21st Century Renewable Fuels, Energy, and Materials Initiative

PI: K. Joel Berry[1]

Co-PI: Susanta K. Das[1]

Team members: Abhijit Sarkar[2], Jianfang Chai[2], Salma Rahman[2], Li Sun[1], James P. Godschalx[2], Claire Hartmann-Thompson[2], Edmund J. Stark[2], Steven N. Kaganove[2], Adina Dumitrascu[2], Christopher Schilling[3] and Steven E. Keinath[2]

[1]Center for Fuel Cell Systems and Powertrain Integration, Kettering University, Flint, Michigan, USA.
[2]Michigan Molecular Institute, Midland, Michigan, USA.
[3]Saginaw Valley State University, Saginaw, Michigan, USA.

DOE Annual Review: MAY 14-18, 2012

Project ID # **FC078**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Overview

Timeline

- Start - October 2010
- Finish - June 2012
- 95% Complete

Budget

- Total project funding
  - DOE - $1,250,000
  - Cost share $312,500
- Funding received in FY11
  - $0
- Planned funding for FY12
  - $0

Barriers

- Barriers
  - **A. Materials and manufacturing costs**
  - **B. Membrane performance and durability**
  - **C. Efficient multi-fuel reforming system**
  - **D. Alternative fuel source without impact on human food chain**
- Targets - **Improve membrane conductivity and durability**
  - **Cost-effective multi-fuel reformer system**
  - **High power density Lithium-Air battery for ease of use and at a reduced cost**
  - **High energy yield agriculture bio-crop**

Partners

- **Michigan Molecular Institute (MMI)** - Polymer membranes and lithium-air battery
- **Saginaw Valley State University** - High energy yield agriculture bio-crop (Miscanthus)

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Relevance

Overall Objectives (2010 – 2012)	• Development of an improved high-temperature PEM fuel cell membrane capable of low-temperature starts (<100°C) with enhanced performance. • Development of a 5kWe novel catalytic flat plate steam reforming process for extracting hydrogen from multi-fuels and integration with high-temperature fuel cell systems. • Development of an improved oxygen permeable membrane for high power density Lithium-Air batteries for ease of use and at a reduced cost. • Development of novel high energy yield agriculture bio-crop (Miscanthus) for alternative fuels with minimum impact on human food chain. • Extend math and science alternative energy education program to include bio-energy and power.

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Plan and Approach

Plan & Approach

80% Complete

➢ Task 1: **High temperature fuel cell membrane**

- Increased proton conductivity
- Improved durability and thermal stability
- Performance evaluation

95% Complete

➢ Task 2: **5kWe catalytic flat plate fuel reformer**

- CFD study of catalytic flat plate reformer
- Design and build the reformer prototype
- Test and evaluate the performance

85% Complete

➢ Task 3: **High power density Lithium-Air battery at a reduced cost**

- Optimize the combination of electrolytes that are best suitable for Li-Air battery
- Design and build the prototype
- Test the prototype for durability and efficiency

100% Complete

➢ Task 4: **Research on high energy yield agriculture bio-crop (Miscanthus)**

- Literature survey
- Develop energy and economic model
- Identify methods to produce alternative fuels from bio-crop (Miscanthus)

90% Complete

➢ Task 5: **Alternative energy education program to include bio-energy and power**

- Develop an educational module to incorporate the project results for bio-energy and power education

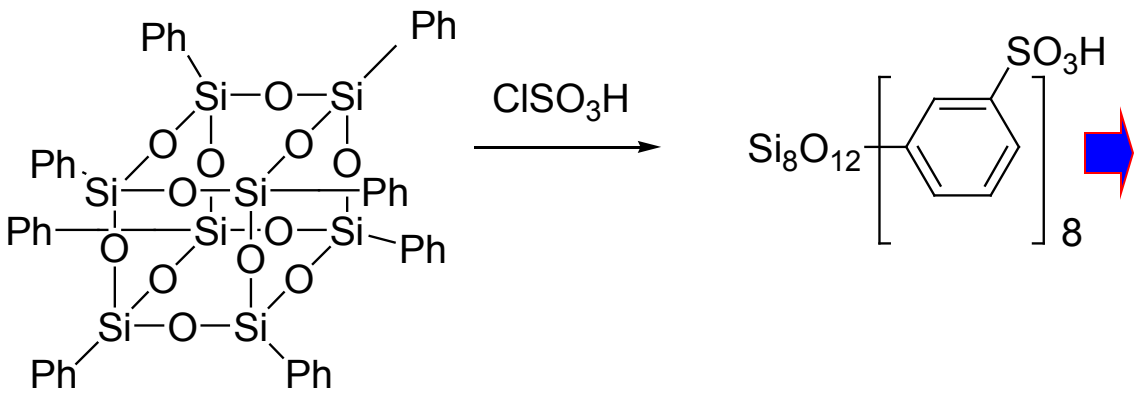
This presentation does not contain any proprietary, confidential, or otherwise restricted information

Approach

Overview for High Temperature PEM Membrane

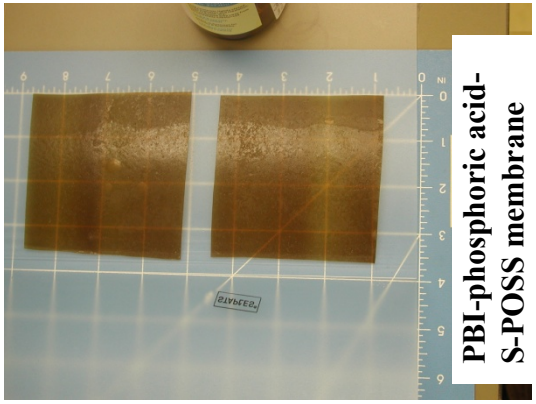
- We used novel patented nano-additive synthesis technology to prepare higher conductivity and more robust high temperature PEM fuel cell membranes

- Patented Nano-additive Synthesis Technology



Synthesis of Sulfonated-Polyhedral Oligomeric Silsesquioxane (S-POSS)

- New Polymer Membrane

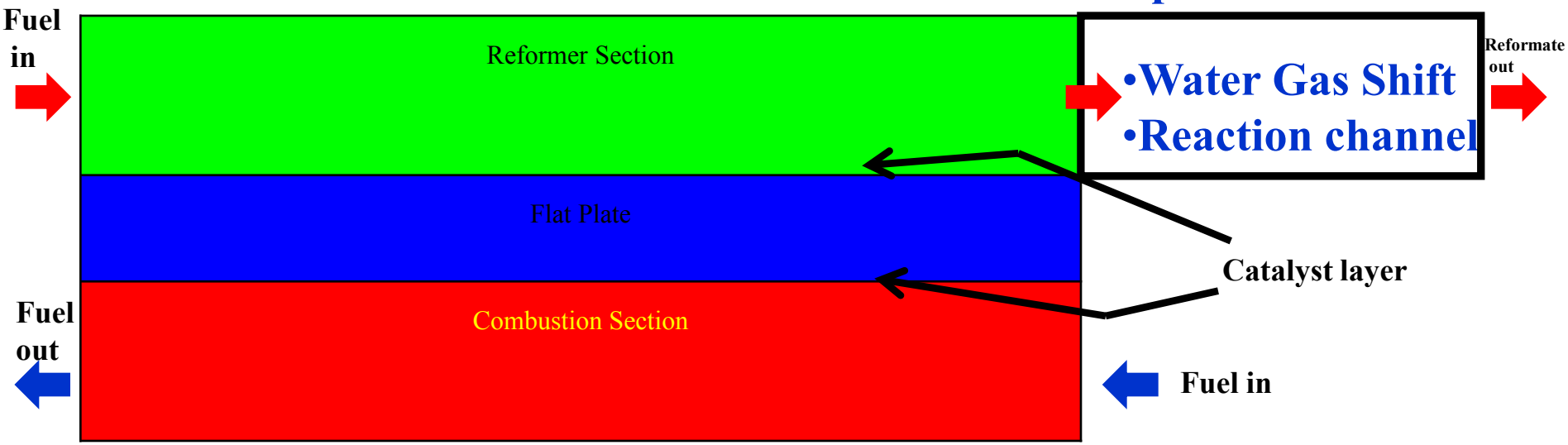


Fabricated Membrane

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Approach

Overview for Flat Plate Reformer Development



- Length of the channel 30 cm
- Width of the channel 2 mm
- Wall (flat plate) thickness 50 µm

Catalyst layer	
Thickness	$20*10^{-6}$m
Pore radius	$10*10^{-9}$m
Porosity	0.4
Tortuosity	4
Thermal conductivity	0.4 W/m.K
Density	2355 kg/m^3
Solid wall	
Thickness	0.0005m
Thermal conductivity	25 W/m.K

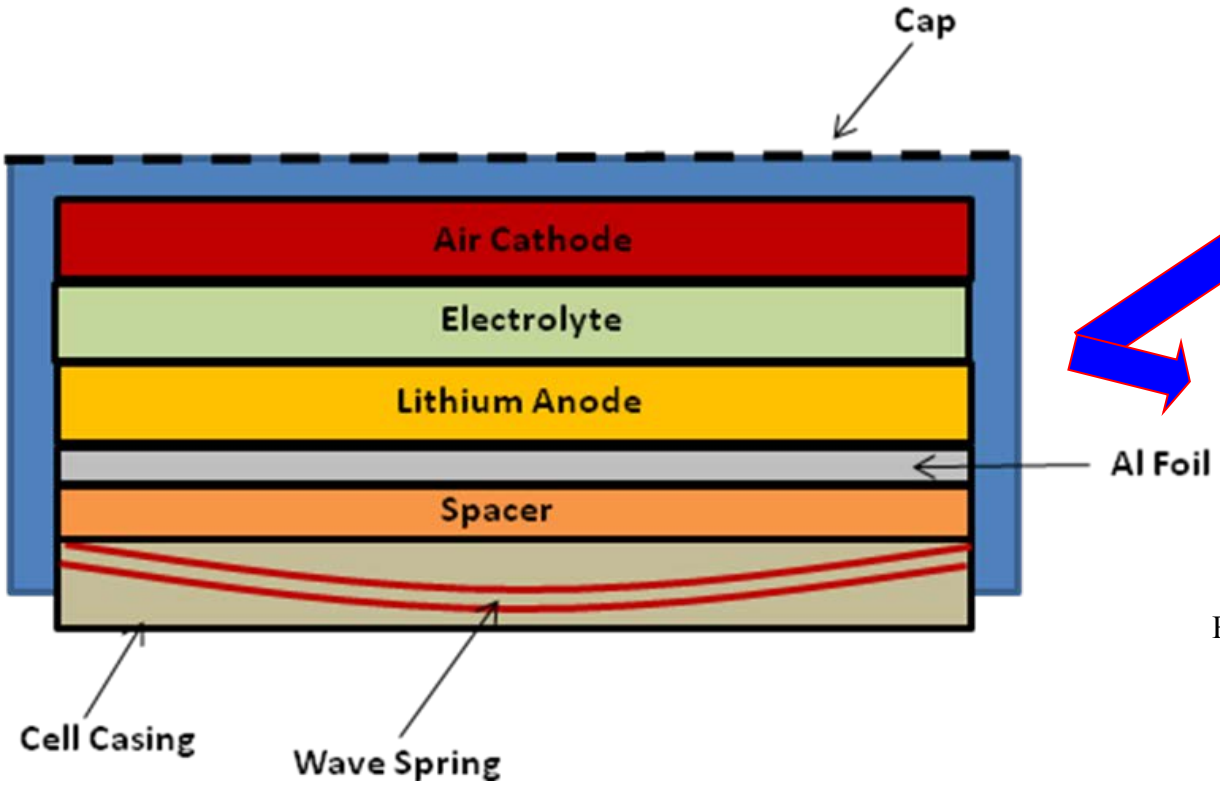
- **Catalyst containing 15.2% Ni supported on magnesium spinel**

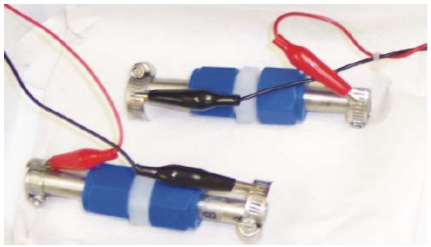
This presentation does not contain any proprietary, confidential, or otherwise restricted information

Approach

Overview for Lithium-Air Battery

- **Schematic Representation of the Proposed Lithium-Air Battery**





Fabricated Lithium-Air Batteries

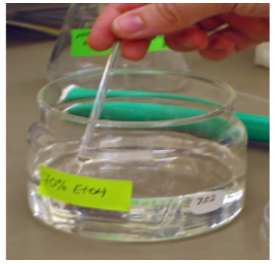
This presentation does not contain any proprietary, confidential, or otherwise restricted information

Approach

Overview for Biofuel from High Yield Energy Crop

- **Approach for biofuel from high energy yield agriculture crop**

Miscanthus Grass



Ethanol (E-85) - Biofuel

Torrefied bio-mass

Pyrolyzed bio-char

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Accomplishments/Progress

Comparison of high temperature membrane conductivity

DAB: 3,3'-Diaminobenzidine

Sample	Water at RT	90°C, 20% RH	90°C, 40% RH	90°C, 60% RH	90°C, 80% RH	120°C, 3% RH	150°C, 5% RH
Literature[2] PBI (low RH)	--	80	--	--	--	160	220
PBI control (815-12) IV = 1.78	55,59	99,110	123,129	135,178	81,100	69,77	71,81
PBI control (829-8) IV = 2.02	55,26	66,96	103,209	152,243	166,176	71,103	79,120
10% S-POSS (815-16) Unwashed, no excess DAB IV = 1.46	74,82 **+37%**	81,109 **-10%**	120,116 **-6%**	128,144 **-13%**	192,204 **+218%**	111,115 **+55%**	117,139 **+68%**
10% S-POSS (829-24) Unwashed, no excess DAB IV = 2.45, near insoluble	15,16 **-61%**	103,66 **+5%**	108,105 **-31%**	109,184 **-26%**	94,164 **-25%**	42,63 **-39%**	54,69 **-38%**
10% S-POSS (829-14) Washed, no excess DAB IV = 1.49	24,43 **-17%**	75,96 **+6%**	134,114 **-21%**	173,128 **-24%**	150,108 **-25%**	84,112 **+13%**	102,153 **+28%**
10% S-POSS (815-20) Washed, excess DAB IV = 2.93	26,26 **-37%**	119,38* **+47%**	181,128 **-1%**	273,254 **+33%**	201,233 **+27%**	125,42* **+44%**	151,40* **+51%**
10% S-POSS (815-24) Unwashed, excess DAB No IV, near insoluble	18,22 **-51%**	12,19 **-80%**	20,28 **-85%**	60,46 **-73%**	66,54 **-65%**	13,21 **-80%**	16,26 **-79%**

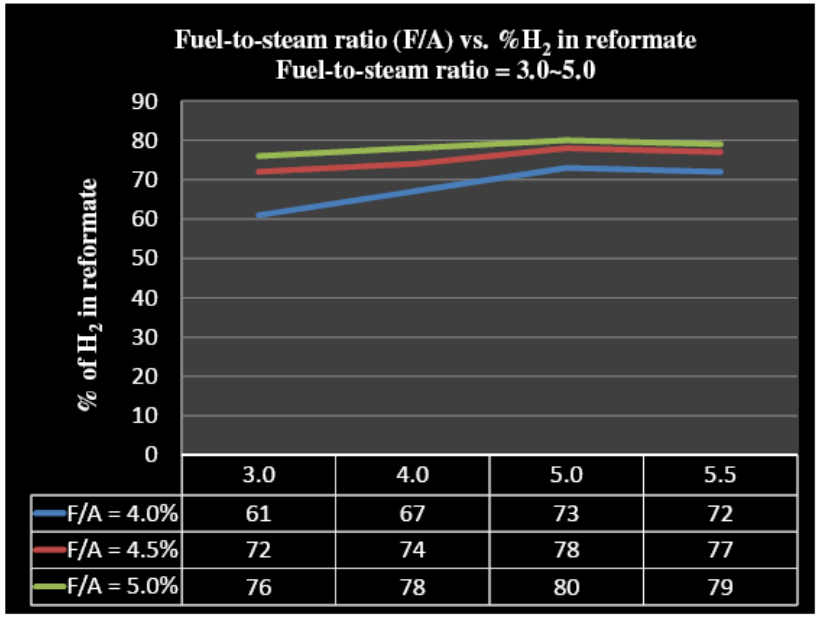
- **The best conductivity across the range of experimental conditions was obtained with washed S-POSS and excess DAB (IV = 2.93, 815-20) with a 44% increase relative to a control at 120°C and a 51% increase relative to a control at 150°C.**

- **Take away statement: The presence of S-POSS in polybenzimidazole (PBI)-phosphoric acid fuel cell membranes results in increased conductivity, increased modulus and improved mechanical properties.**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

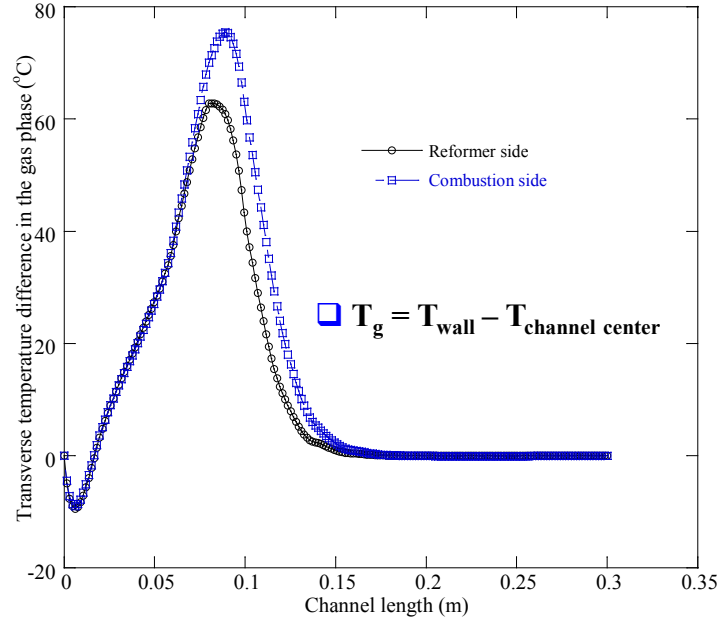
Accomplishments/Progress/Results

- **Validation of catalytic flat plate fuel reformer performance**



	3.0	4.0	5.0	5.5
F/A = 4.0%	61	67	73	72
F/A = 4.5%	72	74	78	77
F/A = 5.0%	76	78	80	79

- **Fuel to steam ratio vs H_2 production by catalytic flat plate fuel reformer.**



- **Transverse temperature difference in both reformer and combustion side.**

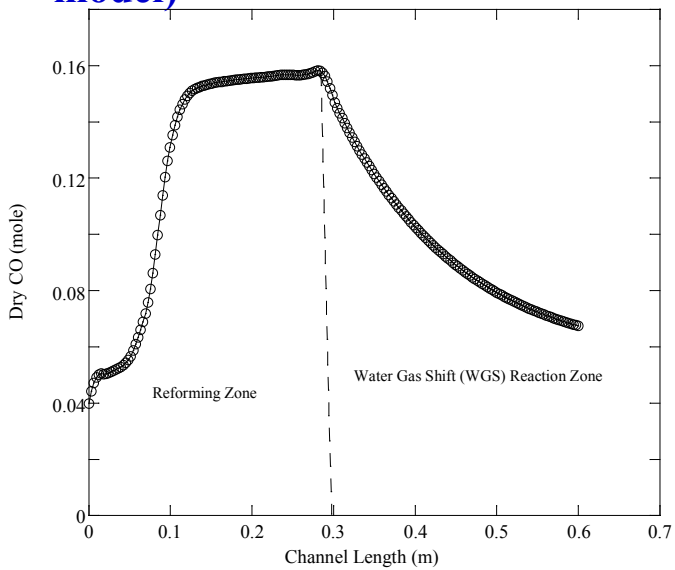
- **Take away statement: In a conventional steam reformer Tg is often greater than 250°C whereas here it is less than 30°C. Virtually no heat loss across the flat plate.**

- **Take away statement: Increase of fuel to steam ratio leads to higher percentage of H_2 production.**

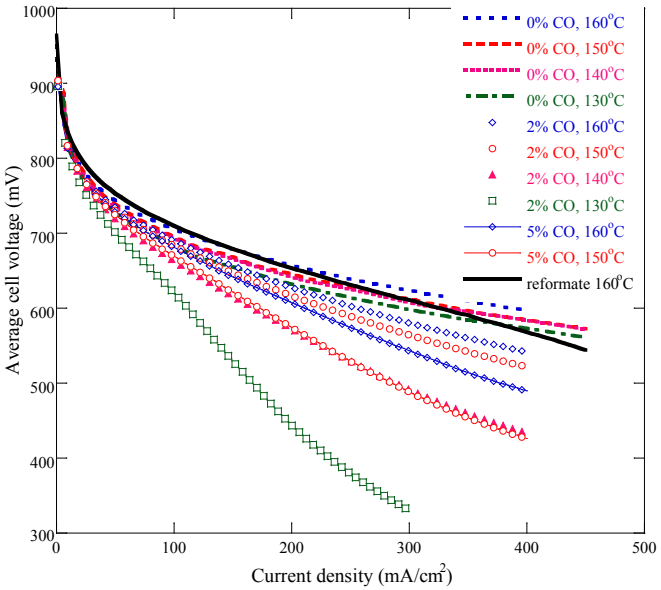
This presentation does not contain any proprietary, confidential, or otherwise restricted information

Accomplishments/Progress/Results

- **Experimental performance evaluation of fuel reformer (developed based on CFD model)**



(a) Production of dry CO with water gas shift (WGS) reaction and optimized reformer geometry.



(b) Polarization curves of a PBI-membrane with 5-cell HTPEMFC stack at different temperatures with different % of CO and reformate. The CO concentrations are indicated in the figure.

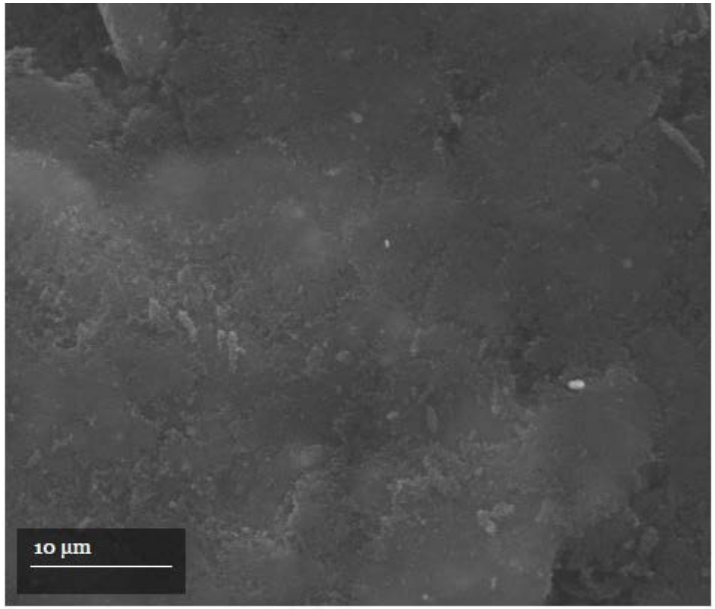
- **Take away statement: Reduction of dry CO is more than 50% with WGS reaction. CO level has changed from 0.158 to 0.072 on a dry basis.**

- **Take away Statement: For the case of reformate, the stack performance is much better (i.e., voltage drop is much lower) compared to 2% CO and 5% CO especially at high current density (0.3~0.4 A/cm^2) at 160°C. This implies that the reformate can be more preferable than 2% CO ~ 5% CO at 160°C.**

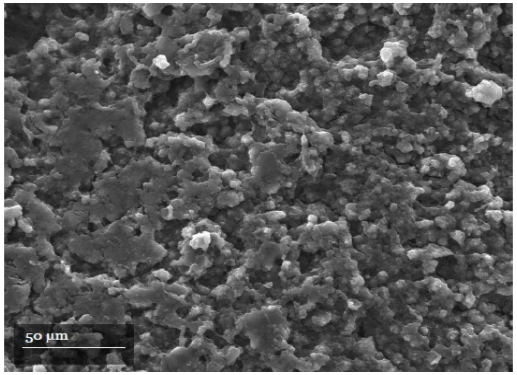
This presentation does not contain any proprietary, confidential, or otherwise restricted information

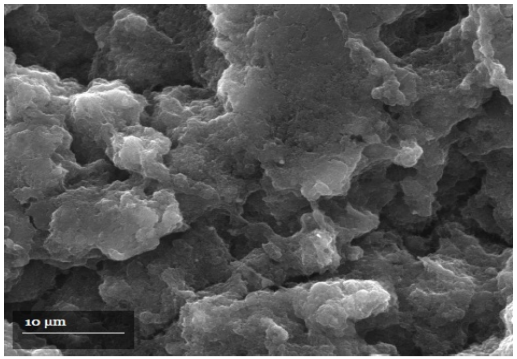
Accomplishments/Progress/Results

Characterization of Lithium-Air Battery Cathode Materials



(a) SEM image of an air cathode before discharge.





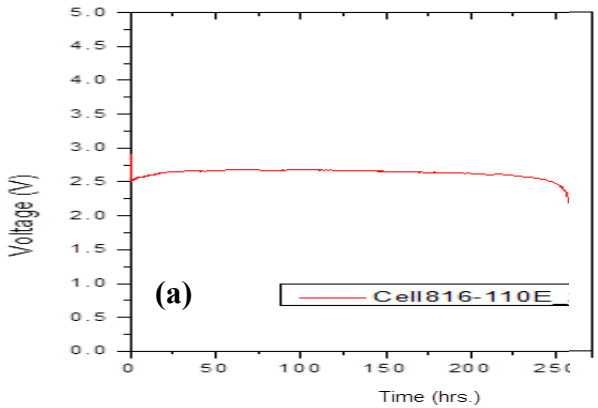
(b) SEM images of an air cathode after discharge.

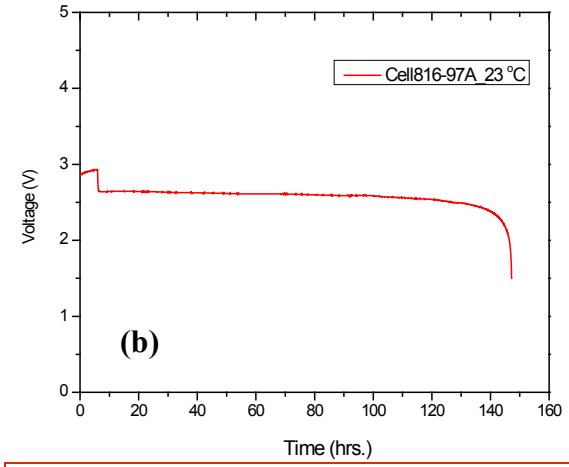
- **Take away statement:** The SEM images provide insight to the fate of cathode materials.
- **Take away statement:** SEM images clearly show that some particles were formed on the surface of the carbon materials, however, further investigation is needed in order to determine the chemical composition of these particles.

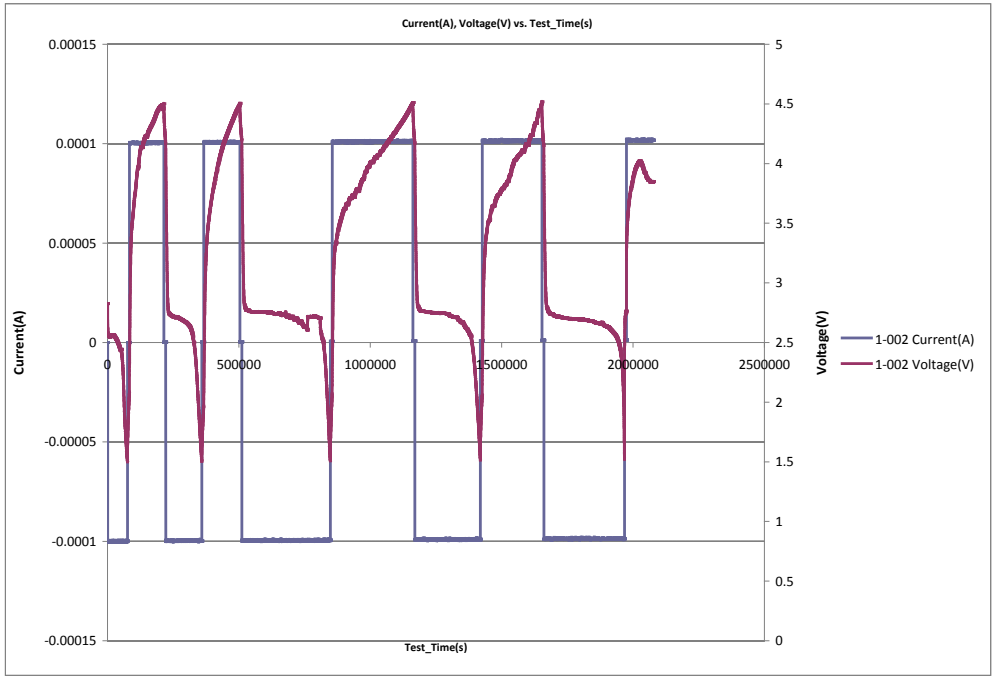
This presentation does not contain any proprietary, confidential, or otherwise restricted information

Accomplishments/Progress/Results

Performance Evaluation of Lithium-Air Battery







- **Charge-discharge cycles testing. The cell shows promising cycle-ability when tested in pure oxygen at room temperature with 0.1 mA/cm^2 current.**

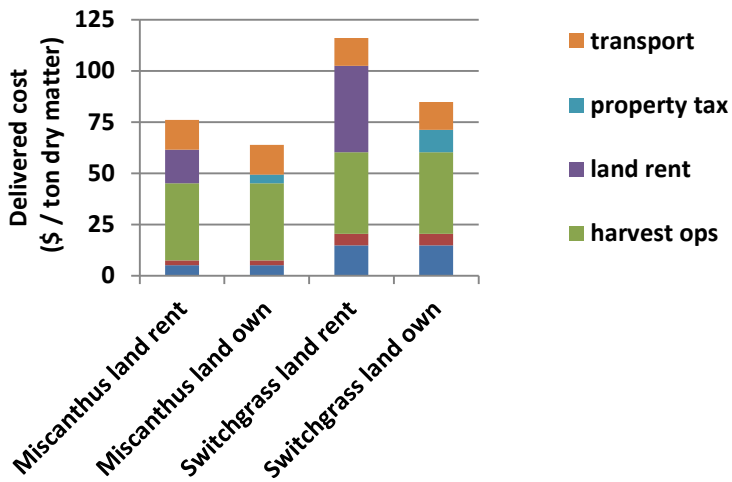
- **The battery cell shows improved performance when tested in oxygen (a) rather than in dry air (b) with 0.1 mA/cm^2 current at room temperature.**

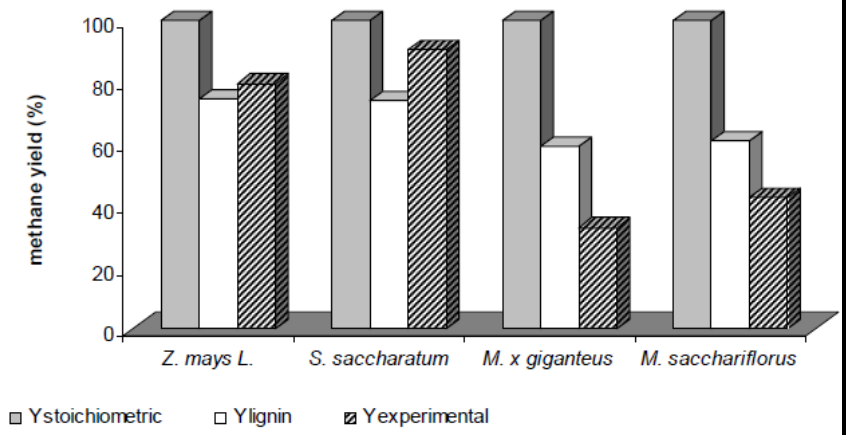
- **Take away statement: The Li-air battery shows one of the highest cell capacity reported to date along with good cycle-ability.**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Accomplishments/Progress/Results

- **Optimization of bio-fuel production using Miscanthus**





- **Effects of land rental versus land ownership on simulated production costs of miscanthus and switchgrass.**

- **Comparison of experimentally measured and theoretically predicted yields of methane from the following silages [Pokoj et al. (2010)]: corn maize (Z. mays L.), sugar sorghum (S. saccharatum), and two types of miscanthus.**

- **Take away statement: Based on the developed model in a northern Midwestern US setting, cost- and energy-balances as well as the sensitivity analysis revealed that miscanthus is more cost- and energy-efficient in terms of costs of land use, harvest operations, and raw-materials transportation.**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Collaboration

PI: Kettering University

- Task 2: **5kWe catalytic flat plate fuel reformer**
  - CFD study of catalytic flat plate reformer
  - Design and build the reformer prototype
  - Test and evaluate the performance

Co-PI: Michigan Molecular Institute (MMI)

- Task 1: **High temperature fuel cell membrane**
  - Increased proton conductivity
  - Improved durability and thermal stability
  - Performance evaluation

Co-PI: Saginaw Valley State University (SVSU)

- Task 4: **Research on high energy yield agriculture bio-crop (Miscanthus)**
  - Develop energy and economic model
  - Identify methods to produce alternative fuels from bio-crop (Miscanthus)

- Task 5: **Alternative energy education program to include bio-energy and power**
  - Prepare an educational module to incorporate the project results for bio-energy and power education

- Task 3: **High power density Lithium-Air battery at a reduced cost**
  - Optimize the combination of electrolytes that are best suited for Lithium-Air battery
  - Design and build the prototype
  - Test the prototype for durability and efficiency

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Future Work

- **Future Work (FY2012)**

- **Performance improvement of high temperature PEM membrane**
  - Optimize a membrane electrode assembly (MEA) using a PBI-phosphoric acid-POSS nano-additive proton exchange membrane
  - Test thermal stability and life-cycle sensitivity
  - Document performance evaluation

- **Design and build 5kWe catalytic flat plate fuel reformer**
  - Test prototype performance and benchmark the results
  - Optimization of reformer system
  - Develop cost analysis for an optimized reformer system

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Future Work

- **Future Work (FY2012)**

- **Explore other avenues for performance enhancement of Lithium-Air battery**
  - **Optimization of processing steps to improve the battery's performance.**
  - **Once a reproducible procedure has been identified, batteries with and without the oxygen permeable membrane will be prepared and evaluated under various atmospheric conditions (i.e., different relative humidity values).**
  - **Final performance evaluation of developed Lithium-Air batteries.**

- **Cost effective procedure for bio-fuel production from high energy yield agriculture crop**
  - **Economic and technical feasibility of procedures to convert the energy crop, *Miscanthus x giganteus (MXG), into either hydrogen or hydrogen carriers suitable for fuel cell use.***
  - **Calculation of optimal combination of bio-fuel production procedures for Miscanthus bio-crop.**

- **Develop a bio-energy education module**
  - **Math and science alternative energy education program for bio-energy and power.**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Summary

Project Summary

Relevance: Helped to develop high temperature PEM fuel cell membrane, Lithium-Air battery and bio-fuel from bio-crop for fuel cell applications.

Approach: Patented nano-additive synthesis technology for high performance membrane, multi-fuel capable reformer based on CFD study, Lithium-Air battery with high-efficiency membrane for oxygen and moisture management.

Technical Accomplishments and Progress: Higher conductivity and more robust HTPEM fuel cell membranes have been developed. Performance evaluation of a multi-fuel reformer has been completed. Preliminary testing of Lithium-Air battery performance evaluation has been completed.

Technology Transfer/Collaborations: Active partnership with MMI and SVSU, including presentations, publications and patents.

Proposed Future Research: Identify factors limiting HTPEM fuel cell performance and Lithium-Air battery performance.

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Authors Contact

Dr. K. Joel Berry
Email: jberry@kettering.edu

Dr. Susanta K. Das
Email: sdas@kettering.edu