21st Century Renewable Fuels, Energy, and Materials Initiative

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Project ID # FC078

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Overview

Timeline
- Start – July 2010
- Finish - June 2011
- 35% Complete

Budget
- Total project funding
  - DOE - $1,250,000
  - Cost share - $312,500
- Funding received in FY10
  - $1,250,000

Overview

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
  - Improved membrane conductivity & durability
  - Cost-effective multi-fuel reformer system
  - High power density lithium-air battery with simple control systems and 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)
Relevance

Overall Objectives (2010 – 2011)

- Development of an improved high-temperature 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 integrate with high-temperature fuel cell systems.
- Development of an improved oxygen permeable membrane for high power density lithium-air batteries with simple control systems and 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 educator program to include bio-energy and power.
Plan and Approach

Plan & Approach

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

➢ 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

➢ Task 3: High power density Lithium-Air battery at a reduced cost.
  - Optimize the combination of electrolyte that is best suitable for Li-air battery
  - Design and build the prototype
  - Test of prototype for durability and efficiency

➢ 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)

➢ Task 5: Alternative energy education program to include bio-energy and power.
  - An educational module preparation incorporating the project results for Bio-Power education

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Approach Overview for High Temperature PEM Membrane

- We used novel patented polymer synthesis technology to prepare robust electrolyte for high temperature PEM fuel cell

Patented Polymer Synthesis Technology

New Polymer Membrane

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Approach Overview for CFD flat plate reformer Modeling

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

- **Solid wall**
  - Thickness: 0.0005 m
  - Thermal conductivity: 25 W/m.K

- **Water Gas Shift**
- **Reaction channel**

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

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Approach Overview for Lithium-Air Battery

- Schematic Representation of The Proposed Lithium-Air Battery
Approach Overview for Biofuel from High Yield Energy Crop

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

  - Miscanthus Grass
  - Torrefied bio-mass
  - Pyrolyzed bio-char
  - Ethanol - Biofuel
Accomplishments/Progress

• Optimization of high temperature membrane casting protocol

- Three control \( m \)-PBI-PPA membranes have been cast to date
- A nitrogen flow system was found to be preferable to a closed nitrogen system
  - Necessary to drive off water to shift the equilibrium toward the desired PBI product
- Storage of PPA under rigorously anhydrous conditions was also found to be key
- The quality of the film was related to the reaction time (mass of PBI)
  - Necessary to determine optimum reaction time
Accomplishments/Progress/Results

• CFD analysis of Catalytic Flat Plate Reformer

  • Schematic of Catalytic Flat Plate fuel reformer

  • Transverse temperature difference in both reformer and combustion side

• In a conventional steam reformer $T_g$ is often greater than 250°C whereas here it is less than 30°C.

• Virtually no heat loss at the very end section of the reformer.
Accomplishments/Progress/Results

• CFD analysis of dry hydrogen and dry CO production with WGS

(a) Production of dry H₂ with water gas shift (WGS) reaction and optimized reformer geometry.

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

- Production of dry hydrogen is increased only 2% with WGS reaction.
- Reduction of dry CO is more than 50% with WGS reaction. CO level has changed from 0.158 to 0.072 on dry basis.

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**Accomplishments/Progress/Results**

- **Comparison of conductivity among ceramic and polymer electrolyte for Lithium-Air Battery**

- **Ceramic electrolyte: Li₂O, Al₂O₃, GeO₂, and P₂O₅**
  - LAGP disc before sintering
  - LAGP disc after sintering

- **Polymer electrolyte: PEO, LiTFSI, BN/Li₂O**
  - PC (BN) disc
  - PC(Li₂O) disc

(a) Ceramic and polymer electrolyte sample preparation.

(b) Conductivity as a function of temperature for ceramic and polymer electrolyte.

- **The ceramic electrolyte has moderate conductivity at reduced temperature.**
- **The polymer electrolyte shows higher conductivity above 35°C.**
- **The big difference in the conductivity among the polymer samples might be attributed to the poor quality of the Pt coating on the surface of the discs.**
Accomplishments/Progress/Results

• Activation Energy in Lithium-Air Electrolyte

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ceramic 1 Conductivity (10⁻⁴ S/cm)</th>
<th>PC(Li₂O) 2 Conductivity (10⁻⁴ S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>3.18</td>
<td>1.78</td>
</tr>
<tr>
<td>35</td>
<td>4.90</td>
<td>4.92</td>
</tr>
<tr>
<td>40</td>
<td>5.64</td>
<td>7.11</td>
</tr>
<tr>
<td>50</td>
<td>7.49</td>
<td>14.1</td>
</tr>
<tr>
<td>60</td>
<td>9.36</td>
<td>23.8</td>
</tr>
<tr>
<td>70</td>
<td>11.6</td>
<td>35.6</td>
</tr>
<tr>
<td>80</td>
<td>13.7</td>
<td>54.4</td>
</tr>
<tr>
<td>90</td>
<td>15.6</td>
<td>71.2</td>
</tr>
<tr>
<td>100</td>
<td>18.0</td>
<td>84.2</td>
</tr>
</tbody>
</table>

(i) Temperature dependent conductivity of Ceramic 1 and PC(Li₂O) 2

(ii) Arrhenius plot of the conductivity of (a) Ceramic 1 and (b) PC(Li₂O) 2

• Polymer electrolyte has higher activation energy than ceramic electrolyte

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• Lithium-Air Battery Fabrication and Characterization

An all solid cell was fabricated utilizing the Ni/C/LAGP based cathode, the PC(Li_2O)/LAGP/PC(BN) solid electrolyte, and a lithium metal anode.

• Primary test result: The highest OCV observed was 2.74 Volt at room air temperature and the cell lasted 16 days before the voltage dropped to below 2.0 Volt.
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

- **Task 5:** Alternative energy education program to include bio-energy and power.
  - An educational module preparation incorporating the project results for Bio-Power education

**Co-PI: Michigan Molecular Institute (MMI)**

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

- **Task 3:** High power density Lithium-Air battery at a reduced cost.
  - Optimize the combination of electrolyte that is best suitable for Li-air battery
  - Design and build the prototype
  - Test of prototype for durability and efficiency

**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)
## Future Work

### Future Work (FY2011-FY2012)

<table>
<thead>
<tr>
<th>Performance improvement of High temperature PEM membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Optimize a membrane electrode assembly (MEA) using PBI-phosphoric acid-POSS nanoadditive proton exchange membrane</td>
</tr>
<tr>
<td>- Test thermal stability and life-cycle sensitivity based on DOE matrix</td>
</tr>
<tr>
<td>- Map membrane conductivity history based on different RH cycles</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Design and build 5kWe catalytic flat plate fuel reformer based on CFD study</th>
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<tbody>
<tr>
<td>- Design layout of the reformer has to be developed</td>
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<tr>
<td>- Build the prototype using the optimized layout</td>
</tr>
<tr>
<td>- Test prototype performance and benchmark the results</td>
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<tr>
<td>- Develop cost analysis for a optimized reformer system</td>
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</tbody>
</table>
Future Work

- **Future Work (FY2011-FY2012)**

- **Explore other avenues for performance enhancement of Lithium-Air Battery**
  - The efforts for the next few quarters will be aimed at the assembly and testing of a working button cell battery utilizing the Ni/C/LAGP based cathode, the PC(Li$_2$O)/LAGP/PC(BN) solid electrolyte, and a lithium metal anode assembled in a 2032 button cell battery case.
  - Once a working battery is produced, efforts will then be focused on optimizing the processing steps to improve on 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).

- **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 giganteous (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 educator program for bio-energy and power.
Summary

Project Summary

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

Approach: Using patented polymer synthesis technology for high performance membrane, multi-fuel capable reformer based on CFD study, Lithium-Air battery based on high conductive polymer materials.

Technical Accomplishments and Progress: Advanced roll to roll HTPEM fuel cell membrane manufacturing procedure has been developed. A design layout of multi-fuel reformer is completed. Preliminary test of Lithium-Air battery performance evaluation is completed.

Technology Transfer/Collaborations: Active partnership with MMI, SVSU, presentations, publication and patents

Proposed Future Research: Seek answers by identifying factors limiting HTPEM fuel cell performance and Lithium-Air Battery.
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