

V.L.8 21st Century Renewable Fuels, Energy, and Materials Initiative*

K.J. Berry (Primary Contact), Susanta K. Das (co-PI), Abhijit Sarkar, Claire Hartmann-Thompson, C.H. Schilling, Steven E. Keinath, Jianfang Chai, James P. Godschalx, Salma Rahman, Li Sun, Edmund J. Stark and Dave Namenye

Center for Fuel Cell Systems and Powertrain Integrations
Kettering University
1700 University Avenue
Flint, MI 48504
Phone: (810) 762-7833
E-mail: jberry@kettering.edu, sdas@kettering.edu

DOE Managers

HQ: Dimitrios Papageorgopoulos
Phone: (202) 586-3388
E-mail: Dimitrios.Papageorgopoulos@ee.doe.gov

GO: James Alkire
Phone: (720) 356-1426
E-mail: James.Alkire@go.doe.gov

Contract Number: DE-EE0003109

Project Start Date: July 1, 2010

Project End Date: June 30, 2012

*Congressionally directed project

- (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.
- 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.

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 reformat 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:

- 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 4×10^3 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 as on-board fuel processing (or fuel reforming) for hydrogen extraction from locally available logistics fuels such as propane, diesel, JP8 fuel (for military), natural gas, methanol, ethanol, synthetic, and bio-renewable fuels [1]. However, the challenge has been the development of an on-board hydrogen fuel reforming “system” that is cost effective, compact, and commercially viable. Since the production of pure hydrogen required additional equipments and cost for fuel reforming, low-temperature PEM fuel cells are not a viable option for use with logistic fuels for large scale global fuel cell markets [1]. As such the primary technical and commercial challenge is the development of a cost-effective fuel cell electric power generation system capable

of using locally available logistics fuels and applicable for small- and large-scale applications worldwide. Traditionally, the approach has been to focus on the development of fuel reforming technology for low-temperature PEM fuel cells, including the removal of fuel impurities [1]. Unfortunately, this approach results in excessive fuel reformer cost, larger reformer size and high complexity. Conversely, our solution is to focus on the development of a more robust “PEM fuel cell combined with fuel reforming system” that is more tolerant of fuel impurities which reduces not only the fuel reformer cost, complexity, and size, but also increases the overall system efficiency. Since a high-temperature PEM fuel cell operates at 160-180°C, it allows the use of non-pure hydrogen (2% CO mixed with hydrogen stream) as a fuel [2] while maintaining the cost and expanding the application flexibility benefits comparable to low-temperature PEM fuel cells. The expected outcomes include: 1) more efficient use of thermal energy or by-product heat as a combined heat and power application resulting in high system efficiency; 2) reduction of balance-of-plant (BOP) components for cooling, water management and purification resulting in reduced maintenance and simpler operations and controls; 3) when using reformed fuels rather than pure hydrogen, the result is increased tolerance to carbon monoxide (CO) which reduce the equipment and capital cost necessary to remove fuel impurities; and 4) will move this emerging technology closer to meeting DOE’s 2015 power density target of 100 W/L for fuel cells and reformed fuels.

In this project, using Michigan Molecular Institute’s (MMI’s) patented [3] nanoadditives-based high-temperature PBI-PPA membranes those are known to be thermally stable up to 200°C with superior proton conductivity, we plan to test the performance of a 25 cm² active area high temperature PEM fuel cell with up to 5% CO mixed reformat directly pumped from the reformer to the cell. At Kettering, we designed and built the multi-fuel reformer based on a rigorous CFD model simulation to use locally available logistic fuels/bio-fuels. Bio-fuels are planned to be extracted from a high energy yield agriculture bio-crop, MG, which is suitable for bio-fuel extraction without any impact on human food chain. For fuel cell energy storage purpose, we are developing and fabricating lithium-air battery with superior charge-discharge capacity. Finally, we intend 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 a 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.

- Develop improved oxygen permeable polymer membranes for high power density lithium air battery and use it to design simple control systems at reduced cost.
- Develop and research of novel high energy yield agriculture bio-crop (Miscanthus) suitable for reformat fuel/alternative fuel with minimum impact on human food chain.

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 of 40 in-oz was measured. Regarding reaction vessels, plain wall resin kettles performed better than indented wall resin kettles (in which reagents were trapped in the

indentations). 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

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

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 reformat 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

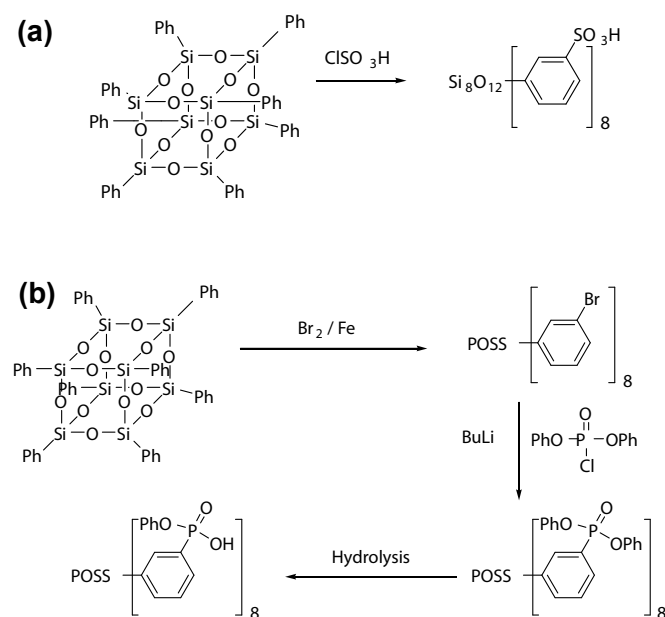


FIGURE 1. (a) Production of S-POSS Nanoadditive (b) Production of P-POSS Nanoadditive

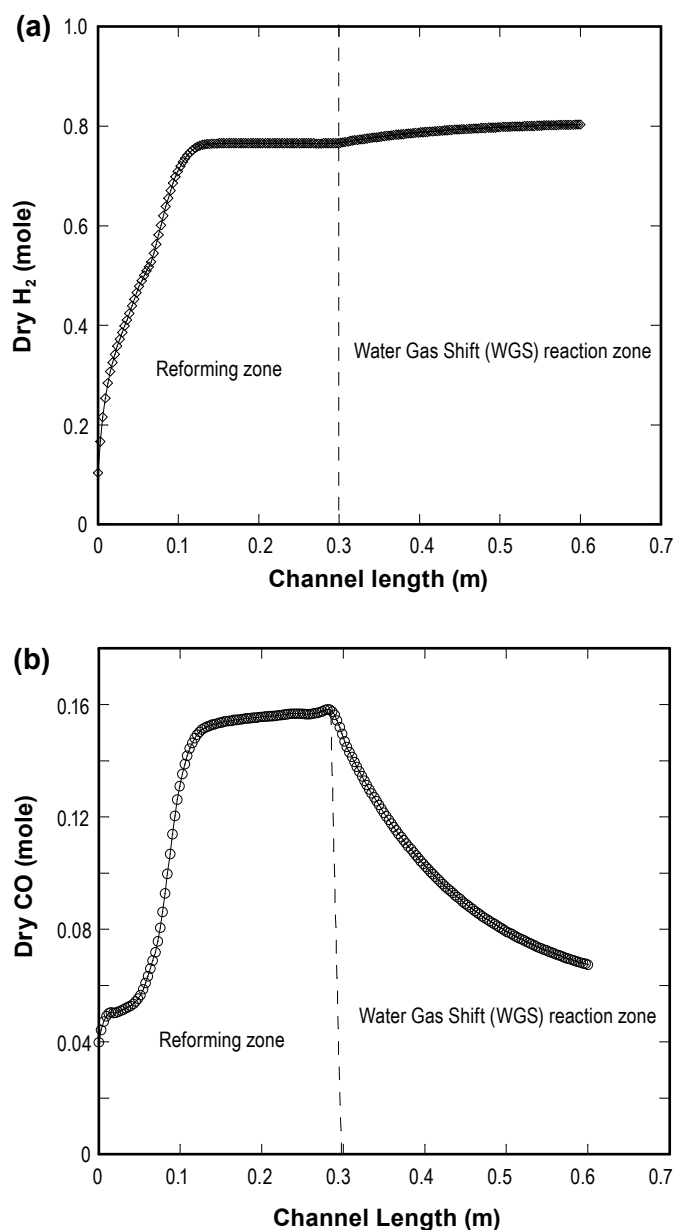


FIGURE 2. (a) Production of Dry H₂ with WGS and Optimized Reformer Geometry (b) Production of Dry CO with WGS and Optimized Reformer Geometry

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(Li₂O), 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(Li₂O) 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(Li₂O)/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 Co₃O₄ 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.

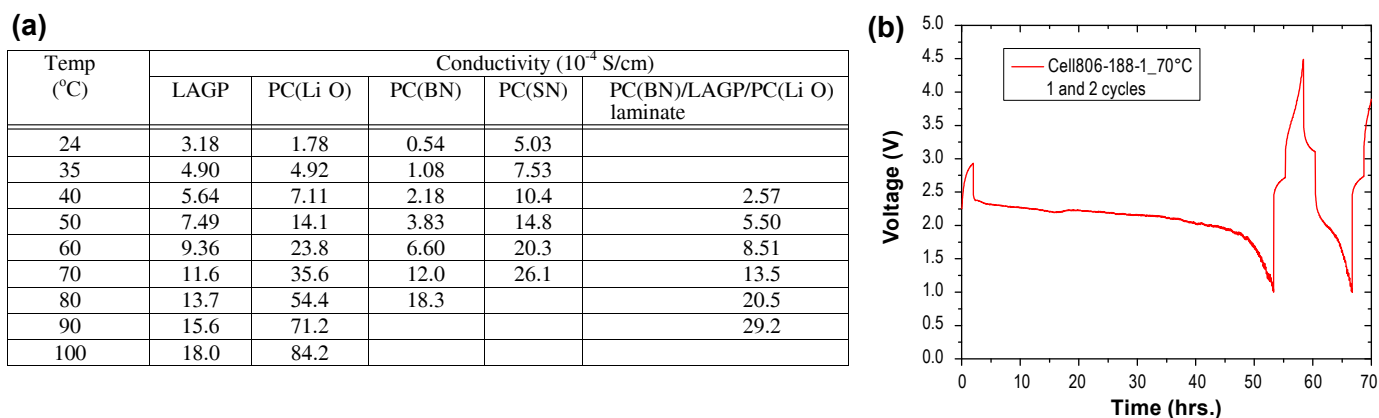


FIGURE 3. (a) Data of conductivity of the solid electrolyte components and three layer stacks. (b) The first two cycles (charge-discharge) of lithium-air battery prototype cell tested at 70°C.

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:

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

In this expression, i_{max} is the crop lifetime in years, ϕ_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 understand 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

1. Larminie J. and Dicks A., *Fuel cell systems explained*, John Wiley & Sons, New York (2000).
2. Susanta K. Das, Antonio R. and K. J. Berry, Experimental Evaluation of CO Poisoning on the Performance of a High Temperature PEM Fuel Cell Stack, *Journal of Power Sources*, Vol. 193, p. 691-698 (2009).
3. Improved Fuel Cell Proton Exchange Membranes, Nowak, R.; Hartmann-Thompson, C.; Bruza, K.; Thomas, L., Meier, D. (Michigan Molecular Institute, USA), WO 2008127645 A1 (2008).
4. Khanna, M., Dhungana, B., and Clifton-Brown, J., "Costs of producing Miscanthus and switchgrass for bioenergy in Illinois," *Biomass and Bioenergy*, Vol. 32, p. 482-493 (2008).