Multiple Fuel and Current Collector Testing in Direct Water Methanol Fuel Cells

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Abstract

Testing of fuel cells, in particular Direct Methanol Fuel Cells (DMFC) is an excellent laboratory exercise that involves chemical thermodynamics, electrochemistry, and experimental engineering generally. The general technology of fuel cells and the more detailed technology of DMFCs are briefly discussed herein. This review highlights the advantages of DMFCs. The apparatus, procedure, and typical results for the educational testing of DMFCs are then presented, and the implications for further research and education are discussed.

Introduction

Taking an active role in developing this alternative energy conversion technology and power resource, students at the United States Military Academy (USMA) are constructing and testing DMFCs. Current fuel cell testing is being conducted at the Academy's fuel cell lab with some consultation from the Georgia Institute of Technology. Students are testing four materials for the current collection electrode, which are aluminum, stainless steel, titanium, and copper. In addition four different fuels - methanol, isopropanol, ethanol, and hydrogen - are also being tested. In addition to the educational benefits, DMFC technology is so new that the final results will help to determine the best fuel and electrode combinations necessary to achieve the optimal cell voltage and power density as well as to engineer the material selection and construction techniques that give the best cell longevity.

The testing will identify the best fuel and electrode combination, and the testing will also be a valuable learning experience for the students involved. Direct Water Methanol Fuel Cells (DMFC) are of special practical importance since they use a convenient liquid fuel. They have already been utilized in many different capacities such as small to medium scale and emergency power generation where batteries would have been utilized Destructive methanol crossover into the polymer electrolyte have been observed for concentrations higher than a 25% mixture by volume of methanol to water, and as this problem becomes prevalent it obviously limits the power and efficiency of the cell. This problem needs to be investigated with other fuels and possibly mitigated. With regard to fuel cell construction, performance is also limited by the design and electrical conductivity of the current collector material. Various materials with high conductivity could be used, but the effects of corrosion over a period of time will eventually affect fuel cell life; consequently, an optimal selection must be made considering the cost,

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durability, and conductivity of the metal. Ultimately, the on-going testing will provide a state of the art experimental experience to the students involved, and test results will help support related development of a promising and convenient power source.

General Background

The fuel cell is a clean and efficient device which electrochemically converts chemical energy into electricity. The fuel cell can employ hydrogen, hydrocarbons, methanol, or other alcohols to produce electricity. All fuel cells consist of an anode, a cathode, and an electrolyte like other galvanic cells. In other cells, such as common dry cells, the chemical reactants are consumed, and then the cell is useless and must be either recharged or discarded. In a fuel cell the fuel source can be replaced continuously while it is in use.

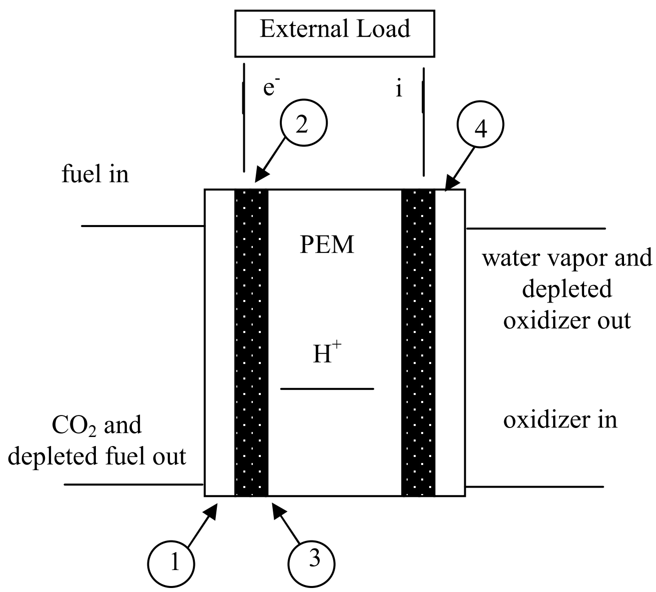

Figure 1. Basic PEM Fuel Cell
1-anode current collector, 2-anode diffusion layer.
3-anode catalytic electrode (CE), 4 -cathode CE

A practical power system contains a fuel cell stack. The stack is a series and/or parallel combination of cells, which are connected to produce a needed amount of direct current at the necessary voltage.

Fuel cell technology not only continues to improve upon existing technology, but also has started to create improved technologies because of the various needs for high efficiency power generation systems. There are several varieties of fuel cells, which can be characterized mainly by electrolyte composition and operating temperature. The different electrolyte compositions, molten, solid, and aqueous play a major role in fuel cell operation parameters, conditions, and applications such as vehicular, stationary, or space craft/station power.

The Alkaline Fuel Cell (AFC) is currently being used in space applications because of its relatively high efficiency and voltage output. It uses aqueous potassium hydroxide as the electrolyte. The AFC is designed to convert pure oxygen and hydrogen into electricity. Due to this fact, the cost for operating a fuel cell of this nature is relatively high; however, the operating temperatures range between 80 to 150 F. [6]

The Phosphoric Acid Fuel Cell (PAFC) uses phosphoric acid electrolyte to generate electricity at more than 40% efficiency. The operating temperatures range between 350 to 400 F.[2] Also, approximately 85% of the heat that the Acid Fuel Cell produces can be and in many cases is used for cogeneration. Because of the increase in industrial applications, efforts have been made to continually upgrade the PAFC and reduce the minor corrosion problems.

The Solid Oxide Fuel Cell (SOFC) is designed to be used in larger, high-power applications such as industrial and even large-scale central electricity generating stations. The (SOFC uses a hard ceramic electrolyte material which is fundamentally different from the previous liquid electrolyte concepts. The approximate operating pressures are between 3-5 atmospheres and temperatures up to 1,800 F. SOFC electrical generating efficiencies average between 65 and 70%.

The Proton Exchange Membrane (PEM) Fuel Cell operates at a temperature range of approximately 65 to 110 F. The PEM fuel cell has very high power density and one of the few fuel cell technologies that can vary its output quickly to meet shifts in power demand. Because of its design, this particular fuel cell is best suit for possible applications in automobiles in which a fast startup is necessary. The Department of Energy has also stated that the Proton Exchange Membrane Fuel Cell is the "primary candidate for light-duty vehicles, for buildings, and potentially for much smaller applications such as replacements for rechargeable batteries." [6]

The PEM uses a thin polymer sheet that is designed to allow hydrogen ions to pass through it. The hydrogen enters on the anode side of the fuel cell where a catalyst is located and causes the hydrogen atoms to release electrons and become hydrogen ions. It is here that the electric current is generated and will be utilized before returning to the cathode side of the fuel cell. The product at the completion of its chemical reaction is water (see chemical reaction 1.6). Direct Water Methanol Fuel Cell (DMFC) technology utilizes the chemical reactions between methanol, water, platinum, and ruthenium to create electricity. Methanol is a hydrocarbon fuel which, at low temperatures, can provide a large amount of electrochemical reactions when mixed with oxygen.[1] The products at the completion of this chemical reaction are water, carbon dioxide, direct voltage (D.C.), and current (see chemical reaction 1.3). Methanol in its pure form is highly corrosive and even in its watered down state corrosion is very likely over a period of time. Isopropyl alcohol can also be utilized in DFMC fuel cell structures. Isopropyl's products at the completion of its chemical reaction are water and acetone (see chemical reaction 1.7).

Table 1. Fuel Cell Reactions

(1) Direct Methanol Fuel Cell

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (1.1)

Cathode: $\frac{3}{2}O_2 + 6H + 6e^- \rightarrow 3H_2O$ (1.2)

Overall Reaction: $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$ (1.3)

(2) Hydrogen Fuel Cell

Anode: $H_2 \rightarrow 2H^+ + 2e^-$ (1.4)

Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (1.5)

Overall Reaction: $H_2 + \frac{1}{2}O_2 \rightarrow 2H_2O$ (1.6)

(3) Direct Isopropanol Cell, Overall Reaction

$CH_7OH + \frac{1}{2}O_2 \rightarrow (CH_3)_2CO + H_2O$ (1.7)

To the military, a low heat signature and minimal noise are important for battlefield survival. Fuel cells inherently have these features, so fuels cells and especially DMFCs are promising. Several areas of research concerning DMFCs still need to be explored in order to effectively utilize them in military and other applications. One area is an improved current collector and another is fuel flexibility.

Research on improving current collector performance by investigating various materials that have a medium to high range of electrical conductivity is currently being explored at the West Point Fuel Cell lab. Similar work is also underway at the Army Research Lab in Adelphi Maryland as well as at a number of fuel cell suppliers.[7] The goal is finding an improved or optimal current collector material. The current collector must not only have high electrical conductivity but also resist corrosion and dissipate heat well. ASTM tables[9] for average levels of material thermal and electrical conductivity were consulted concerning the material selection process for current collectors. Several promising materials were then identified and tested.

The lab is also engaged in developing fuel flexibility. Due to the wide variety of vehicles and equipment that move on to a battlefield, the military prefers bulk supplies that can be utilized by the majority of equipment. The most common fuel in the military is JP-8, which is used in all tanks and wheeled vehicles; however, other fuels such as commercial diesel fuel can be used in military vehicles achieving some fuel flexibility. To develop some similar fuel flexibility, the West Point fuel cell lab in conjunction with Georgia Institute of Technology is currently exploring a number of fuel variants that could work in a DMFC stack configuration. Currently direct hydrogen gas, isopropanol, and ethanol have proven to work in a basic DMFC during preliminary testing. This testing demonstrates that some fuel flexibility may be possible in DMFC applications.

The fuel cell lab is also promoting education. Cadets at the United States Military Academy School of Mechanical Engineering are currently learning how to construct a DMFC at the fuel cell lab. Cadets are taught not only basic chemical reactions and how cell oxidation occurs, but also how to improve the efficiency of the DMFC stack. Initially students work with the established MEA construction of Pt-Ru/Pt and Nafion 117 and a titanium current collector. As part of the engine and power plants course, a number of labs in which testing and optimization of various fuels for fuel cell power were conducted. At the end of the lab, the experimental fuel cell utilizing the ideal fuel mixture is connected to a model electric vehicle to race against fellow students. The more advanced students will also explore improving the current collectors during their yearlong senior capstone projects.

The work at West Point is part of a much larger overall effort. Recent advances in fuel cell technology and the decline in cell construction cost, have prompted studies in improving efficiency of fuel cells, in particular DMFCs. Several areas of focus for improving fuel cell efficiency are: (1) MEA construction, where the Nafion polymer is varied or manipulated in some way to decrease methanol crossover. (2) Fuel cell stack design, where the casing for the fuel cell is designed to allow better oxidation, natural oxidation on the cathode, or improved fuel follow on the anode side. (3) Fuel flexibility, where different concentrations and types of fuels are tested, the methanol concentration is varied to identify the highest concentration allowable before crossover can occur, or entirely different fuels are introduced and the results compared with methanol. (4) Current collector design, where construction and type of current collectors are tested in the areas of electrical and thermal conductivity as well as corrosion resistance. The United States Military Academy is currently working in the last two areas of interest.

Academic Research

As the cost of oil continues to increase and this as well as other natural resources begins to dwindle, the search for alternative power sources continues to increase. Exposing students to the general function and application of fuel cell technology will pave the way for even greater advancements for fuel cells as well as other possible alternative power technologies. Universities that look to improve their labs in the areas of automotive hybrid technology, power plant construction and power generation, or may just desire to have a well-rounded lab curriculum should consider utilizing direct water methanol fuel cells. The experimental apparatus and procedure that can be readily replicated elsewhere is described next. This apparatus is suitable for instructional labs as well as basic research on fuels and materials.

Small 3x3cm or 10x10cm Direct Water Methanol Fuel Cells (DMFC) (See figure 1.2) are relatively simple to construct and easy to maintain. DMFC's are ideal for class instruction, not only for their small size but also for a readily available and easily handled fuel source, methanol. Although methanol in its pure form is extremely hazardous to the skin and eyes and is very volatile, the fuel cell needs only 10-25% methanol solution and 80-75% water by volume. This dilution of methanol decreases the hazards to the skin and eyes and is no longer volatile. Since undergraduate engineering students have a background in thermal sciences and basic power consumption, efficiency will always be a major interest and a worthwhile feature to explore.

Objectives

The objectives of this project are the educational experience and two research topics. One is finding the most efficient DMFC current collector among some of the most commonly used materials in past fuel cells: titanium, copper, steel, and aluminum. Current collector materials will be compared in the areas of voltage, current, heat dissipation, and corrosion resistance. The second objective of this project is to find the ideal fuel source utilizing a basic DMFC stack configuration, and then matching it with the ideal current collector. The different fuels, methanol 20%, isopropyl alcohol 20%, ethyl alcohol 20%, and hydrogen gas, will be compared in the areas of cell power density, and voltage with and without an applied load.

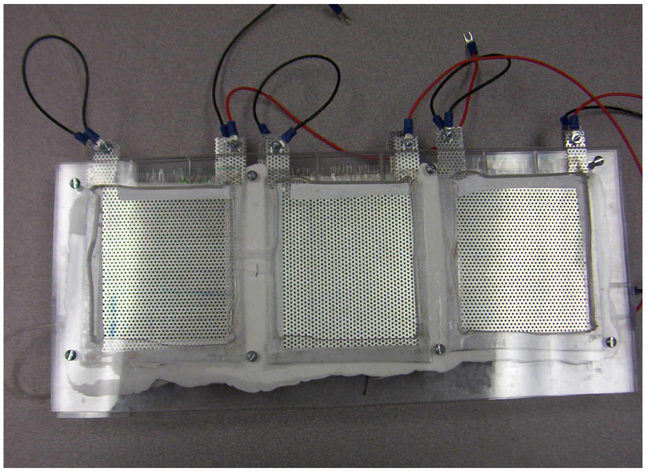

Figure 2: 10cm DMFC Fuel Cell Stack Constructed by USMA Cadets

Apparatus

The equipment and materials needed for fuel cell construction are: Teflon sheet, Nafion 117 polymer membrane which is platinum-coated perfluorosulfonic acid, Nafion 117 liquid solution, platinum powder, platinum-ruthenium powder, isopropyl alcohol, carbon cloth, distilled water, temperature regulated press, temperature regulated vacuum chamber, Plexiglas sheets, and titanium, copper, aluminum, or steel perforated plates.

First prepare the ink-like platinum and platinum ruthenium solutions that are used to create the catalytic electrodes. The solutions are created by mixing 20% distilled water with 40% Nafion polymer solution dissolved in alcohol. Then take 7% to 15% of this solution and mix it with 93% of finely divided particles of platinum for the cathode or 85% platinum ruthenium for the anode.

Next the actual membrane electrode assembly (MEA) is created. It is recommended that the following steps be performed in the order exactly as stated. The construction of the MEA begins with cutting two 10cm by 10cm pieces of Teflon sheet. This will be the transfer surface for the platinum and platinum ruthenium, which will be the catalytic electrode surfaces in the MEA. For quality control, weigh and record each Teflon square, and then set them on top of a heating element, which is kept at around but not exceeding 100°F. Coat one Teflon square with platinum black ink solution until the Teflon surface can no longer be seen. Coat the second Teflon square with platinum ruthenium black ink solution until the Teflon surface can no longer be seen. After the solutions dry on the Teflon, both Teflon squares should be at least 4 milligrams heavier. Cut one 10 x 10 cm Nafion-117 polymer square and dry it for 40 minutes in a temperature controlled vacuum press at 60°C. Place the two Teflon squares on each side of the Nafion polymer sheet with the coated sides are face down on the sheet and immediately place under a heated press until the temperature and pressure increase to 257°F and 500psi, wait one minute and remove. Pull the Teflon squares slowly away from the Nafion, the platinum and platinum ruthenium sides should stay on the Nafion. Immediately immerse into distilled water then remove. To ensure proper final assembly, label the platinum side of the MEA as O_2. This process completes the preparation of the basic MEA.

Next cut two 3x3cm sections of a the felt-like carbon diffusion layer material, cover each coated side of the MEA and place under the heated pressing machine until the temperature and pressure increase to 257 °F and 500 psi, wait one minute and remove. Construction of the cell is now complete except for the current collection electrode. Corrosion resistant materials such as titanium or graphite can be used to secure the MEA in the cell housing and is the medium that will transmit the D.C. voltage created by the chemical reactions on the membrane. The cell housing can be constructed by using Plexiglas, glass, or any non-corrosive water impermeable material.

Procedure

After construction and assembly of the MEAs and fuel cell casings were completed, students began to run a series of tests to determine if the fuel cell was constructed properly. The first test was for fuel leakage utilizing a simple fluid flow pump that can be purchased at a local fish aquarium pet store, pump distilled water into the fuel cell to maximum capacity and visually inspect for leakage. Once all leaks have been corrected by tightening the screws slowly in the general area while not over stressing the Plexiglas so that it does not crack, proceed with the voltage testing.

Empty the distilled water solution and pump a 20% methanol solution into the fuel cell. While visually inspecting for leaks use a DC multimeter and thermal couple to record the voltage and temperature. Since four different current collectors are being utilized in four separate fuel cell stack configurations, first check each individual cell for improper MEA placement. This can be determined by the voltage level, if the voltage level does not exceed 0.3 volts after 5 minutes or 0.2 for copper, then the MEA will need to be reversed so that the cathode oxidation side is facing outward.

Next conduct the open circuit voltage testing. Allow the fuel cells to operate for 30 minutes while recording temperature, voltage, and time. After 30 minutes, empty the fuel cells and flush with distilled water. Wait approximately 1 hour or whenever the residual chemical reactions have completed and the cell temperature has returned to room temperature. Repeat these steps after changing fuels. Initial testing has been limited to this open circuit testing. Future cell testing will include load and longevity voltage testing.

Results

Preliminary results for the different current collectors utilizing 20% methanol as a fuel show that the titanium yields the highest voltage with steel close behind, but copper had the lowest temperature while aluminum had the highest. Although the temperature ranges for each of the current collectors are of no surprise, the peak voltage was. Copper, which is a very good conductor of electricity, did not perform as well. Initial assumptions are that the methanol chemical reactions degrade the electrical conductivity.

Preliminary results for the different current collectors utilizing 20% isopropyl alcohol as a fuel show a very quick start up in chemical reactions and quickly achieved its peak voltage. At 30 minutes all the different current collectors had nearly the same voltage and varied only slightly in temperature.

Preliminary results for the different current collectors utilizing 20% methanol as a fuel show that the highest voltages for all cells occurred within the first 5 minutes of testing and then dropped significantly even though the temperatures continued to increase. In addition, the temperatures at 30 minutes were fairly similar to that of Isopropyl alcohol.

Conclusion

The preliminary results look very promising in the area of alternative fuels. The performance of isopropyl and ethyl alcohol when compared to the commonly used methanol fuel shows more research in the area of voltage performance over a longer period of time must be explored. Voltage load testing will also occur in the near future. Titanium was the initial top performer with all three fuels but was second in the area of temperature. Also, after completion of initial testing of the steel current collector fuel cell, corrosion apparently in the form of some sort of rust could visibly be seen over 60% of the surface area. Due to the flushing and introduction of the various fuels, we were unable to determine which fuel specifically caused the corrosion. Although methanol is the most corrosive fuel of the three tested, future tests will reveal which fuel or fuels caused the corrosion. Hydrogen gas will also be tested as an alternative fuel and will assist in the determination of the ideal fuel and current collector combination.

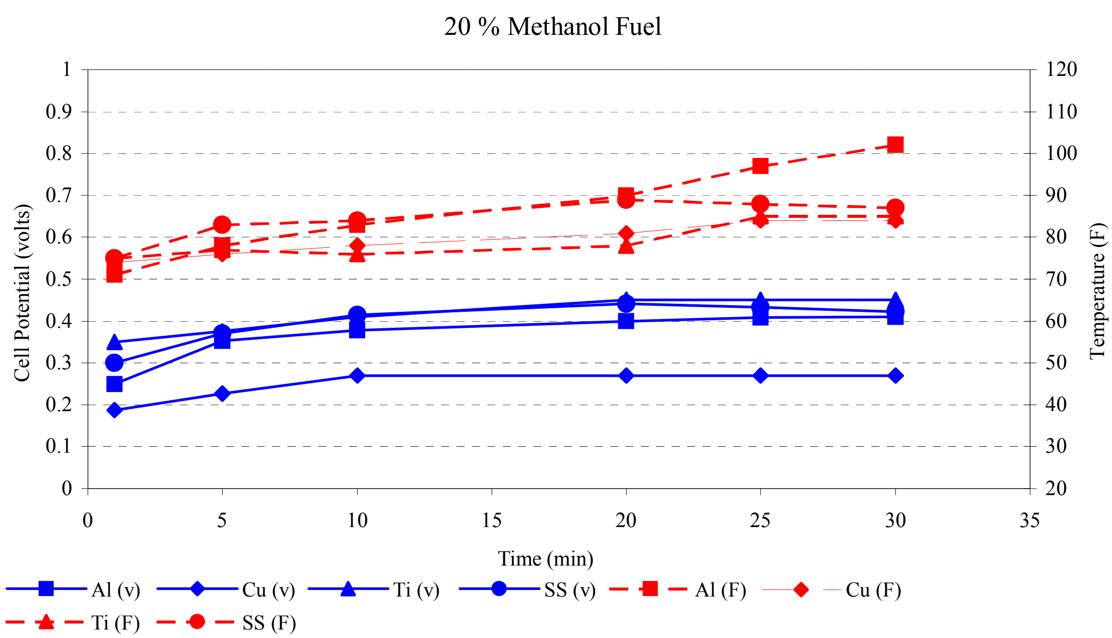

Figure 3. Results of Cell Testing with Different Current Collectors Utilizing 20% Methanol Fuel

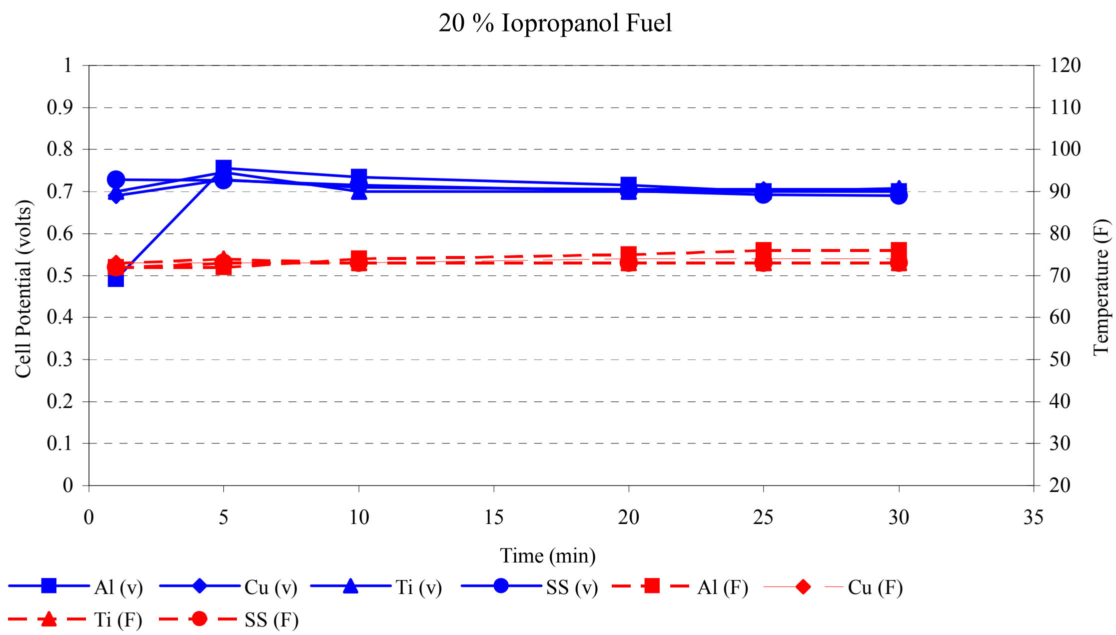

Figure 4. Results of Cell Testing with Different Current Collectors Utilizing 20% Isopropanol Fuel

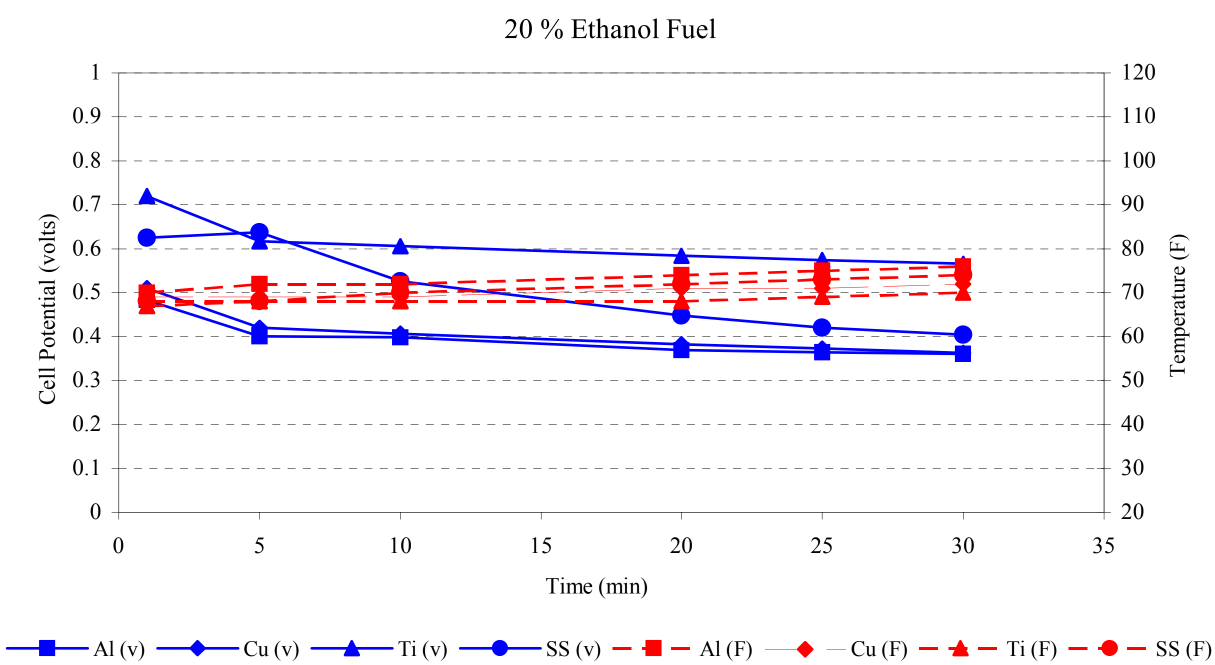

Figure 5. Results of Cell Testing with Different Current Collectors Utilizing 20% Ethanol Fuel

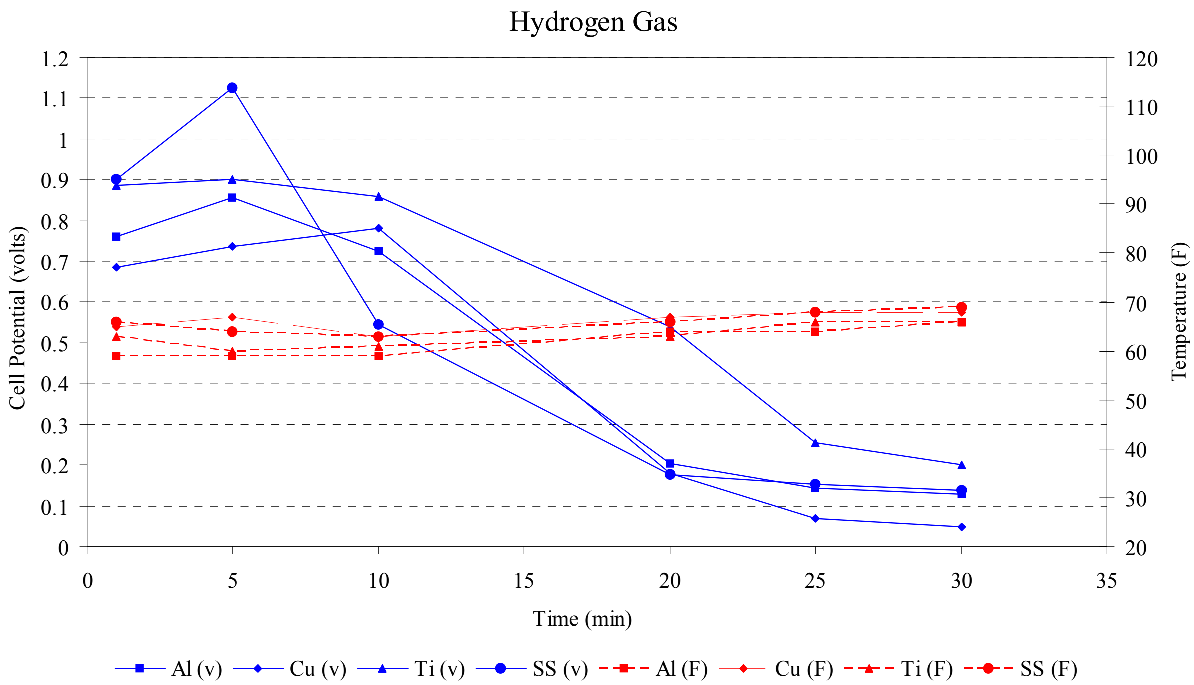

Figure 6. Results of Cell Testing with Different Current Collectors Utilizing Hydrogen Gas

(Hydrogen Gas flow was stopped after 2 minutes into testing)

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Biographical Information

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Has more than 25 years experience in graduate and undergraduate engineering education. Supervised more than ten Ph. D. thesis students, more than twelve M. S. thesis students, more than twenty M. S. special research project students, and numerous undergraduate students engaged in research and design projects. Has published more than forty refereed papers and over fifty major research reports along with numerous other papers and reports. Holds several patents.

MAJ DAWSON PLUMMER
Has more than 5 years experience in undergraduate engineering education. Trained, educated, and mentored more than fifty United States Military Academy Cadets who were later commissioned as officers in the United States Army. Has authored and Co-authored four research papers in the areas of fuel cells and multiphase fluid flow that were published in various journals. Currently has over ten years of service in the United States Army and has attended various specialty schools.