Fiscal Year (FY) 2011 Objectives

- Research, develop and fabricate an improved high-temperature proton exchange membrane (PEM) fuel cell membrane capable of low-temperature starts (<100°C) with enhanced performance.
- Research, develop and fabricate a 5 kWe novel catalytic flat plate steam reforming process for extracting hydrogen from multi-fuels and integrate with high-temperature PEM fuel cell systems.
- Research and develop improved oxygen permeable membranes for high power density lithium-air battery with simple control systems and reduced cost.
- Research and develop a novel high energy yield agriculture bio-crop (Miscanthus) suitable for reformate fuel/alternative fuel with minimum impact on human food chain.
- Extend math and science alternative energy educator program to include bio-energy and power.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

| (A) Durability | (B) Cost | (C) Performance |

Technical Targets

This project is conducting fundamental studies to develop a new class of high-temperature PEM fuel cell materials capable of conducting protons at elevated temperature (180°C), multi-fuel reformer system, high power density lithium-air battery, and high energy yield bio-crop cost analysis and production model. If successful, insights gained from these studies will be applied toward the design and manufacturing of advanced membrane materials, lithium-air battery and multi-fuel reforming system that meet the following DOE 2015 targets:

- Cost: $20/m² for high-temperature PEM membrane.
- Improved membrane conductivity and durability.
- Cost-effective multi-fuel reformer system.
- High power density lithium-air battery with simple control systems at a reduced cost.
- High energy yield agriculture bio-crop cost analysis and production model.

FY 2011 Accomplishments

- Polybenzimidazole (PBI)-polyamide (PA) membrane with good mechanical integrity has been successfully fabricated and a reproducible fabrication method has been developed where molecular mass was a function of the mechanical stirrer torque. Fabricated PBI-PA membranes with high molecular mass and good mechanical integrity. Sulfonic acid polyhedral oligomeric silsesquioxane (POSS) nanoadditive (S-POSS) was already prepared on the 100-g scale. Phosphonic acid POSS (P-POSS) nanoadditive was also prepared on the 2-g scale.
- The developed high-temperature PBI-PA-based PEM membrane is capable of meeting proton conducting membrane materials requirement at a cost of 60% below the DOE targets for 2015. Fabrication of a membrane electrode assembly (MEA) (Pt/C-membrane-Pt/C) is currently underway subject to exact real-world fuel cell operating conditions.
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- Optimized design of a multi-fuel catalytic flat plate steam reformer with combustion and reforming catalyst separated by solid flat plate boundary is completed based on a computational fluid dynamics (CFD) model simulation results. Based on the optimized design, a first generation fuel reformer prototype has been fabricated. Currently we are testing the multi-fuel reformer prototype to generate data to benchmark the performance.
• Fabricated numerous button cell lithium-air battery prototypes to evaluate performance of various components. Characterized various battery properties including charge-discharge cycle testing, open-circuit voltage (OCV), and total charge-discharge capacity. Characterized electrolyte conductivity and electrode polarization resistance for improved performance of lithium-air battery. Fabricated an oxygen permeable membrane for lithium-air battery cathode with an oxygen permeability of $10^4$ to $4 \times 10^5$ barrer and a moisture permeability of 1 to 5 barrer.

• Two primary methods have been demonstrated at scale for the production of ethanol from cellulosic biomass crops, Miscanthus giganteus (MG) as a feedstock for ethanol: (i) giganteus hydrolysis and fermentation; and (ii) gasification and microbial reaction. The main output of this task will be a comprehensive cost- and energy-balance for the production of MG and its conversion to ethanol by each of these methods. A spreadsheet model has been developed that enables the practitioner/bio-crop producer to evaluate the role of key agronomic factors on MG production costs and net energy balance relative to those of alternative energy crops.

• Learning objectives for the alternative energy educator program (workshop) are being developed. The development of the instructional design document including instructional strategy methodologies has begun. The identification and/or development of learning activities that will engage the participants in the learning process are also in process.

Introduction

Low-temperature PEM fuel cells operate at 80°C and requires nearly pure (99.9999%) hydrogen [1]. However, the lack of a hydrogen refueling infrastructure has been a significant barrier for commercialization, especially for large volume markets such as commercial transport, military, silent watch, residential homes, telecommunications, and waste fuel processing to power applications [1]. To leverage the significant commercial potential of this emerging technology globally, the solution has always been considered to extend math and science alternative energy educator program to include the research results in bio-energy and power generation topics.

Approach

• Use patented novel polymer synthesis technology to prepare high-temperature proton exchange polymeric media that has been designed primarily to have high proton exchange capability at elevated temperature.

• Using CFD model results, design and fabricate a 5 kWe novel catalytic flat plate steam reforming system for extracting hydrogen from multi-fuels and integrate with high-temperature PEM fuel cell systems.
Results

In the past year, the main focus has been on S-POSS and P-POSS nanoadditive synthesis, and development of a method for synthesizing high molecular mass PBI in PPA, and casting mechanically robust membranes from the same PBI-PPA reaction solution. The S-POSS synthesis has been completed on a 100-g scale (one-step process, Figure 1a) and the P-POSS synthesis has been completed on a 2-g scale (three-step process, Figure 1b, in which the first two steps have been scaled up to 10-50 g). In order to achieve maximum molecular mass, and therefore the best film integrity upon casting for the PBI syntheses in PPA, it was determined that a precise 1:1 monomer ratio was of paramount importance, we found that 4% solids in PPA was optimum, and minor deviations in either direction caused a significant decrease in molecular mass (see Table 1). A digitally controlled stirrer was used and the torque (related to viscosity and molecular mass) was monitored during the reaction. After 24 hours at 205°C, a plateau torque value was measured. Regarding reaction vessels, plain wall resin kettles performed better than indented wall resin kettles (in which reagents were trapped in the indents). Films were cast by pouring the hot PPA mixture onto a substrate and spreading it using a doctor blade. Final membrane thickness can be controlled by adjusting the doctor blade setting (where the size of the gap determines the film thickness). Granite and glass substrates were evaluated and granite was selected because it had a flatter surface to ensure uniform film thickness, and appeared resistant to temperature and acid exposure. The membrane thickness in the final MEA should be able to be controlled by varying the time, temperature, and pressure during the MEA pressing process.

### TABLE 1. m-PBI Inherent Viscosity as a Function Of Reaction Conditions

<table>
<thead>
<tr>
<th>Reference</th>
<th>Time (hrs)</th>
<th>Temperature (°C)</th>
<th>% Solids in PPA</th>
<th>Inherent viscosity (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>805-13</td>
<td>168</td>
<td>205</td>
<td>6.52</td>
<td>1.597</td>
</tr>
<tr>
<td>805-18</td>
<td>96</td>
<td>205</td>
<td>6.18</td>
<td>0.866</td>
</tr>
<tr>
<td>815-1</td>
<td>24</td>
<td>205</td>
<td>3.75</td>
<td>1.585</td>
</tr>
<tr>
<td>815-4</td>
<td>72</td>
<td>205</td>
<td>4.00</td>
<td>2.419</td>
</tr>
<tr>
<td>815-9</td>
<td>48</td>
<td>205</td>
<td>4.00</td>
<td>2.247</td>
</tr>
<tr>
<td>815-12</td>
<td>48</td>
<td>205</td>
<td>3.99</td>
<td>1.779</td>
</tr>
</tbody>
</table>

During the past year, by taking into account the effect of channel length, inlet gas velocity and catalyst layer thickness for flat plate reformer system we optimized the multi-fuel reformer system with water-gas shift (WGS) reaction in order to build a flat plate reformer prototype for real world testing. Figure 2a represents the production of dry H₂ with WGS reaction and optimized reformer geometry for methane reforming. The reformer geometry is optimized based on the optimized channel height, inlet velocity and catalyst layer thickness. From Figure 2a we see that the production of dry hydrogen only went up by 2% (mole fraction of H₂ from 0.76 to 0.78) with the WGS reaction. It is due to the fact that no methane is available in the WGS zone to produce H₂. Figure 2b represents the production of dry CO with the WGS reaction and optimized reformer geometry. From Figure 2b we see that the amount of dry CO was reduced by more than 50% (mole fraction of CO went down from 0.158 to 0.072 on dry basis) with WGS reaction. Therefore, it is advantageous to include WGS reaction with the optimized fuel reformer geometry especially in order to get low CO-rich reformate H₂. We already built a flat plate fuel reformer based on this optimized simulation study and the real world testing is underway to evaluate the effect of different parametric conditions.

For the lithium-air battery, in the past year, the main focus has been on fluorinated hyperbranched polymer (HBP) synthesis for oxygen permeable membrane fabrication, cathode development, solid electrolyte development, cell fabrication, and cell characterization. The fluorinated HBP was synthesized using MMI’s patented bimolecular non-linear polymerization technology and used
in the oxygen selective membrane fabrication. A commercial porous PTFE/polypropylene (PP) support coated with the fluorinated HBP has been prepared. The evaluation for oxygen and moisture permeability is currently being carried out. Air cathodes for the lithium-air battery were based on nickel foam (current collector), carbon (electrical conductor), lithium aluminum germanium phosphate (LAGP)-based ion conductor, and PTFE (binder). The LAGP/C ratio was varied from 75/25 to 25/75 in order to obtain the best cell capacity and performance. A cobalt catalyst was explored which was found to enhance the cell capacity. The use of a solid ceramic electrolyte greatly improves safety and durability of the cells, but requires the cells to operate at elevated temperature for best performance. In addition, the rigid ceramic electrolyte can suppress dendrite formation from the lithium anode during the charging process. A literature process was replicated as a starting point to develop an optimum battery. A three-layer electrolyte comprising a LAGP ceramic center sandwiched between two polymer electrolytes was used. A polymer electrolyte was used as a protective layer to prevent the direct contact of Li metal with the ceramic disc. In addition, the polymer layers also improve the contact between the electrolyte and both the anode and cathode. Several kinds of polyethylene oxide (PEO)-based polymer electrolyte layers were prepared. PC(Li$_2$O), PC(BN), and PC(SN) discs were obtained by ball mill mixing followed by pressing at elevated temperature. The three layer PC(BN)/LAGP/PC(Li$_2$O) electrolyte was obtained by lamination of the three layers at elevated temperature. The conductivities of these solid electrolytes were measured and shown in Figure 3a. Solid button cells were fabricated utilizing the Ni/C/LAGP/PTFE based cathode, the PC(Li$_2$O)/LAGP/PC(BN) solid electrolyte, and a lithium metal anode. The cells were tested under dry air using a 0.1 mA discharge current. The OCV of the cells were above 3.1 V, however, the cells did not show any discharge capacity at room temperature. When the cells were tested at elevated temperature (60-80°C) they did show some discharge capability even in the absence of any catalyst in the cathode. The cell capacity increased with an increase of the amount of carbon in the cathode. In addition, as expected, the specific cell capacity was greatly enhanced with the addition of a Co$_3$O$_4$ catalyst to the cathode (1,160 mAh/g C). Although the cells showed some promising properties, the maximum discharge current allowed was small. The internal resistance of the cells was very high at room temperature (>2,000 ohm) and decreased with an increase of temperature. However, the same or even higher internal resistance with a single layer polymer electrolyte compared to that of a three layer electrolyte suggests that interfaces, not the electrolyte itself, are the main factors for the high internal resistance and thus a low discharge current. A cell with a liquid electrolyte wetted interface between the solid electrolyte and the Li anode showed significantly improved cell capacity as shown in Figure 3b. To improve on the small discharge current, alternative polymer and gel type electrolytes are being explored. HBP materials based on organosilane and polyethylene glycol (PEG) are under development. Siloxanes are nonvolatile, nonflammable, highly resistant to oxidation, nontoxic, have a low $T_g$, and are environmentally benign. PEG is effective in solvating lithium salts and thus is lithium ion conducting. To further improve on the electrolyte, polar molecules are attached to the HBP periphery. For example, the reaction of tetrakis(dimethylsiloxy)silane with diacrylated PEG was carried out in toluene in the presence of platinum catalyst. A portion of the Si-H end groups (50-90%) are converted into polar groups such as cyclic carbonate, which can increase solvation and ion pair separation ability of the HBP.
In addition, it was expected that fast molecular motion of the hyperbranched side chains would contribute to fast ionic transport.

For high energy-yield bio-fuel agriculture crop MG production, during the past year, we developed a spreadsheet model for predicting the costs of production of MG relative to other energy crops (eg. switchgrass). Results of these studies are drawn together with the purpose of providing the U.S. Department of Energy with a convenient and flexible method of calculating production costs relative to alternative energy crops. The method is based on a standard, cost-accounting approach reported in earlier studies on MG production by Khanna et al. [4]. Using discount methodology [4], that analysis accounts for the outputs generated and the inputs required (cash flow) over the lifespan of the crop. The main result is a calculation of net present value, which is the total margin over the crop lifetime, converted into equivalent value in today’s money. With that method, a breakeven price is calculated as the price in current dollars needed to offset all production costs over the lifetime of the crop discounted to current prices divided by the discounted value of successive crop yields.

\[
\text{Breakeven price} = \frac{\sum_{i=0}^{i_{\text{max}}} C_i / (1 + r)^i}{\sum_{i=0}^{i_{\text{max}}} \phi_i / (1 + r)^i} \tag{1}
\]

In this expression, \(i_{\text{max}}\) is the crop lifetime in years, \(\phi_i\) is the yield per hectare in year \(i\), \(r\) is the discount rate, and \(C_i\) is the cost of production per hectare in year \(i\). Currently, we are performing detailed sample calculations to guide the user in building a spreadsheet model. Costs of production are split between one-time establishment costs in year one, and annual maintenance and harvesting operations in each subsequent year. Costs of production are further split among the primary unit operations of rhizome propagation, crop establishment, cultivation, harvesting, baling and storage, and delivery to a bio-energy plant.

Conclusions and Future Directions

From FY 2010 to the current date has resulted in a great knowledge expansion regarding manufacturing processes of new high-temperature PEM materials, lithium-air battery development and fabrication process, and multi-fuel reformer prototype development. We now understood the manufacturing process of new materials and the performance validation protocols in quantitative terms at least at the laboratory-based manufacturing stage. We have a good understanding of the polymer chemistry, thermodynamics and electro-kinetics. This information is critical to develop new high-temperature membrane materials for fuel cell applications where chemical treatment, polymer casting, and performance evaluations are of the utmost importance. Although the DOE deliverables of our project to date have been achieved, this year we intend to submit final project report after finishing the following attributes:

- Having developed a reliable method of membrane fabrication, PBI-PPA membranes carrying S-POSS or P-POSS at appropriate loadings will be prepared, compared with PBI-PA control membranes, and characterized for in-plane proton conductivity, tensile strength and elongation to break, phosphoric acid content (via titration), and morphology and domain structure. The best method of making MEAs to specifications suitable for utilization in fuel cell stacks will be developed. MEAs will be evaluated in stacks and also used to make through-plane conductivity measurements.
- Evaluate the multi-fuel reformer performance for different parametric conditions and further refinement of multi-fuel reformer will be performed if needed.
- Further refinements to the cathode formulation, electrolyte composition, solid electrolyte fabrication, and/or button cell fabrication will be made and the resultant batteries will be tested to insure that a reproducible system is obtained. Lithium-air batteries
will then be fabricated incorporating the fluorinated HBP-based membranes and tested under varying relative humidity conditions to determine how effective the membranes are towards enabling oxygen permeation while retarding moisture permeation. Prototype battery fabrication will require switching to a pouch type battery with non-ceramic electrolytes to achieve the desired voltage and power output.

- Develop a detailed cost- and energy-balance for miscanthus production.

References


