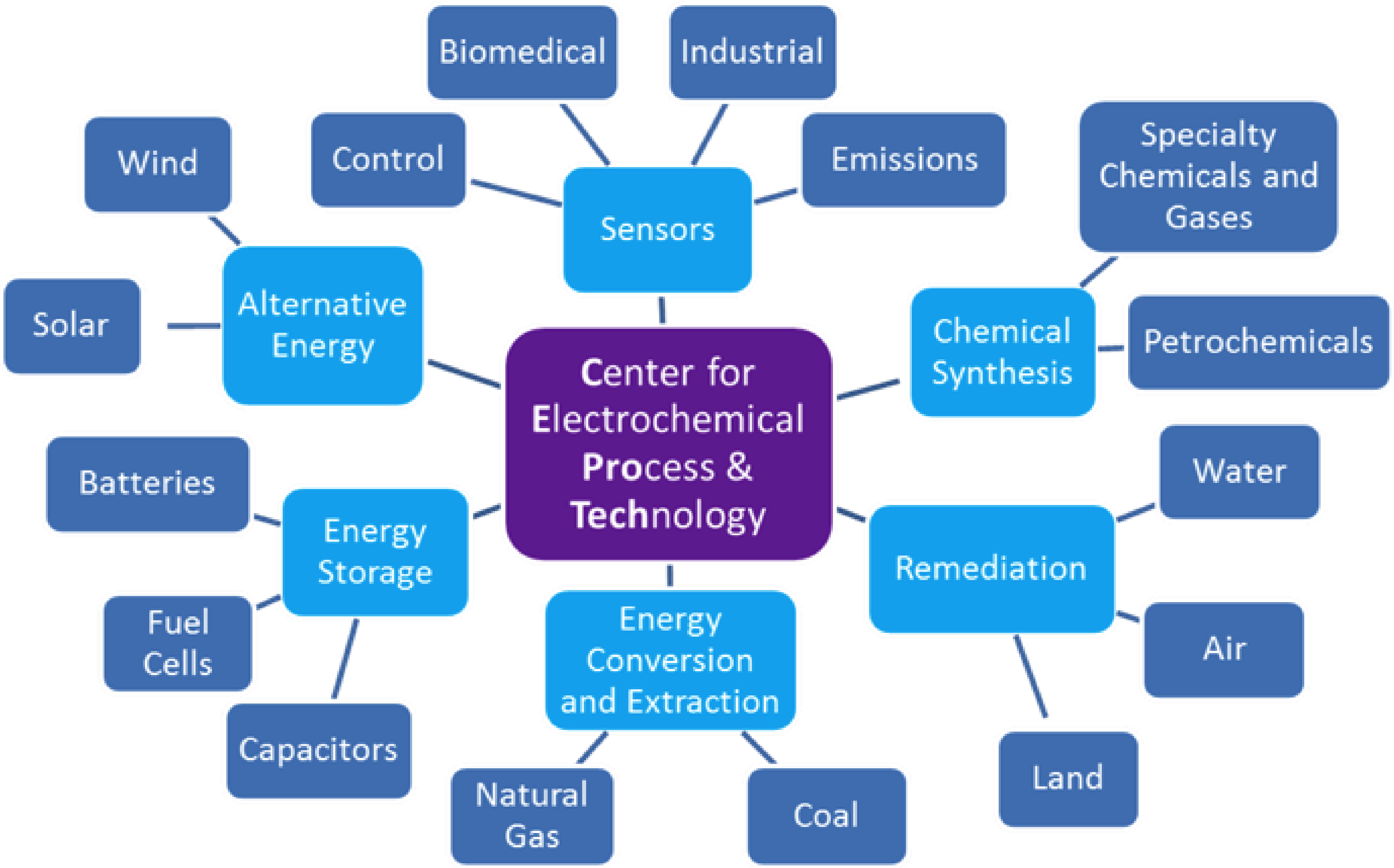
EPSuM Consortium

Phase I, planning grant (roadmap)

- The US National Institute of Standards and Technology (NIST) awards grant to Ohio University CEProTECH in June, 2014 (http://www.nist.gov/amo/70nanb14h052.cfm)
- Goal of the Grant:
  - Develop a technology roadmap to support, sustain, and enhance U.S. manufacturing capacity in the chemical industry and allied sectors
  - EPSuM will implement electrochemical science and technology to to address major technical barriers in the manufacturing of chemicals and materials

Applications, Industrial Adoption, and Case Studies

Applications

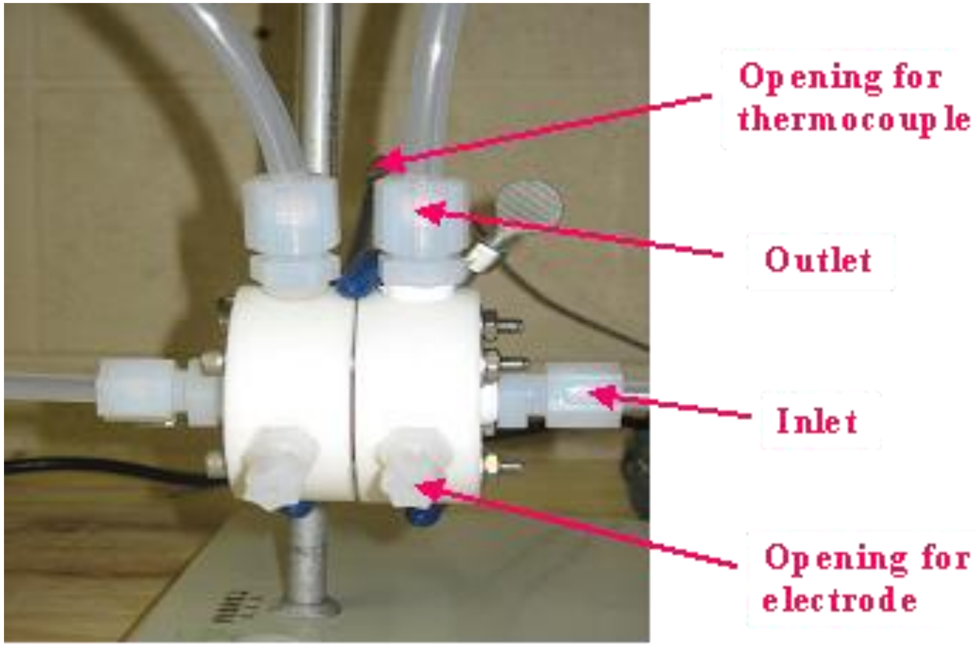


Electrolysis of Solid Fuels

- Highly efficient conversion of coal and other solid fuels to hydrogen, fuels, and chemicals with carbon dioxide capturing

What is Coal Electrolysis?

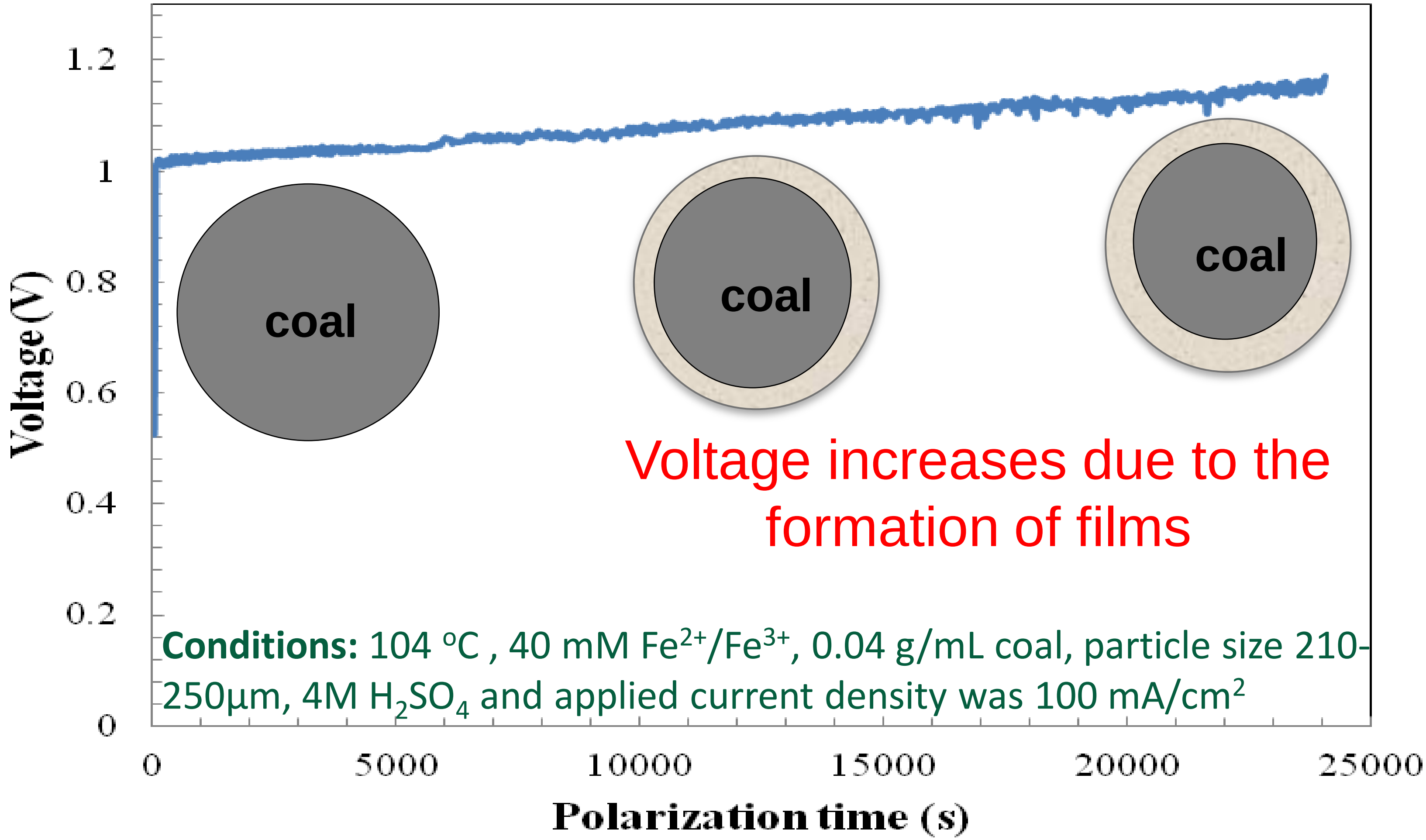
- Efficient process for the conversion of coal to hydrogen, liquid fuels, and high value products with carbon capturing



Continuous Coal Electrolytic Cell*

* X. Jin, G. G. Botte, J. Power Sources, 171 (2007) 826-834

Cell Voltage Profile



Conditions: 104 °C , 40 mM Fe^{2+}/Fe^{3+}, 0.04 g/mL coal, particle size 210-250µm, 4M H_2SO_4 and applied current density was 100 mA/cm^2

Hypothesized/Proposed Reactions for Coal Electrolysis

Cell Compartment/Reactions	Current Efficiency
Anode	
$2n \sim C + 2H_2O \rightarrow 2n \sim \left(C - OH\right) + 2H^+ + 2e^-$	85-75%
$\left(\frac{1}{2}\right) C + H_2O \rightarrow \left(\frac{1}{2}\right) CO_2 + 2H^+ + 2e^-$	15-25%
Cathode $2H^+ + 2e^- \rightarrow H_2$	100%

Energy Consumption: Comparison with Water Electrolysis at 80 ^oC*

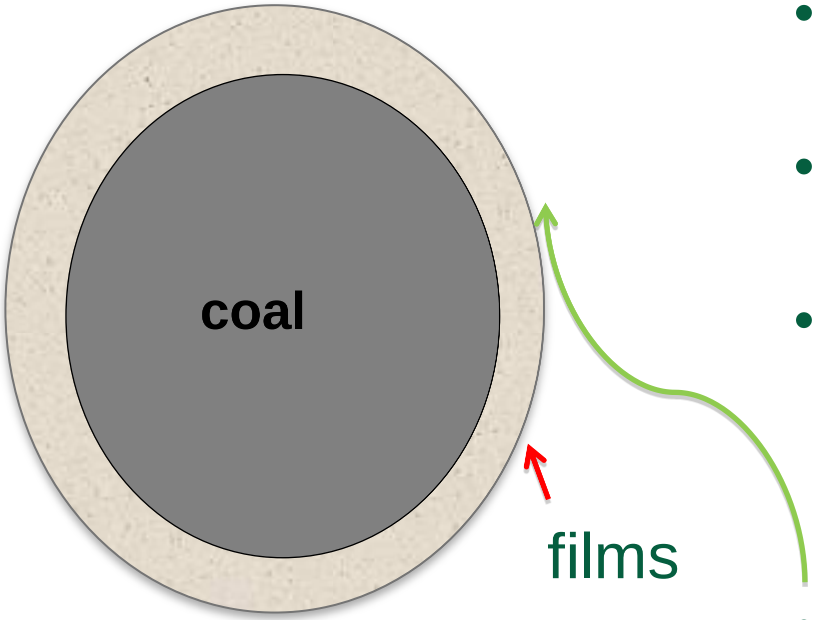
Entry	Result
Faradaic Efficiency Hydrogen Production Faradaic Efficiency Coal to CO_2	98% 12%
Energy consumption (w-h/g H_2) Theoretical: 5.6 w-h/g H_2	22.5
Energy consumption (w-h/g H_2) Theoretical: 33 w-h/g H_2	44

49% lower than water electrolysis

* N. Sathe, G. G. Botte, J. Power Sources, 161 (2006), 513-523

Formation of Films

Proposed mechanism



- Films constituted by COH and iron
- Surface of coal may contain O and H from water
- Surface of coal particles can be oxidized as

$$C + H_2O \rightarrow CHO + H^+ + e^-$$

- Films are rich in H and O

Coal Electrolysis To Fuels and Blends

Extracted oil/fuel after electrolysis

G. G. Botte, Center for Electrochemical Engineering Research, Ohio University

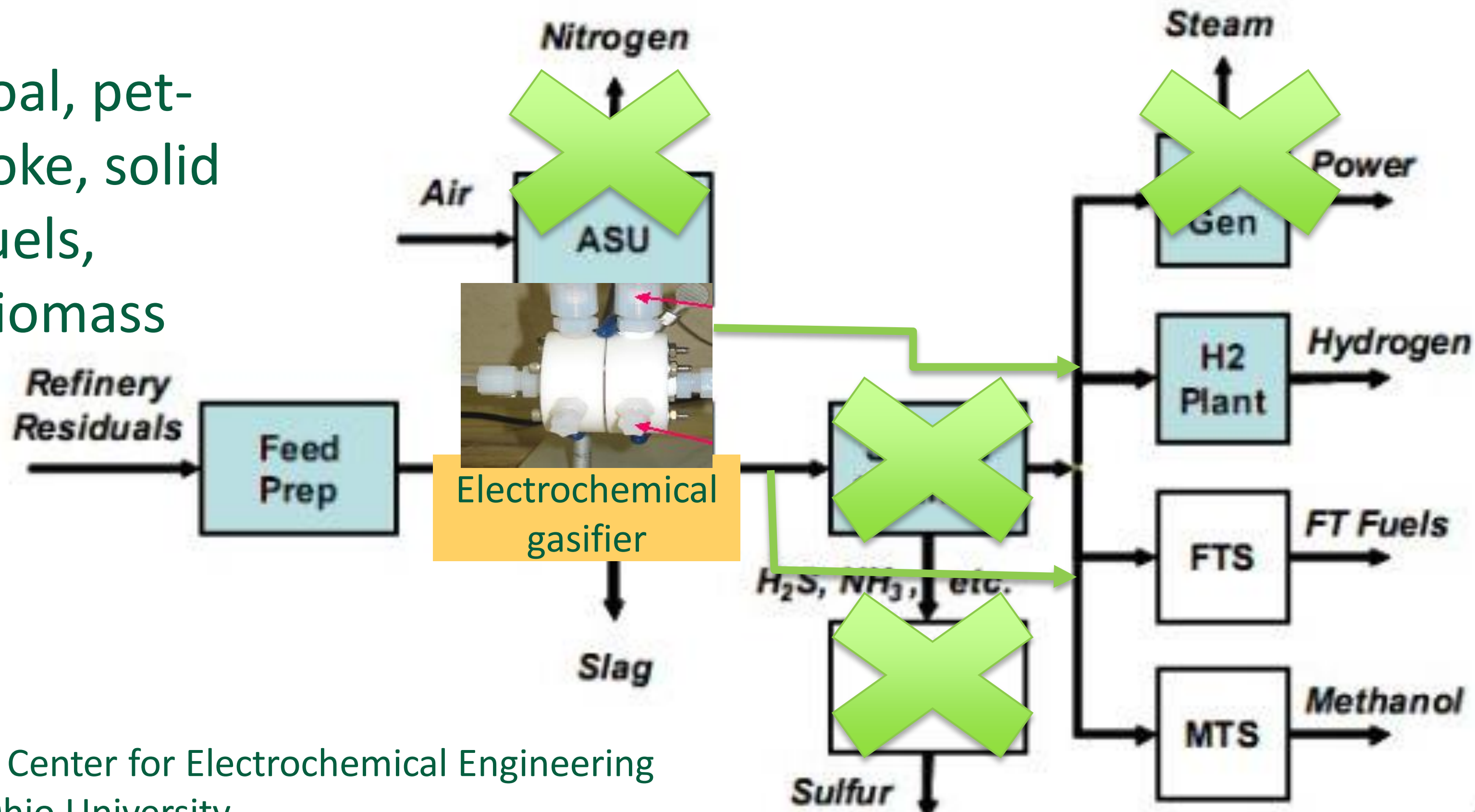
Advantages and Summary

- Electrolysis of coal can provide hydrogen more efficiently than other technologies (efficiencies greater than 80%)
- Fuels / blends can be extracted from electrolyzed coal char at low temperature and pressure
- Electrolysis of coal provides a way to produce hydrogen while capturing the carbon (with minimum CO_2 emissions)
- Technology is ready to move from bench-scale laboratory to pilot-scale prototype
- Alternatives for other solid fuels and slurries
- Applications in flow batteries

Vision of Electrochemical Conversion and Gasification

Electrochemical gasification can increase selectivity and minimize separation costs

coal, pet-coke, solid fuels, biomass



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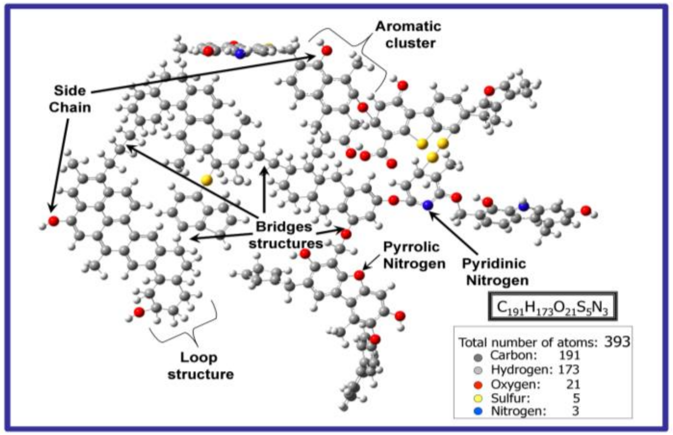
Synthesis of Carbon Nanostructures and Graphene

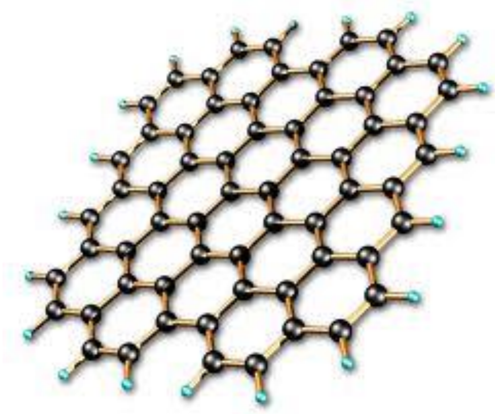
- Carbon-based nanotubes, nano sheets and graphene are synthesized from inexpensive sources
- Applications include batteries, super capacitors, solar panels, superconductors

High Value Products

Synthesis of graphene from coal has been demonstrated

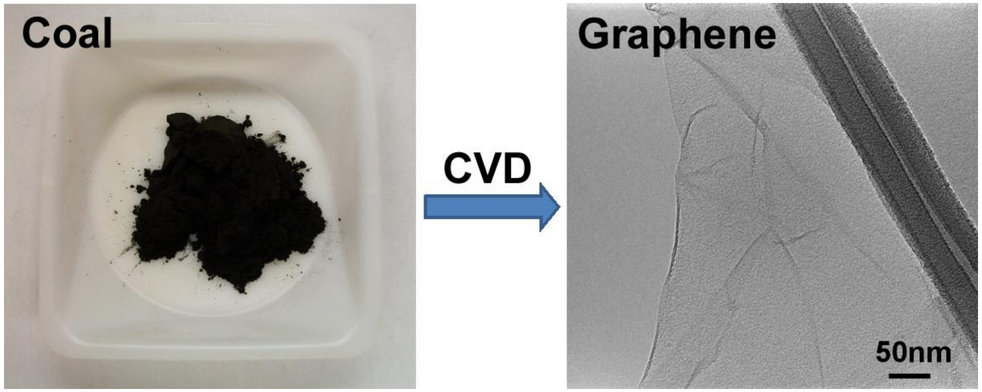


C2G



Coal

Graphene



S.H. Vijapur, D. Wang and G.G. Botte, ECS Solid State Lett. (2013), 2 (7), M45-M47

Advantages and Summary

- Decrease Cost
- Improve Reliability
- Protect National Security
- Electrolysis leads to light components in coal that enable the synthesis of graphene
- Technology is ready to move from bench-scale laboratory to pilot-scale prototype

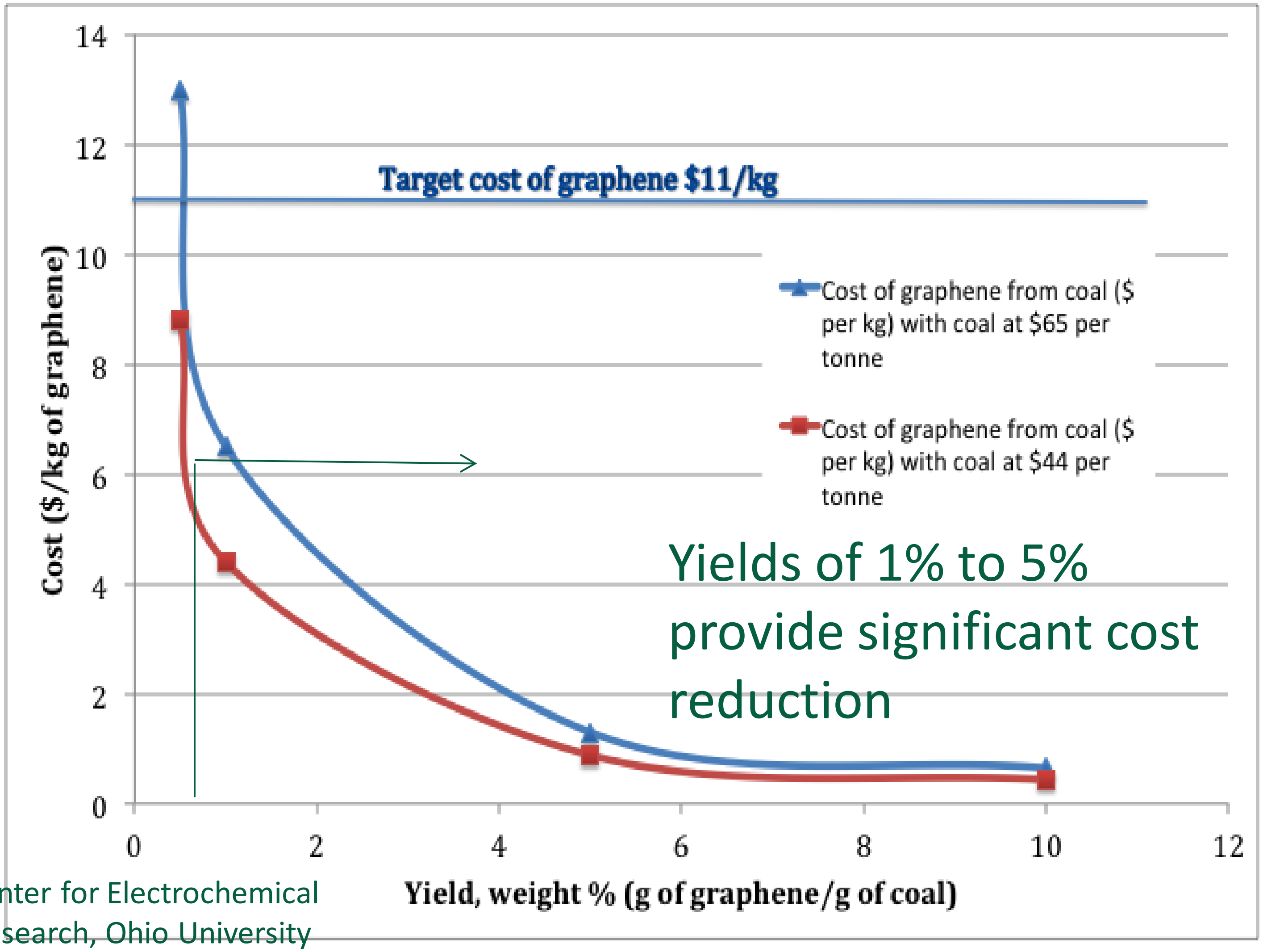
Applications: batteries, capacitors, water filtration, etc.

Graphene on Cu Sheet made by CEER from Pittsburgh No. 8

Applications: functionalized polymers, elastomers, fillers

Graphene sheets made by CEER from Pittsburgh No. 8

Stability on the cost of feedstock



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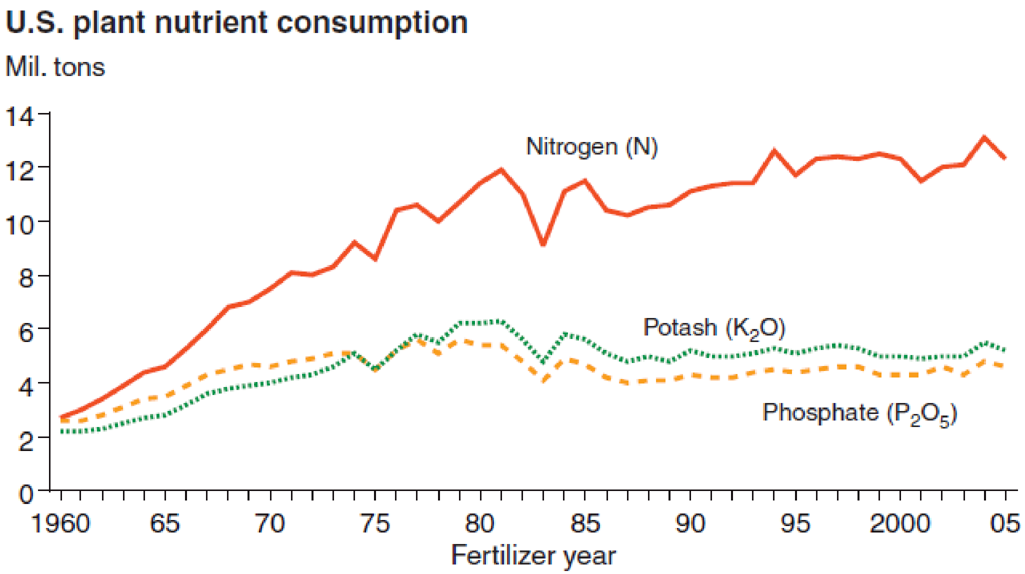
Fertilizer Production

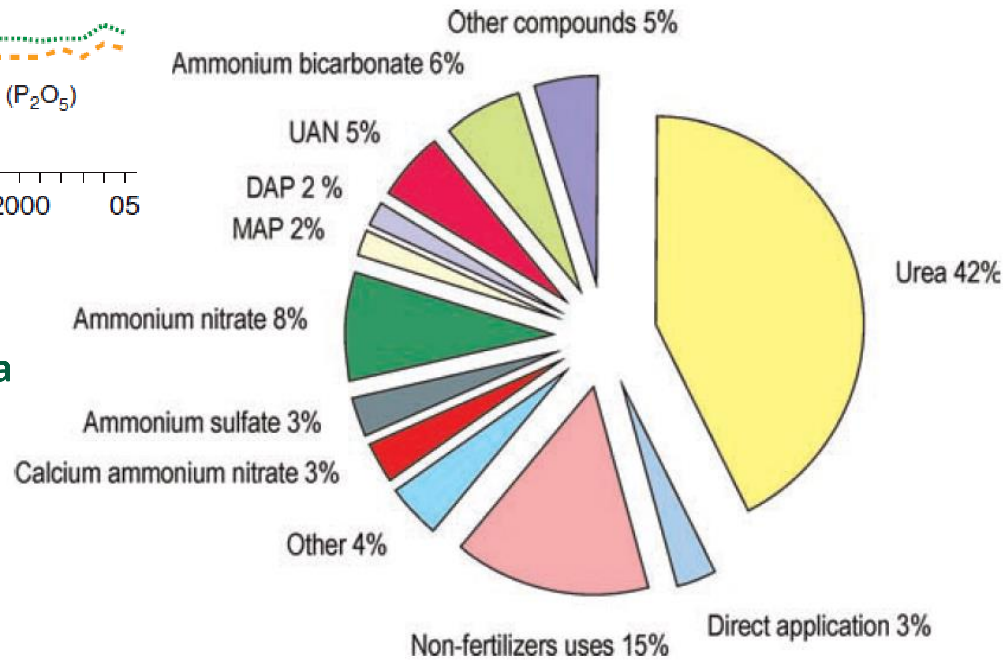
Fertilizer Production

Ammonia



Nutrient Consumption

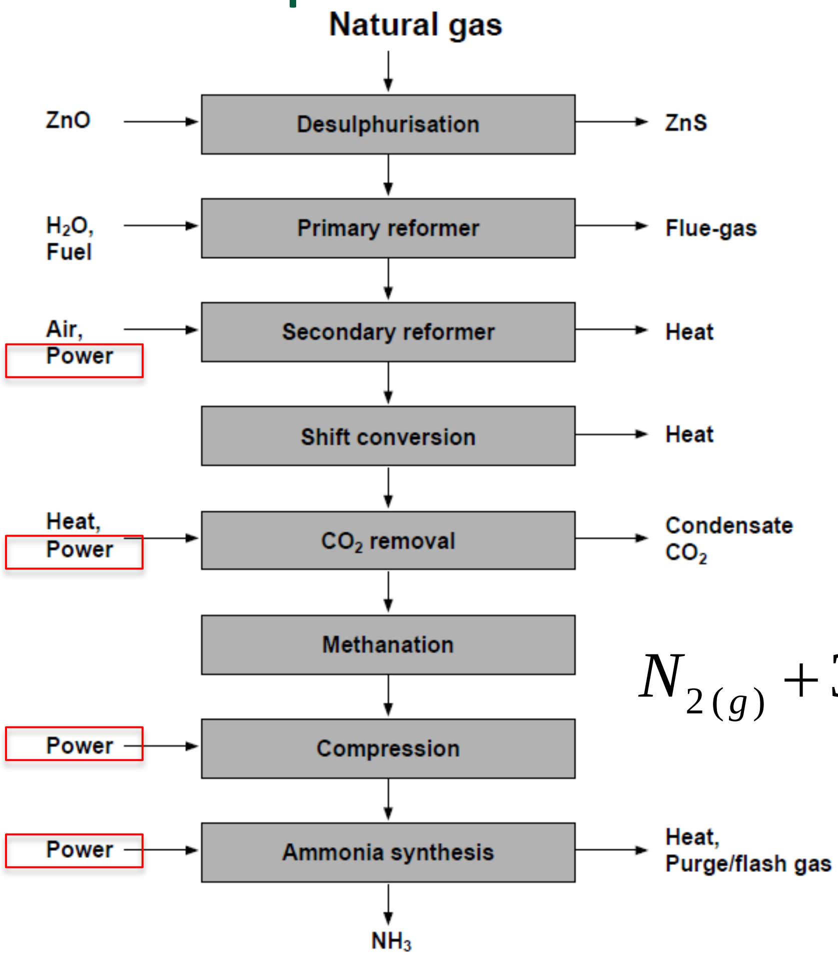
Applications of Ammonia



M. Appl, in *Ullmann's Encyclopedia of Industrial Chemistry* (2012)

Fertilizer Production

Ammonia production and natural Gas (Haber-Bosch Process)



$$N_{2(g)} + 3H_{2(g)} \xrightarrow[\text{High Temperature and Pressure}]{\text{Catalyst}} 2NH_{3(g)}$$

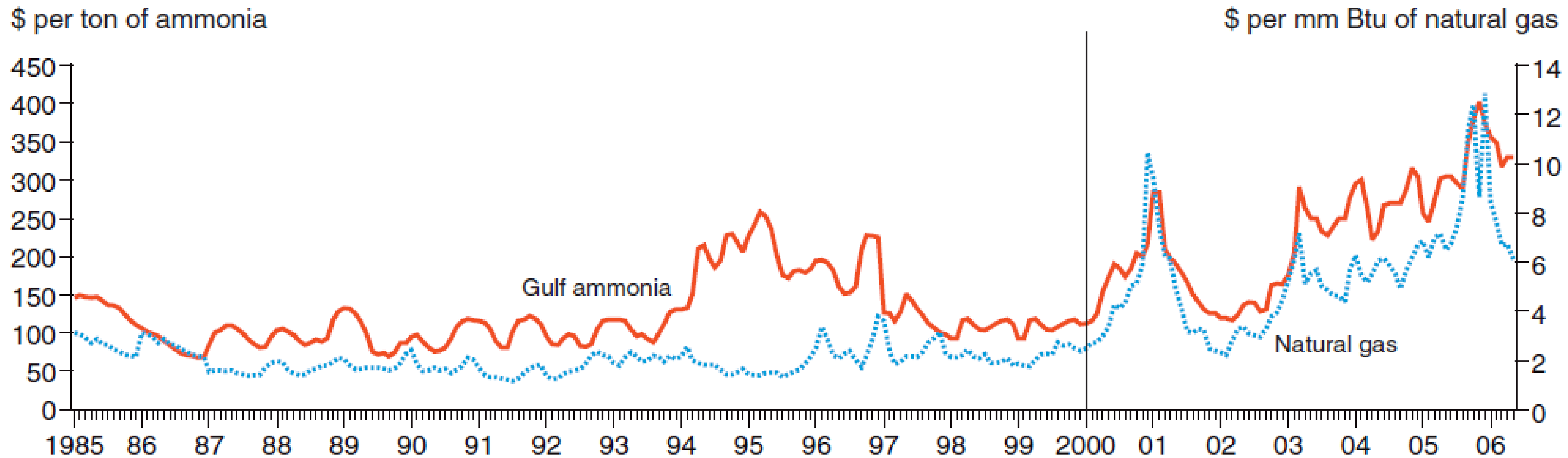
European Fertilizer Manufacturer's Association, Production of Ammonia (2000)

Fertilizer Production

Enhancing the Haber Bosch Process

- Feedstock
- Process Conditions
- Catalyst Development

Monthly U.S. prices of natural gas and ammonia



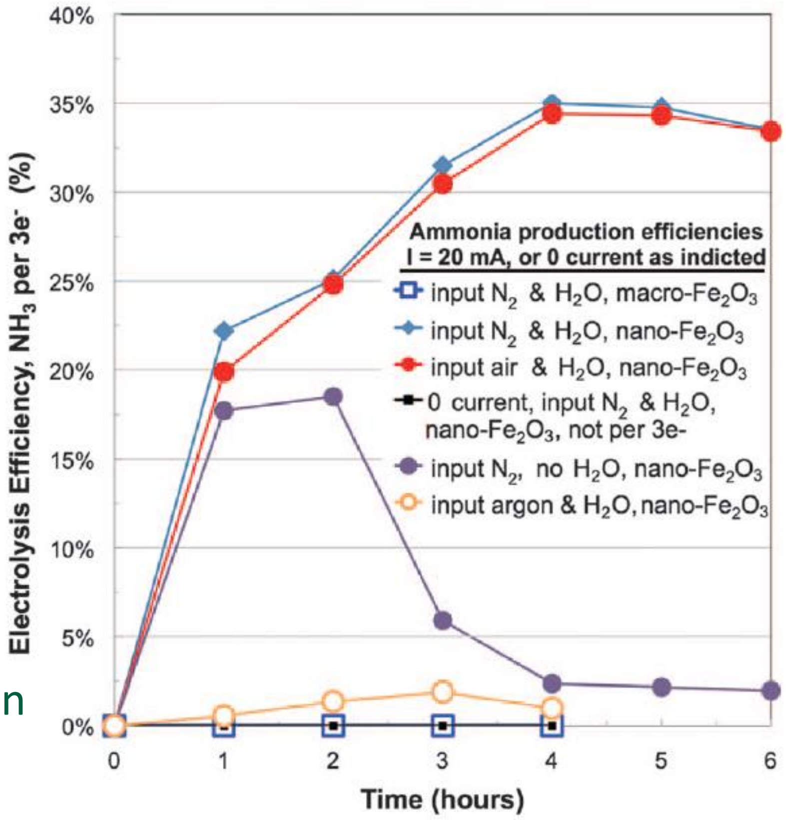
Source: USDA, Economic Research Service using data from TFI (b).

M. Appl, in *Ullmann's Encyclopedia of Industrial Chemistry* (2012)

Fertilizer Production

Ammonia synthesis via steam electrolysis

- Steam Electrolysis as an alternative to steam reformation of methane
  - Molten NaOH-KOH mix, Ni electrodes and suspended Fe_2O_3
  - 1 bar and 200 °C: NH_3 production at 1.2V and 2 mA/cm^2
  - 25 bar and 250 °C: NH_3 production at 1.0V and 2 mA/cm^2
- Process efficiency
  - 35% coulombic efficiency for ammonia synthesis
  - 65% coulombic efficiency for hydrogen production

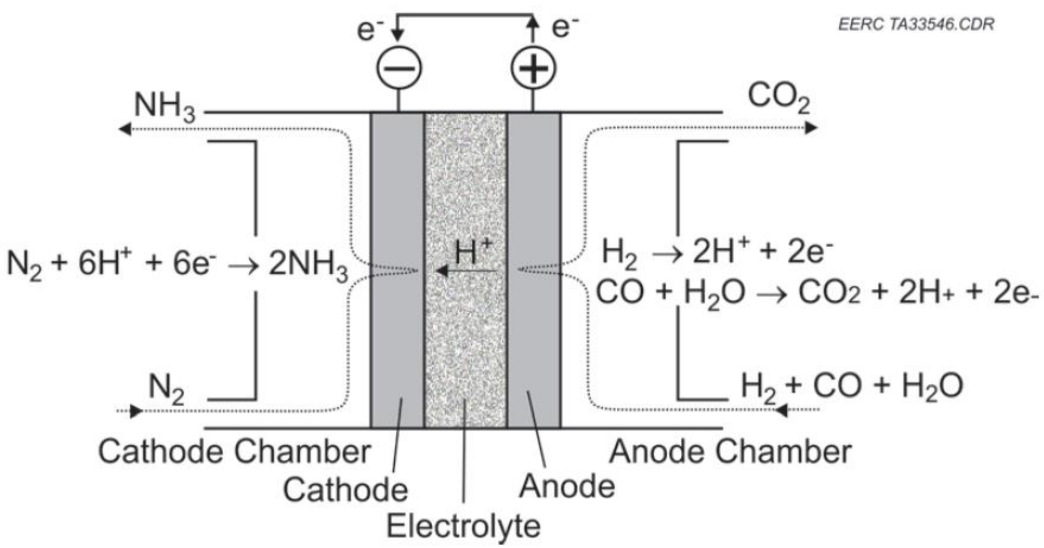


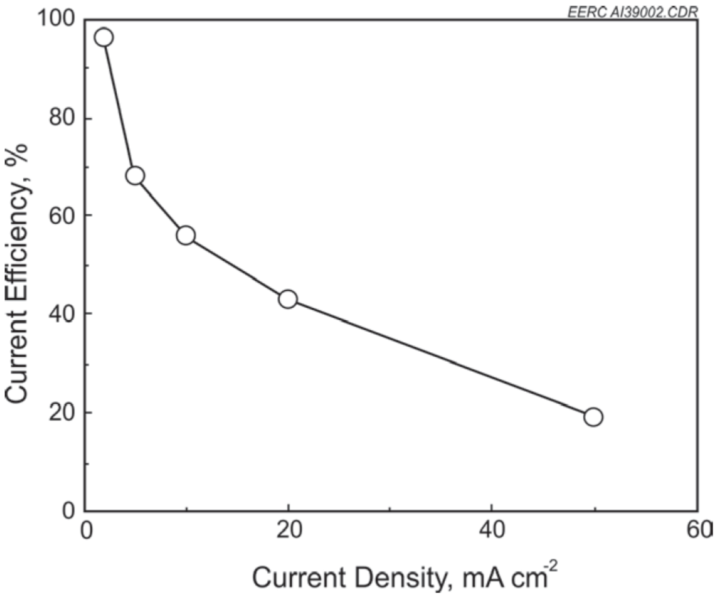
S. Licht *et al.*, Ammonia synthesis by N_2 and steam electrolysis in molten hydroxide suspensions of nanoscale Fe_2O_3, Science **345**, p637 (2014)

Fertilizer Production

Ammonia synthesis via electrolysis (solid state)

- Alternative approach kept syngas input but examined:
  - Solid-state electrolyzer
  - Catalyst development
  - Process conditions optimization: temperature, pressure and electrolyte



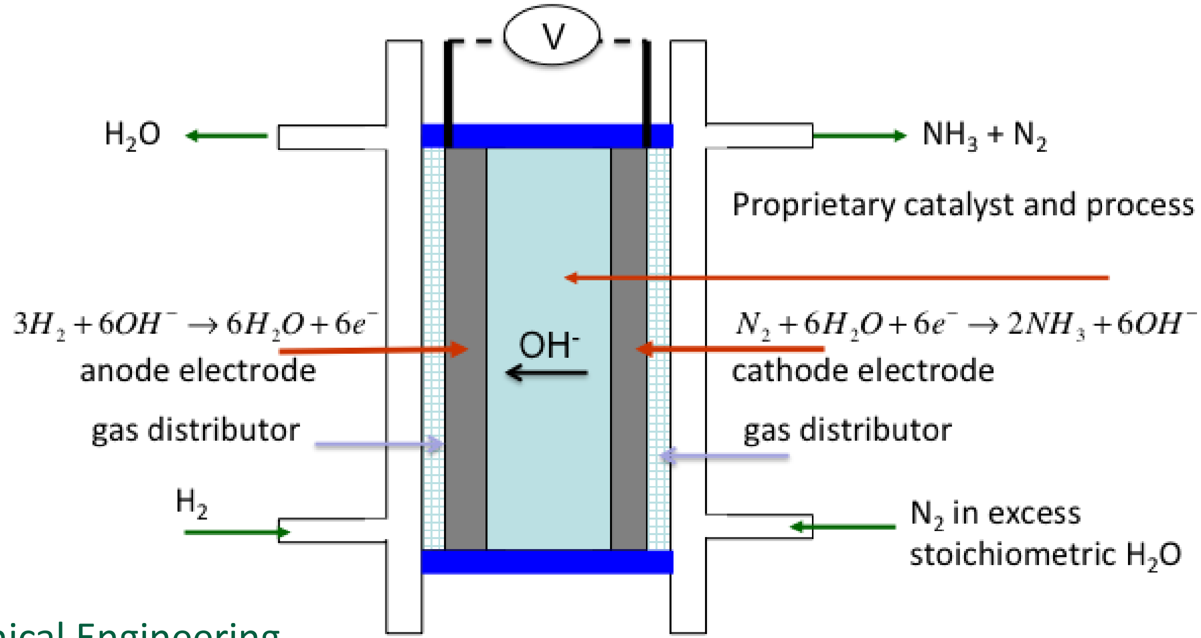


J. Jiang, A. Ignatchanko, T. Aulich, Renewable Electrolytic Nitrogen Fertilizer Production (2010)

Fertilizer Production

Electrochemical synthesis of ammonia in alkaline media

- Substitutes compression and synthesis steps in the Haber-Bosch
- 30% and 50% energy and CO_2 reduction in the Haber-Bosch process
- Under development



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Other Applications

- Electrochemical reduction of CO_2 to high value chemicals
- Shale gas water treatment
- Electrochemical conversion of natural gas
- Many others