Session 3649

A STUDENT-ORIENTED FUEL CELL PROJECT AT PITTSBURG STATE UNIVERSITY (II): LOW PRESSURE-BASED FABRICATION PROCESS FOR THE MOLTEN CARBONATE FUEL CELL (MCFC) ELECTROLYTE MATRIX SUPPORT.

Christopher C. Ibeh, James W. Fonda/Shannon Birk
Pittsburg State University(PSU), Pittsburg, KS/University of Kansas(KU)

Abstract

There is an on-going student-oriented effort at Pittsburg State University to develop and fabricate a resilient and crack-free molten carbonate fuel cell (MCFC) electrolyte matrix support that is capable of functioning at the 650 ^{o}C operating temperature of the MCFC system. Students of the heat transfer, thermodynamics and plastics courses, and PSU/NSF-REU (Research Experiences for Undergraduates) summer program work on this project, in response to the EPA/Energy industry's search for pollutants-free, non-combustion energy systems. The project utilizes a compression molding-controlling fabrication process, and electrical performance of produced MCFC matrices are determined via resistivity analyzer measurements. Low pressures of less than 5000 psi yield the best results; high pressures tend to fracture the matrix. Room temperature volume resistivities of $10^3 – 10^5$ ohm-m have been achieved; a range much better than those of typical insulative materials ($10^{13} – 10^{16}$ ohm-m). Current efforts focus on reducing the resistivity values of fabricated MCFC matrices from the semi-conductive to the conductive range.

Introduction

In a previous paper[(1)] presented at the 1999 ASEE Conference in Charlotte, NC, the concept and use of the term (project) paper was espoused. The term paper embodies such concepts as choice of topic relevant to course content, literature search for development of knowledge base, experimentation for acquisition and analyses of data, report writing for development and improvement of communication skills, and report presentation for effective communication skills. The ultimate goal is to inculcate in the student the need for creativity and critical thinking skills. In this effort, the early 1990's students of the thermodynamics and heat transfer courses at Pittsburg State University were faced with the task of choosing projects to work on for their term papers.

Thermodynamics being the "study of energy and energy systems,"[(2)(3)(4)] and from the first law of thermodynamics, heat is a form of energy, the students were interested in projects that are energy-oriented, and they also wanted something that is meaningful, current and futuristic. The fuel cell represents such an energy system. The fuel cell is a non-combustion based energy system and meets EPA's and DOE's criteria for cleaner, pollutants-free environment[(5)(6)(7)(8)].

Considering that there are four major fuel cell systems under development: the Phosphoric Acid Fuel Cell (PAFC), the Molten Carbonate Fuel Cell (MCFC), the Solid Oxide Fuel Cell (SOFC) and the Polymer Electrolyte Membrane Fuel Cell (PEMFC), the students realized that for meaningfulness they had to focus on one type of fuel cell. To accomplish this, a simple Carnot efficiency feasibility analysis was performed on the four fuel cell systems:

$$\eta_t = 1 - (T_L/T_H);$$

where η_t is thermal efficiency, and T_L and T_H are the lowest and highest temperatures of a given system. For this analysis, T_L is the ambient temperature and T_H is the operating temperature of the system. Based on this, the SOFC with operating temperature of 1000 ^oC would have the highest efficiency followed by the MCFC at 650 ^oC. The PAFC and PEMFC operate at 200 ^oC and 80 ^oC respectively. The high operating temperatures of the MCFC and the SOFC unlike the PAFC and PEMFC, make them amenable to internal fuel reformation and direct use of hydrocarbon fuels instead of just hydrogen. Ofcourse, the students chose to work on the MCFC because of valid concerns of being able to handle the 1000 ^oC requirements of the SOFC in the laboratory.

Originally, the objective was to fabricate and assemble a complete molten carbonate fuel cell(9); while this is still true, the current approach is to design and fabricate a crack-free, resilient molten carbonate fuel cell electrolyte matrix capable of functioning at the 650 ^oC operating temperature of the MCFC. The high temperature-related cracking of the electrolyte matrix and the associated leakage of the electrolyte matrix material, and short circuiting, has been cited as a reason for the delay in full commercialization(10) of currently operating MCFC systems.

The Molten Carbonate Fuel Cell (MCFC) System

The MCFC is a non-combustion, electrochemical reactions-based energy system. In the MCFC, the electrochemical reaction between hydrogen and oxygen results in an electrical potential, and water, heat and carbon dioxide as by-products. (Carbon dioxide, a major component of the photosynthesis cycle is not as deleterious as carbon monoxide and nitrous oxides from combustion-based systems. Also, the MCFC requires introduction of carbon dioxide with oxygen at the cathode to maintain the carbonate level of the electrolyte system. Hence, the carbon dioxide by-product can be utilized as part of the feed air stream, thereby enhancing efficiency). With respect to the electrochemical reactions of the MCFC, the major components are the anode, cathode and electrolyte matrix. The molten carbonate electrolyte matrix serves primarily as a medium for conduction of carbonate ions ($CO_3^=$) from the cathode where they are generated to the anode where they react with the hydrogen ions (H^+) generated at the anode. The electrolyte also serves as a separator and electrical insulator for the electrodes. The MCFC electrolyte matrix plays a critical role, and by design should be impermeable to the gas streams, to prevent intermixing of the fuel (CH_4, H_2, CO) and oxidant streams(8)(10). Hence, it is important to have a void or crack-free electrolyte matrix; cracks in the electrolyte matrix are sources for electrolyte leakage and consequent resistive voltage loss in the MCFC. Equations 1, 2 and 3 are representative of the reactions of the MCFC. Hydrogen reacts with carbonate ions at the anode

$2H_2 + 2CO_3^= \text{--->} 2H_2O + 2CO_2 + 4e^-$ ----- EQ. 1
$4e^- + O_2 + 2CO_2 \text{--->} 2CO_3^=$ ---------- EQ. 2
$2H_2 + 2CO_2 + O_2 \text{--->} 2H_2O + 2CO_2$ ----- EQ. 3

and gives up electrons to become hydrogen ions. The electrons given up by hydrogen at the anode travel through the circuit to the cathode, and in the process cause an electrical potential to exist at the load. At the cathode, the air stream (oxygen and carbon dioxide) pick up the electrons to produce carbonate ions. The overall MCFC reaction is as per equation 3 and reflects the fact that carbon dioxide occurs at both the anode and cathode; carbon dioxide is a reactant at the cathode but a product at the anode.

Considering the critical role of the MCFC electrolyte matrix, the current effort focuses on the achievement of MCFC electrolyte matrix properties and characteristics via matrix composition formulation and fabrication process modification. The use of our in-house developed, low pressure molding fabrication process and polyolefin binder-based formulation accomplishes this.

Experimental Section

The strategic educational role of the term project is embodied in the experimental requirement; the term project requires the student to spend additional time (than the usual laboratory time) working with equipment and instrumentation in the effort to generate data and answers to the questions raised by the term paper topic. Typically, the student goes through the usual laboratory exercises with the approach that there is no need for mastery of the instrumentation. The term paper provides a setting to change this; to be able to successfully implement the term project, the student would need to correctly operate the equipment and instruments. The instructor facilitates this by providing specialized training on the equipment and instrumentation for the term project. This specialized or additional training on instrumentation synchronizes the goals of the student with that of the instructor, and ensures that useful and meaningful data is generated in the process. Mastery and utilization of instrumentation in project implementation provides the student with additional understanding of the subject of study; this learning concept is aptly stated by the motto of the college of technology at Pittsburg State University, “By Doing Learn.”

The major equipment used in this study are:
Polydimethyl siloxane-silicone oil heated C. W. Brabender Two-Roll Mill, Model 011, PH-2000,
Thermo-Electric Manufacturing Company Electric Oven, Model No. F-1730-1,
Blue M Electric Company Electric Muffle Furnace, Model No. 30A-1C, Serial No. 995,
Wabash Hydraulic Press, Moel No. 50-18-2TRM, and Carver Auto M 25 Ton Press,
Signatone Four-Point Probe Resistivity Analyzer With Plastic Head (SP4-625-85TC),
Amray 1200C Scanning Electron Microscope,
TA Instruments Differential Scanning Calorimeter (DSC 10),
Mettler AE100 Analytical Balance, and
Type K Thermocouple Electronic Digital Thermometer, Model No. 15-077-14.

The materials used in this study are:
Lithium aluminate, lithium carbonate, potassium carbonate from Aldrich Chemicals,
Polyisobuthylene (Vistanex) Grade 100, Exxon Chemicals,
Polyethylene, polypropylene, Fina Oil & Chemical Company,
Acrylonitrile butadiene styrene (ABS), Borg Warner Company.

The experimental procedure consists of five main stages:

1. Sintering; 90% by volume lithium aluminate is coated with 10% by volume lithium/potassium carbonate (62:38 mole%) mixture in an oven at 600 ^{o} C for about 45 minutes.
2. Mixing of coated lithium aluminate with binder material at 150 ^{o} C.
3. Blending of coated lithium aluminate and binder mixture at 150 ^{o} C.
4. Low pressure compression molding of blended mixture.
5. Performance testing of compression molded electrolyte matrix sheets via the resistivity analyzer and scanning electron microscope.

Results

Table 1: Resistivity (Ohm-m) Of Electrolyte Matrix Support Versus Current (I) (Nano-Amps) At Various Pressures (Weight-Equivalent) With Binder In Place (11)

Nano Amp (I)	Resistivity (Ohm-m)										
	< 0.5 Tons	0.5 Tons	1 Ton	1.25 Ton	1.5 Tons	2 Tons	2.5 Tons	3 Tons	5 Tons	10 Tons	20 Tons
1	1.5E6	1.5E6	1.5E6	5.0E5	9.0E5	8.0E5	1.0E6	8.0E5	8.0E5	2.9E5	8.0E5
3.5	3.9E5	4.0E5	3.5E5	1.5E5	2.2E5	2.3E5	3.0E5	2.0E5	2.0E5	1.1E5	2.2E5
10	1.5E5	1.6E5	2.0E5	6.0E4	9.0E4	8.0E4	1.0E5	8.0E4	9.0E4	6.5E4	9.4E4
30.5	6.0E4	7.0E4	9.0E4	2.5E4	4.0E4	3.0E4	4.0E4	2.8E4	3.8E4	3.0E4	3.5E4
100	4.0E4	5.0E4	6.8E4	2.1E4	3.0E4	2.1E4	2.2E4	2.1E4	2.8E4	2.8E4	2.3E4
300	2.0E4	3.0E4	1.2E4	1.0E4	1.6E4	1.0E4	1.2E4	1.0E4	1.8E4	1.5E4	1.2E4
1000	1.0E4	2.0E4		7.0E3	1.0E4	6.0E3	7.0E3	6.5E3	1.5E4	1.0E4	8.0E3
3000	4.5E3			2.0E3		2.5E3	2.5E3	2.5E3		5.0E3	
1E04	2.2E3			1.5E3		1.3E3	1.2E3	1.3E3			

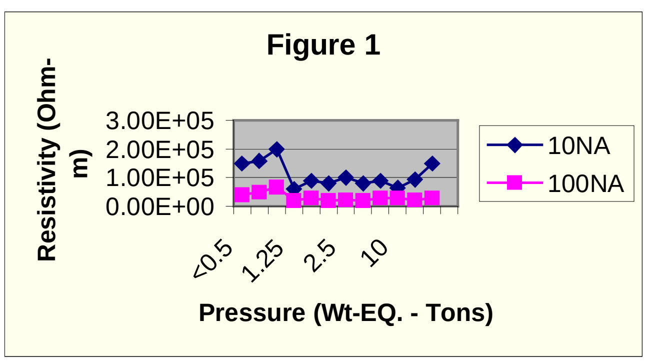

Figure 1: Resistivity Of Electrolyte Matrix Versus Fabrication Pressure At Various Nano-Amps.

Table 2: Resistivity (Ohm-m) Of Electrolyte Matrix Support Versus Current (I) (Nano-Amps) At Various Low Pressures (Psi) With Binder In Place[12]											
(I)	Resistivity (Ohm-m)										
Nano -Amp	175 psi	200 psi	300 psi	400 psi	450 psi	500 psi	600 psi	700 psi	800 psi	900 psi	1000 psi
10	1.4E4	1.2E5	7.7E4	1.E5	4.9E4	1.1E5	1.8E5	1.5E5	1.1E5	7.7E4	1.1E5
100	4.0E4	3.3E4	1.8E4	2.0E4	2.4E4	2.5E4	3.8E4	2.8E4	3.2E4	2.0E4	3.4E4

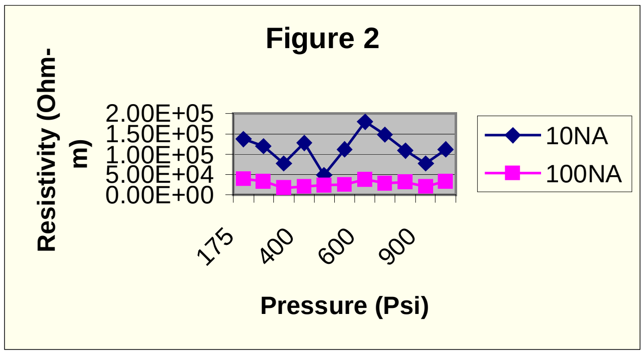

Figure 2: Resistivity Of Electrolyte Matrix Versus Fabrication Pressure At Various Nano-Amps.

Data on Tables 1 and 2 and Figures 1 and 2 are those of in-lab produced MCFC electrolyte matrix with polyisobutylene-based binder. Earlier and previous research [(11)(12(13)] with polyethylene, polypropylene, polyisobutylene and ABS (acrylonitrile-butadiene-styrene) as binders in MCFC electrolyte matrix indicate that polyisobutylene yields the best result in terms resistivity and potential conductivity. Hence, most of the current studies are on electrolyte matrices with polyisobutylene-based binders. Table 1 has data on the resistivity of MCFC electrolyte matrix at various fabrication weight-equivalents of pressure (up to 40 tons). Some of this data is also presented on Figure 1. Based on these and laboratory observation that high fabrication pressures tend to fracture the electrolyte matrix, the current research direction is to verify low fabrication pressure effects. Data on Table 2 and Figure 2 represent part of this effort; data on Table 2 are those of 1 square inch MCFC electrolyte matrix samples compression molded at 175 psi to 1000 psi pressures.

Discussion of Results

To date, most of the MCFC electrolyte matrix produced in our laboratory have resistivity values in the semiconductor range (10^3 – 10^5 ohm-m) [(11)(12)(13)]. Ofcourse, these are room temperature measurements; the MCFC operates at 650 ^{o} C, and any meaningful resistivity evaluations of the MCFC electrolyte matrix would need to reflect this. The electrolyte matrices are expected to have lower resistivities at higher temperatures. The current lack of high temperature resistivity analyzer head is a limitation of this research. To simulate or approximate high temperature behavior, the binder composition of the electrolyte matrix is burnt off prior to resistivity testing. This is accomplished by heating the sample in an oven at 600 ^{0} C for about 30 minutes; in the actual MCFC operation, the start-up process or the ramping from ambient to 650 ^{o} C accomplishes this. Hence, the choice of low temperature combustible materials such as polyolefins as binders in the molten carbonate fuel cell system. The resistivity values of electrolyte matrix samples with binder burnt-off tend to fall in the lower portion of the observed resistivity spectrum of ($10^3 – 10^5$ ohm-m). Data of Table 2 and Figure 2 indicate that lowest resistivities are achieved at fabrication pressures of 300 to 400 psi range and also in the 900 psi region. These reductions in resistivity are not dramatic and may suggest the refinining of fabrication process such as including higher fabrication pressures up to 5000 psi as suggested by data of Table 1 and Figure 1. Reductions in resistivity can also be achieved by modification of the electrolyte matrix composition. Current formulation centers around lithium and potassium carbonates; it may be necessary to include sodium carbonate in the formulation and to vary the lithium aluminate-carbonate ratio. However, preliminary investigations indicate that variation of the lithium aluminate-carbonate ratio to a higher carbonate level may result in lower electrolyte matrix support strength level. Achievement of the ultimate electrolyte matrix properties will require a careful balance of properties involving a combination of matrix reformulation and fabrication process modification. Use of the Scanning Electron Microscope (SEM) will play a vital role in determining the correlation between the effects of pressure on the morphology of fabricated electrolyte matrices and their consequent resistivities.

Pittsburg State University has secured the approval of Oak Ridge National laboratory (ORNL) for the establishment of a "Remote Electron Microscopy Site." This will facilitate the morphology studies of the fuel cell project.

Conclusion

The Student-Oriented Fuel Cell Project at Pittsburg State University is an on-going effort that provides students a "hands-on" education in the areas of design, development, formulation and fabrication of Molten Carbonate Fuel Cell (MCFC) electrolyte matrix support.

The in-house developed fabrication process for the MCFC electrolyte matrix support is viable, and is currently capable of producing electrolyte matrix support with resistivities in the semi-conductive range ($10^{-1} – 10^8$ ohm-m) [11][12][13][14][15].

The in-house developed fabrication process for the MCFC electrolyte matrix needs to be modified in an effort to achieve lower resistivities. Process modification will be in the areas of matrix composition reformulation and fabrication pressure variation.

There is a need for SEM studies to correlate the effects of fabrication pressure on electrolyte matrix morphology, and how these influence or relate to matrix resistivity, strength and overall performance.

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CHRISTOPHER C. IBEH

Christopher C. Ibeh is an Associate Professor of Plastics Engineering Technology at Pittsburg State University, Pittsburg, Kansas. He is also the Director of the Pittsburg State University, National Science Foundation-sponsored "interdisciplinary Materials Research Experiences for Undergraduates (REU)" program. Dr. Ibeh has a B.S. and an M.S. in Natural Gas Engineering from Texas A & M University, Kingsville, Texas, and a Doctor of Engineering degree from the department of Chemical Engineering, Louisiana Tech University, Ruston, Louisiana. Dr. Ibeh's areas of research interest include: plastics in fuel cells, biodegradable plastics for low temperature applications, and simulation techniques for optimization of processing parameters of polymeric materials.

SHANNON BIRK

Shannon Birk is a graduate of Fort Scott Community College, Fort Scott, Kansas. She is currently enrolled in the school of Pharmacy at the University of kansas (KU). Ms. Birk was one of the 9 REU student-participants of the 1998 PSU/NSF-REU summer program during which she worked on the fuel cell project.

JAMES FONDA

James Fonda is a graduate of Mineral Area College, Park Hills, MO. He is currently an exchange student in Britain where he is studying British Politics for his Humanities and History credit hours at the University of Missouri-Rolla. Mr. Fonda was one of the 9 REU student-participants of the 1999 PSU/NSF-REU summer program during which he worked on the low fabrication pressure effects on the Molten Carbonate fuel Cell Electrolyte Matrix.