

Development of Prototype Pultruded Structural Fuel Cell

by

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Abstract

Multifunctional composite materials offer the opportunity to combine features and introduce multiple functions in a single structure. The combination of structural support with the ability to produce power will be especially useful in many applications. Thoughtfully integrating these material advantages will lead to reductions in part count, installation effort, system weight, and cost. Fully-integrated, holistic design, material specification, fabrication, and assembly processes can offer tremendous gains in productivity in the manufacture of composite structures integrating multifunctionality. The current research focuses on the production of a multifunctional fuel cell through the pultrusion process. This product combines fuel cell technology with composite material technology to achieve a design that produces electrical power while displaying mechanical integrity. A design such as this, which would serve both to provide an electrical power source and to oppose mechanical loads that the system may experience during its operation, could prove beneficial for many space-restricted systems such as unmanned aerial vehicles or mobile military housing. Even further functionality could be achieved by utilizing the excess heat generated during fuel cell operation to heat a thermal reservoir or interior space in cold climates. This paper describes the manufacturing of a pultruded structural fuel cell and the characterization of the resulting functionality.

Introduction

The Pultruded Structural Fuel Cell (PSFC) is a multifunctional system that allows for the integration of

a fuel cell to generate electrical power while serving as part of a structure, be it a house, car, ship, tank or free-standing power source. This combination of functions allows for improved use of mass and space resulting in lighter, more transportable vehicles and structures and potential energy savings. The technology is particularly of interest to the U.S. Army, which is transitioning to a lighter and more agile force capable of rapid deployment. The creation of multifunctional materials which may perform multiple tasks can aid in this transformation [1,2]. In particular, materials that can produce power in addition to withstanding structural loads will allow for more efficient design.

In this study, the development of a multifunctional direct methanol fuel cell, ultimately manufactured through the continuous pultrusion process, is investigated. This cell combines composite materials with fuel cells to create a structure that will take advantage of the benefits of each technology. Composite materials are used extensively in U.S. Army structural applications due to their light weight, high strength and stiffness properties. Fuel cells produce power as long as they are supplied with fuel, thus eliminating the necessity of recharging or replacing batteries. A multifunctional fuel cell will produce power while simultaneously demonstrating mechanical integrity that will allow it to also become part of a structure. Potential applications for a cell of this type include unmanned aerial vehicles [3], troop carriers and housing materials.

In addition to incorporating multifunctionality, it is important that the material be producible in a cost effective manner for large quantities. Previous attempts to develop structural fuel cells have been conducted on a relatively small scale [1,3,4] and used hand layup or vacuum assisted resin transfer molding (VARTM) processes. The hand layup process involves the stacking of prepregged plies of reinforcing fabric and resin. The technique is very labor intensive technique and is difficult to scale to high volume or large components. The VARTM process is capable of producing large parts, though is still significantly less efficient than pultrusion. This paper focuses on developing a composite fuel cell through the highly efficient pultrusion process.

Because pultrusion is a continuous, automated process, it has the potential to create multifunctional composite fuel cells quickly and in high volumes. Reinforcing fibers and structural foam are continuously pulled through a bath of resin, through forming guides and finally through a heated die to create a constant cross section part [5]. It is envisioned that the fuel cell can be manufactured in a similar fashion within the pultruded material. A schematic of the pultrusion process including fuel cell assembly is shown in Fig 1.

Structural fuel cell elements (unit cell) would be produced in a continuous process and be able to be joined (adhesively bonded, span joined) to produce a panel or assembled sections, as shown in Fig. 2, that could be transported and joined to other sections and joints to form a practical structure. The exterior composite structure provides the load carrying capacity of the system and provides the containment and manifolding necessary to operate the fuel cell.

The fuel cell within the core of the system in the configuration shown requires little contribution of the core to carry the shear and normal stresses that would be present in a monolithic sandwich configuration. The fuel cell portion of the system would be composed of several components required to produce the electricity including the membrane electrode assembly (MEA), connections and diffusion layers for the fuel and products, and electrodes for the developed power.

Experimental Prototypes

Vacuum Assisted Resin Transfer Molding

Vacuum assisted resin transfer molding (VARTM) was the first manufacturing process used to create a multifunctional fuel cell at Virginia Tech. A custom MEA obtained commercially was used as the cell's chemical reaction site. The assembly was comprised of a ionic polymer catalyst loaded membrane with carbon cloth layers on each side. The membrane had a total area of 30 cm² (10 cm × 3 cm) and an electrode active area 22.5 cm² (9 cm × 2.5 cm). The catalyst loadings for the anode and cathode layers of the MEA were 2.0 mg/cm² of platinum-ruthenium and 4.0 mg/cm² of platinum, respectively.

Open cell aluminum foam was used as an electrical conductor/fuel distributor for the MEA. The 0.32 cm thick foam had a porosity of 20 pores per inch and a density of 8%. The length and width dimensions of the foam were 9 cm and 2.5 cm (the same dimensions as the active area of the MEA), respectively. A piece of foam was positioned on each side of the membrane electrode assembly. Next, holes were drilled along the inner faces of two 0.32 cm thick, 0.64 cm wide, hollow rectangular brass tubes. These tubes were then welded to two solid brass tubes to create a rectangular structure capable of delivering reactants to the fuel cell. One of these brass structures was used on each side of the cell. A thin sheet of brass was welded to each of the brass structures and laid onto each aluminum foam piece so that the electricity that the cell produced during its operation would eventually be conducted into the brass structure. Next, a sheet of silicon gasket material was placed on each side of the assembly to seal the cell and prevent leakage of the reactants during cell operation. A closed-cell foam

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core material was then added on each side of the cell to give the cell its structure in preparation for the resin transfer molding process. Fig. 3 shows the components of one half of the fuel cell along with the central membrane electrode assembly.

Once the fuel cell assembly was created, it was wrapped in plane weave glass fabric to prepare it for the VARTM process. Derakane 510A-40 vinyl ester resin was used along with Norox MEKP 925H initiator and Cobalt Napthenate 6% promoter for this process. The mass ratios of the components of the mixture were about 100 parts resin to 1 part initiator to 0.1 part promoter. The process was allowed to proceed for one night, and the completed cell was retrieved the next morning. The completed fuel cell is shown in Fig. 4.

Tests to evaluate the electrochemical capabilities of the cell were performed on a fuel cell test station manufactured by Fuel Cell Technologies, Inc. The fuel used during the tests was a methanol/de-ionized water solution which was 8% methanol by volume. All tests were performed at room temperature. The methanol solution was fed to the cell at a flow rate of 2 cm³/min with the aid of an external peristaltic pump.

Lower than expected fuel cell performance prompted an interest in reactions that may be occurring between the different materials that existed within the cell. This was accomplished with the help of a Field Emission Scanning Electron Microscope (FESEM) with Energy Dispersive X-ray Spectroscopy (EDS) capabilities. The microscope was used to evaluate the elemental composition of methanol solution which had traveled through the cell as well as aluminum foam which had been inside the cell during the chemical reactions. The methanol solution was set on a glass substrate and onto a hot plate to force the water to evaporate before it was examined under the microscope.

Pultrusion

The next multifunctional fuel cell was created using the pultrusion process. A custom membrane electrode assembly was also ordered from fuelcellstore.com for this cell. This assembly consisted of a Nafion 117® membrane which had a total area of 195 cm² (30 cm × 6.5 cm) and an electrode active area of 126 cm² (28 cm × 4.5 cm). Electrode loadings for this assembly were also 2.0 mg/cm² of platinum-ruthenium on the anode side and 4.0 mg/cm² of platinum on the cathode side.

Channeled 60% graphite/40% polyphenylene sulfide monopolar plates were used as electrical conductors/fuel distributors in this cell. The dimensions of the plates were approximately 30.5 cm × 5.7 cm. A custom aluminum mold was designed for their production. The

plates were created with a laboratory press by compression molding a wetlay precursor at 300°C and a load of nearly 66,725 newtons for approximately 10 minutes. Once the plates were produced, two holes were drilled through each of them to create inlet/outlet locations for fuel and gas reactants. An example of a pressed composite monopolar plate is shown in Fig. 5.

Custom polyvinyl chloride (PVC) fittings were created to allow for fuel and air connections. These fittings were attached to the holes in the plate using silicone sealant. Matching external fittings were also designed. A pair of fittings is shown in Fig. 6.

After the fittings were attached, the fuel cell assembly was created using each of the aforementioned components and a silicon gasket sealing material. The MEA was first placed in between two gaskets. A monopolar plate (with the attached fittings) was then placed on each side of the cell to complete the fuel cell assembly. Additional sealing was also provided using high temperature tape around the edges of the plate and on top of each fuel/air coupling. Custom, rectangular-shaped polyisocyanurate foam insulation was used to add structure to the fuel cell. The foam came in lengths of approximately 2.4 m. The width and thickness dimensions of the foam were approximately 5.7 cm and 3.7 cm, respectively. The foam dimensions allow for slight compression as part is pulled through the die. A section approximating the dimensions of the fuel cell assembly was removed from the center of the foam and replaced by the assembly to complete the preparation for the pultrusion. This resulting multifunctional foam core was then prepped for pultrusion by wrapping the ends of the fuel cell section with high temperature adhesive tape to prevent snagging during pultrusion. A diagram of the pultruded fuel cell is shown in Fig. 7.

Pultrusion of the prototype structural fuel cell was conducted at Strongwell Corp. using a standard die for a 6.35 x 4.13 cm tube with 0.318 cm wall thickness tube. The inner mandrel that would normally be used to fabricate a tube was replaced with the structural foam containing sections with the fuel cell assembly. The pultrusion materials (from the inside to the outside) consisted of the foam core/fuel cell assembly, an inner mat of M8643 E-Glass, 45 glass rovings (228 m/kg yield), and finally a 28 g Nico outside mat. Fig. 8 shows sections of the pultrusion process at Strongwell.

Once the pultrusion of the direct methanol fuel cell was complete, the cell location along the length of the beam was found with an electronic stud finder. Then an HP Faxitron 43804N cabinet x-ray device was used to obtain images of the cell so that the locations of the PVC fittings could be determined. Figure 9 displays radiographic images of a composite fuel cell.

After the locations of the fittings were known, holes were drilled into the cell so that inlet/outlet connections (which were compatible with the fuel cell test station) for the fuel and air reactants could be made. The connections consisted of hollow PVC base materials with standard Swagelok cores inserted. Electrical connection was made by installing a screw through the composite outer skin and foam until it contacted the monopolar plate. A section of pultruded fuel cell connected to the testing station is shown in Figure 10.

Electrochemical testing conditions

Electrochemical tests were performed on the cell at room temperature using a test station manufactured by Fuel Cell Technologies, Inc. An external peristaltic pump was used to feed a 2 M methanol solution to the anode side of the cell while air was fed to the cathode side. Polarization curves were obtained at various cell operating conditions. Unless otherwise indicated, pump flow rates were maintained at 2 cm³/min for all tests. Air flow rates were varied between 200 sccm and 1000 sccm.

Results and Discussion

VARTM cell

Fig. 11 shows an electrochemical curve obtained from the fuel cell test station for the cell manufactured through the VARTM process. This test was conducted at room temperature with a methanol flow rate of 2 cm³/min and an air flow rate of 250 sccm. The performance of the cell was less than ideal. The expected open circuit voltage for a direct methanol fuel cell such as this one is approximately 0.7 V. Also, current densities on the order of 100 mA/cm² or more should be expected from a cell of this type under similar operating conditions [6,7]. This cell, however, only reached an open circuit voltage of nearly 0.4 V. At 0.1 V, the cell achieved a current density of approximately 5.5 mA/cm². Furthermore, a test performed nearly one month after the cell's manufacture, showed that the open circuit voltage of the cell had dropped to less than 0.1 V.

The results of the SEM/EDS investigation are shown in Figs. 12 through 14. Figure 12 shows a microscopic image of the waste methanol solution residue that remained on the glass substrate after the water was evaporated. Figs. 13 and 14 are the spectrum of a clean glass substrate and the spectrum of the residue respectively, at location 5 from Fig. 12

Fig. 13 shows that oxygen and silicon are the major elements present in the glass substrate. These can be compared with high aluminum and oxygen concentrations in the methanol that traveled through the fuel cell.

It is evident that the conductive aluminum foam inside the fuel cell dissolved during the fuel cell operation.

Figs. 15 and 16 show SEM/EDS spectra from the analysis of the aluminum foam. Fig. 15 is a spectrum of a clean piece of aluminum foam while Fig. 16 shows a spectrum obtained from a piece of aluminum foam that was removed from the fuel cell once its operation ceased.

The figures obtained from the SEM/EDS study seem to support the idea that corrosion was a major issue for the fuel cell which was created through the VARTM process. Literature seems to agree with this idea. The environment that fuel cells experience makes corrosion or dissolution of metals very likely. Dissolved metal ions can poison the membrane and therefore lower the conductivity of the cell. Coating metallic plates with conductive layers which adhere well to the base metal without exposing it is commonly recommended [8].

Pultrusion Cell

Fig. 17 displays polarization curves obtained from the pultruded composite fuel cell at various air flow rates. Varying this flow rate seemed to have minimal effect on the power produced by the cell. The open circuit voltage reached at each flow rate was approximately 0.55 volts while each cell achieved a current density of just over 4 mA/cm² at 0.1 V

Overall, the electrochemical performance of the pultruded cell was also much lower than what should be expected from a direct methanol fuel cell. Several steps were taken to investigate the cause of the reduced pultruded fuel cell performance. Initially, the fuel cell was disassembled as seen in Fig 18. Resin was not found in interior of cell, however, the Nafion membrane was discolored in several locations. The change in color could possibly be due to excessive temperatures, exposure to styrene or hydration level of the membrane. In addition, a strong fermented odor was observed that was likely due to trapped contaminated moisture in the cell after testing. It is not believed however that either the discoloration of the membrane or the odor account for the large reduction in performance of the structural fuel cell.

To further investigate the cause of the reduced fuel cell performance, the flow characteristics of a cell during operation were investigated using radiography. Radiographic images of the cell were taken at a rate of 1 per second. Nonionic, low osmolar radiographic contrast medium (Omnipaque 350) was injected into the fuel inlet line. Minimal flow through channels was observed, as shown in Fig. 19. Most fuel "short circuited" following a path along the ends of the channels directly from the inlet to the outlet. Channel configurations similar to that used on these monopolar plates have shown to be effective

at routing the fuel over the entire membrane surface. However, the inclusion gasketing material to seal out the resin during pultrusion, may have caused the development of the shorter flow route.

Conclusions

The concept of a modular multifunctional composite fuel cell has been proposed and the ability of the vacuum assisted resin transfer molding and pultrusion processes to manufacture this cell have been proven. The metallic aluminum foam in the cell produced through the VARTM process seemed to contribute to its poor short-term performance and lack of ability to demonstrate any long-term performance. Corrosion and dissolution of the aluminum foam created problems with the fuel cell operation. Any corrosion layer on the surface of the aluminum surely increases the electrical resistance of the cell and therefore negatively affects its overall output. Non-metallic conductive materials or metallic materials with conductive coatings may be used to improve cell performance.

The pultruded fuel cell is promising technology that has been manufactured and will be fully tested in the near future. Pultrusion is one of the most efficient composite manufacturing techniques. Fuel cells manufactured through this process could be completed quickly and in high volumes. The cell that has been developed contains no metallic conductors and was therefore expected to exhibit performance superior to that of the cell produced by VARTM. The power produced by this cell (as well as the cell produced through the VARTM process) was lower than that which should be expected from a typical direct methanol fuel cell. Further investigations revealed that poor fuel flow resulted in the use of only a small percentage of the active area of the MEA to produce power. It is anticipated that the design of the current pultruded fuel cells may be modified to bring the power generation up to the level of conventional direct methanol fuel cells. In future research mechanical testing of the pultruded composite fuel cell during operation will be undertaken to further characterize the technology.

Acknowledgements

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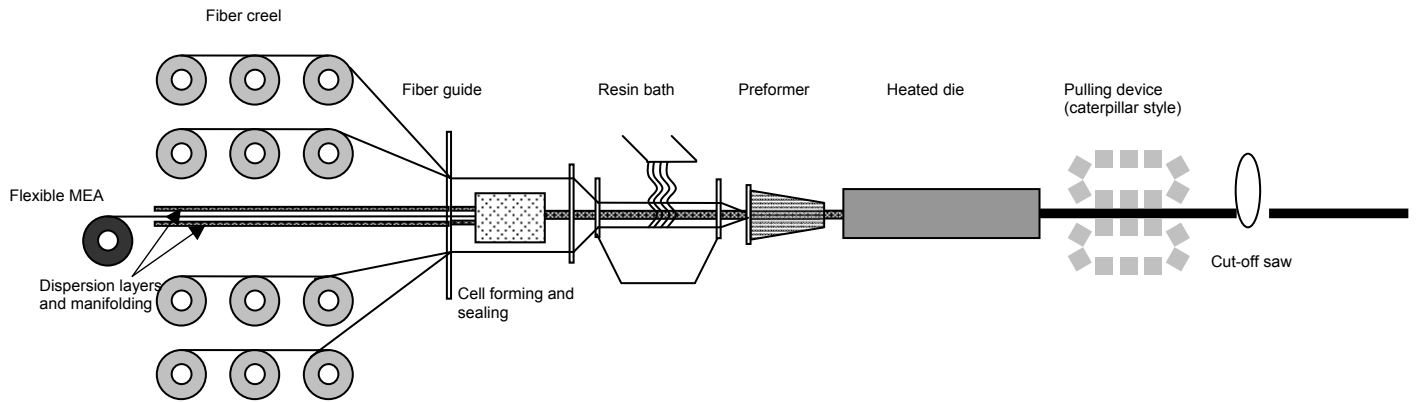


Figure – 1. Schematic of pultrusion process with fuel cell assembly.

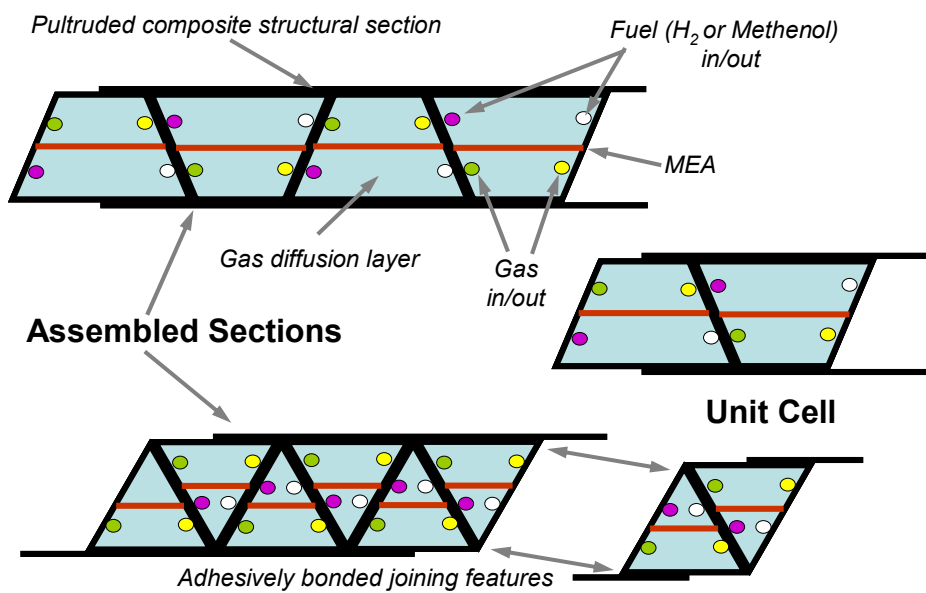


Figure – 2. Conceptual diagram of pultruded fuel cell panel.



Figure – 3. Components used to build the VARTM fuel cell assembly.



Figure – 4. Multifunctional fuel cell constructed through the VARTM process.



Figure – 5. Channeled composite monopolar plate (pre drilling).

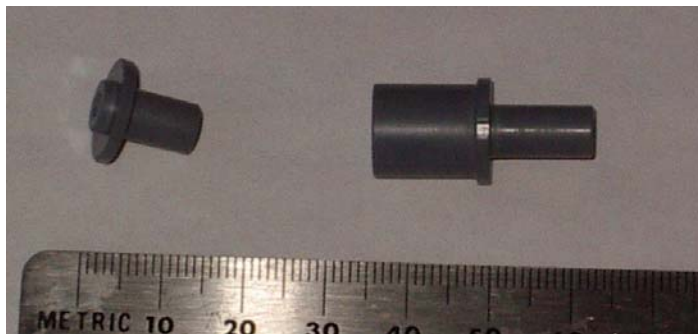


Figure – 6. Internal (left) and external (right) fitting for fuel cell air and fuel connections.

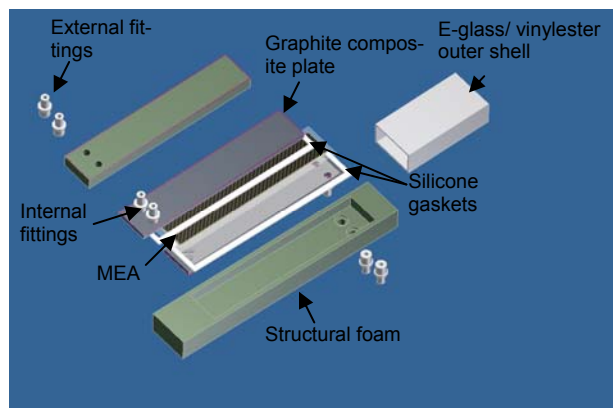


Figure – 7. Schematic of pultruded fuel cell including fuel/air connection.

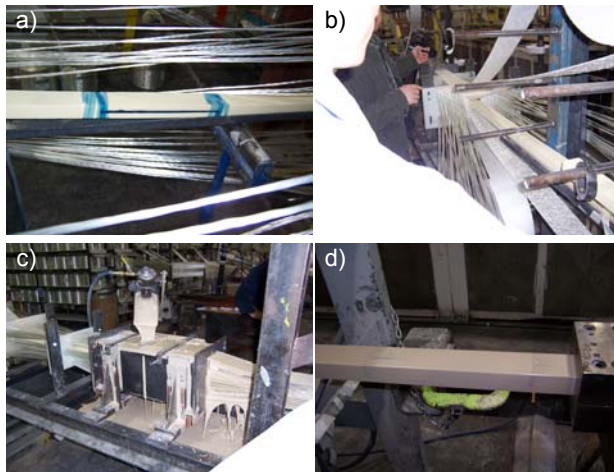


Figure – 8. a) Fuel cell embedded into foam being loaded onto pultrusion machine. b) The surfacing veil was marked to later identify the location of the embedded cells. c) Resin bath. d) Pultruded sandwich composite with embedded fuel cell exiting die.

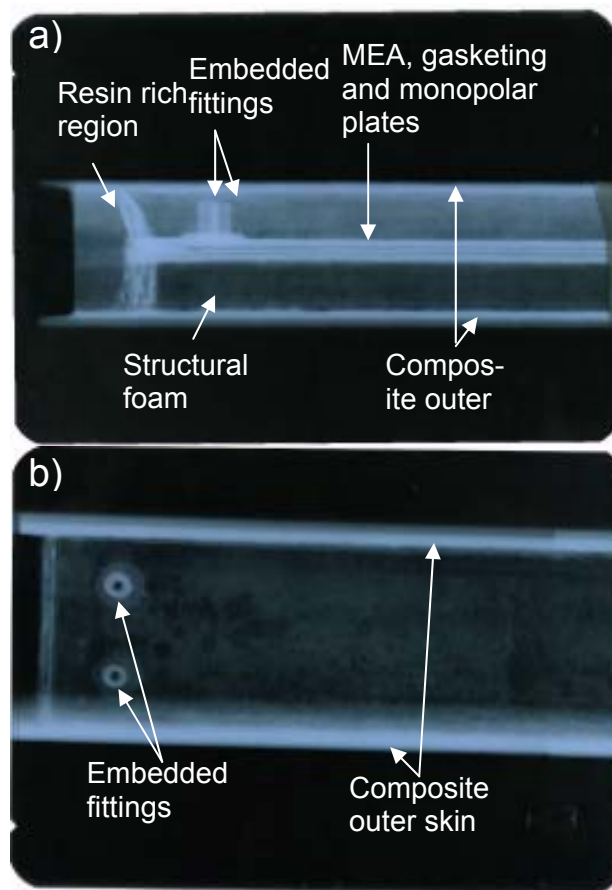


Figure – 9. a) Side view radiograph of pultruded fuel cell. b) Top view radiograph of the pultruded fuel cell beam.



Figure – 10. Fuel cell connected to test stand.

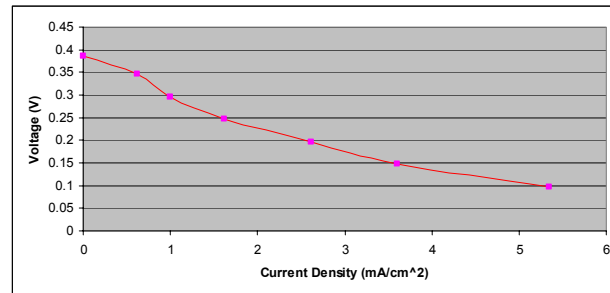


Figure – 11. Electrochemical curves from the composite fuel cell produced by VARTM.

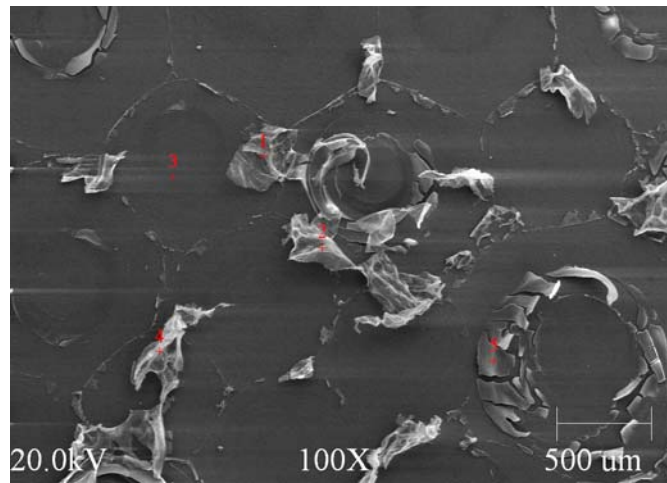


Figure – 12. SEM image of fuel cell waste methanol residue.

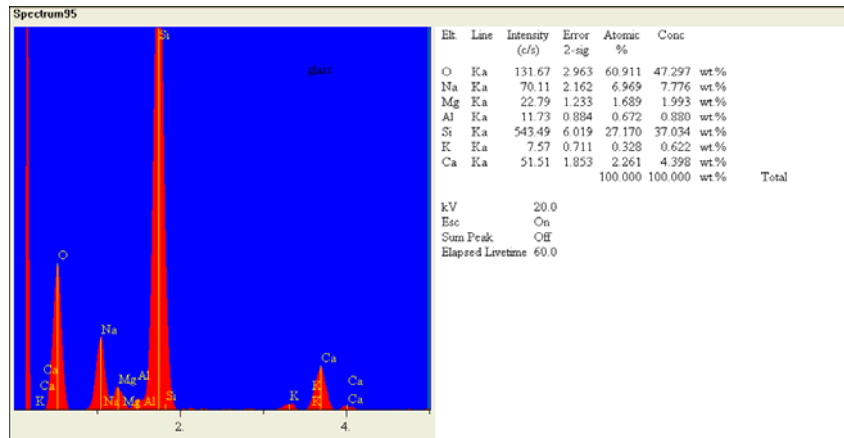


Figure – 13. EDS spectrum of a clean glass substrate.

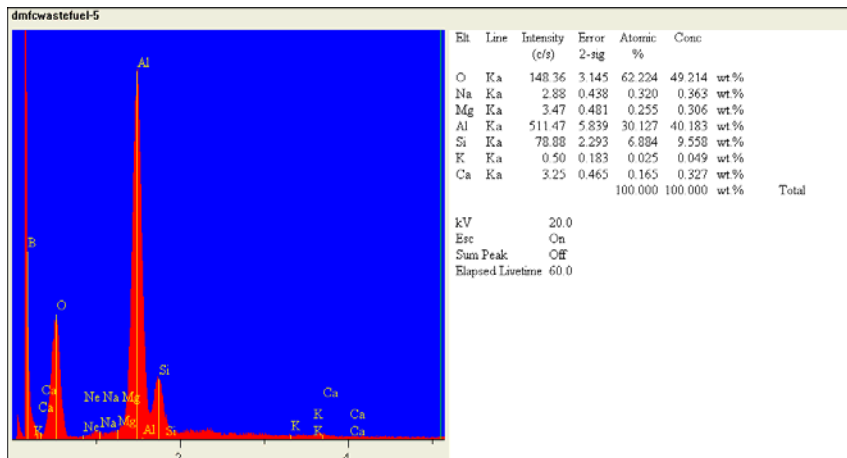


Figure – 14. EDS spectrum of the composition found in the waste residue (in Fig. 12. at location #5).

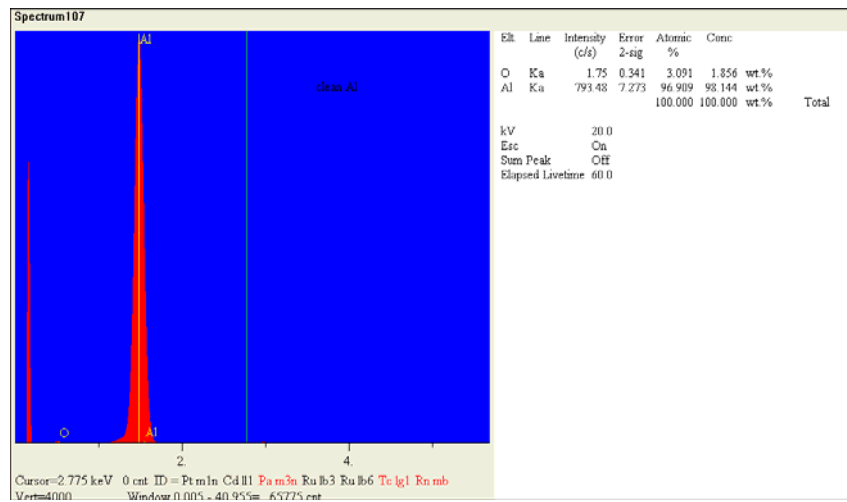


Figure – 15. EDS spectrum of a clean aluminum foam sample.

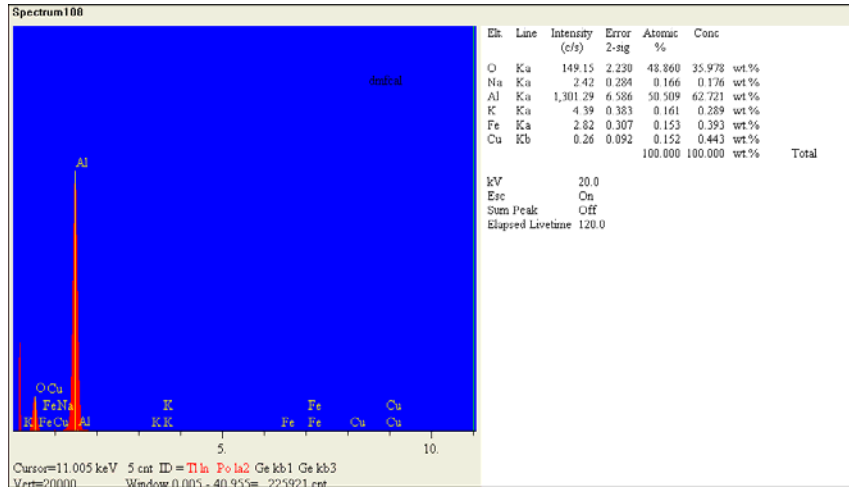


Figure – 16. EDS spectrum of an aluminum foam sample that was removed from the fuel cell.

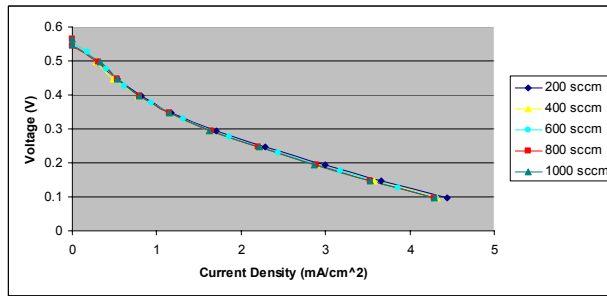


Figure – 17. Polarization curves from the pultruded cell at various air flow rates.



Figure – 18. Disassembled pultruded fuel cell.

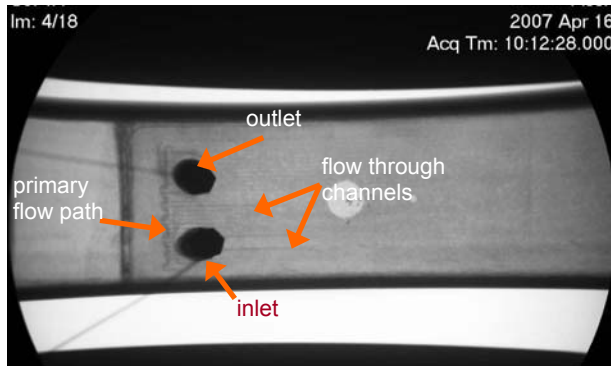


Figure – 19. Schematic of pultrusion process with fuel cell assembly.

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