Electrochemical Pathway for Sustainable Manufacturing (EPSuM)

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Webinar
National Academies’ Government-University-Industry Research Roundtable (GUIRR) & University-Industry Demonstration Partnership (UIDP)
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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) $A \rightarrow A^+ + e^-$
  - Cathode (Reduction) $B + e^- \rightarrow B^-$
  - Electrolyte
  - Divided or Undivided Reactor

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)
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
- In-situ Electrochemistry

Molecular scale

Microscopic and macroscopic models

Unit Operations

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

Rapid Evaluation and Prototyping

Water and Air sustainability
Energy Storage and Conversion
Sustainability of Resources
Process Efficiency
Advanced Manufacturing

Fast Transfer of Technology/Manufacturing

Design, Synthesis, Characterization of Materials
Electrodes, electrolytes, membranes, separators

Process and Systems Modeling
First principles, multiscale modeling, economic models, life-cycle
Planned Consortium: Electrochemical Pathway for Sustainable Manufacture (EPSuM)
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 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*

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/cm²

Voltage increases due to the formation of films
## Hypothesized/Proposed Reactions for Coal Electrolysis

<table>
<thead>
<tr>
<th>Cell Compartment/Reactions</th>
<th>Current Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td></td>
</tr>
<tr>
<td>$2n \sim C + 2H_2O \rightarrow 2n \sim \left( C \quad OH \right) + 2H^+ + 2e$</td>
<td>85-75%</td>
</tr>
</tbody>
</table>
| \[
\left( \frac{1}{2} \right) C + H_2O \rightarrow \left( \frac{1}{2} \right) CO_2 + 2H^+ + 2e
\] | 15-25%             |
| **Cathode**               |                    |
| $2H^+ + 2e \rightarrow H_2$ | 100%               |
## Energy Consumption: Comparison with Water Electrolysis at 80 °C*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faradaic Efficiency Hydrogen Production</td>
<td>98%</td>
</tr>
<tr>
<td>Faradaic Efficiency Coal to CO₂</td>
<td>12%</td>
</tr>
<tr>
<td>Energy consumption (w-h/g H₂)</td>
<td>22.5</td>
</tr>
<tr>
<td>Theoretical: 5.6 w-h/g H₂</td>
<td></td>
</tr>
<tr>
<td>Energy consumption (w-h/g H₂)</td>
<td>44</td>
</tr>
<tr>
<td>Theoretical: 33 w-h/g H₂</td>
<td></td>
</tr>
</tbody>
</table>

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 CO₂ 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

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

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

Yields of 1% to 5% provide significant cost reduction

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

Ammonia

Nutrient Consumption

Applications of Ammonia

Fertilizer Production

Ammonia production and natural Gas (Haber-Bosch Process)

\[ N_2(g) + 3H_2(g) \xrightarrow{\text{Catalyst \atop \text{High Temperature and Pressure}}} 2NH_3(g) \]

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

$ per ton of ammonia

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

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$_2$O$_3$
  – 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$_2$O$_3$, 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

Fertilizer Production

Electrochemical synthesis of ammonia in alkaline media

- Substitutes compression and synthesis steps in the Haber-Bosch
- 30% and 50% energy and CO₂ reduction in the Haber-Bosch process
- Under development

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

- Electrochemical reduction of CO₂ to high value chemicals
- Shale gas water treatment
- Electrochemical conversion of natural gas
- Many others