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ENHANCEMENT OF PERFORMANCE OF MICRO DIRECT ETHANOL FUEL CELLS BY STRUCTURAL MODIFICATION

by

SINDHUJA VALLURI

A THESIS

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Jonghyun Park, Advisor Frank Liou Ming Leu

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ABSTRACT

Direct Ethanol Fuel Cells (DEFC's) are becoming more important in current energy conversion devices because of their higher efficiency compared to other fuel cells. However, the performance of current DEFC's is not efficient in providing energy to meet increasing energy demand. The objective of this work is to make the cell compact and at the same time improve performance. For this purpose, we have removed gasket and endplates to make structure compact and increased surface area by developing a new corrugated structure. This work also uses 3D printing technology Fused Deposition Modeling (FDM) to make pocket backing case to improve sealing and production time. Studies of flow rate effects and elevated temperature impact on the performance of new cells have been made by comparing conventional cells. With the avoidance of the endplates and gaskets by using the proposed pocket model of assembly, the weight of the fuel cell decreases significantly. The corrugated structure has a surface area that is nearly 30% greater than conventional designs, which allows the use of membranes for wider catalytic coatings. Increased surface area greatly improves cell performance by enhancing available reaction sites. 3D printing cells can seal the better than the general structure of the cell and also reduce weight by removing the bolts. In summary, the proposed cells exhibit improved performance under all loading conditions, including increased flow rate and increased temperature.

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1. INTRODUCTION

The batteries have a wide range of applications in the powering the vehicles, mobiles, laptops and other portable devices. The Li-ion batteries and nickel-based batteries are trying to be in pace with growing energy needs and has been succeeded in powering various electronic devices. However, due to the advancement in the technology and development of variety of applications, the power generated is not meeting the needs. There has been an increasing pressure on the battery manufacturers to develop high energy density batteries to be used in the portable electronic world with high end applications. So, fuel cells became the possible solution for powering portable devices replacing the rechargeable batteries [1].

The increasing demand for clean energy and less emissions led to the development of fuel cells. Fuel cells (from hydrogen) generate water as the product decreasing the emissions produced by other electricity production like fossil fuels [2]. Earlier electrical power generating systems used to convert the chemical energy to heat energy and then heat energy to electrical energy [3]. But the fuel cells convert the chemical energy directly into the electrical energy by the reduction and oxidation reactions that occur at anode and cathode [4]. Generally fuel cells are used in the form of stacks to produce greater electric potentials by arranging multiple number of fuel cells in series as single fuel cells generate relatively less electric potentials. And, the amount of potential generated by fuel cells depends on various factors like the type of fuel cell, size of the cell, temperature at which cell is operated and the flow rates of the fuel and oxygen.

Compared to batteries, the fuel cells have greater energy density [5]. The plot illustrating energy density of different energy sources is shown below in Figure 1.1.

Figure 1.1. Energy densities plot

Considering the environment safety and the increased prices of fossil fuels, paved a path for the research in the field of renewable energy resources [2, 6]. Fuel cells has applications in various fields' i.e. stationary, transport, portable and micro power. For example, in portable applications where there is no grid connection, electric power from fuel cells instead from diesel generators avoids harmful emissions. Also, usage of fuel cells in telecommunication system has grown far and there is an estimate working duration of 5h for a laptop with fuel cell instead of a battery [7].

The basic structure of any fuel cell includes two electrodes i.e. anode and cathode separated by an electrolyte connected through an external circuit. The block diagram of a fuel cell containing the anode, cathode and electrolyte is shown in Figure1.2 below. The

electrodes of the cell are exposed to gas or liquid (source of hydrogen) and oxidant (source of oxygen). The structure of the electrodes should be porous in nature because the fuel and the oxidant should be permeable through them. The catalyst particles at anode separates the hydrogen from fuel into protons and electrons from which they take different paths to reach cathode. The electrolyte allows only protons to pass through it and not the electrons. The electrolyte is thus sometimes called as proton exchange membrane. The protons migrated through the electrolyte to cathode react with oxygen to produce water. Electrons are carried through an external circuit to reach the cathode where they conduct electricity. The ionic charge flow through the electrolyte is balanced by the electron flow in the circuit which generates an electric power [2, 8].

Figure 1.2. Block diagram of a fuel cell

The main components of a fuel cell include the flow field plate, current collector, gas diffusion layer and the membrane electrode assembly. The flow field plate includes the anode and the cathode flow field plates. Generally, flow field plates are called as bipolar plates (back plates) if there are multiple number of fuel cells arranged in a stack

and the flow pattern will be on both sides of the plates like the one shown in Figure 1.3 [39]. In a single fuel cell, the flow pattern will be just on one side of the plate. The design for flow field plates has become a matter of interest for researchers since many days. The performance of the cell depends on the flow field configuration i.e. channel length and the number of channels can also affect the performance. There are different kinds of flow patterns which includes pin type, serpentine and interdigitated designs. The flow field plates supply the reactant fuel and gases through the flow channels to the electrodes and provide the structural support for membrane electrode assemblies to facilitate water management in the cell [9]. The flow field plates usually account for three fourth of total weight of the cell.

Figure 1.3. Fuel cell stack

The current collectors are the source of collecting the current produced from the electron transport in the external circuit. These are generally placed between the flow field plates and the gas diffusion layer (GDL). The flow design should be inscribed on the current collector also which enables the flow of fuel along the channels from the flow field plate to the gas diffusion layer. Gas diffusion layer (GDL) acts as a backing material

for the membrane electrode assembly (MEA) which is typically a porous material made of carbon fibers which helps in current collection and acts as an electrical bridge between flow field plates and electrode. This allows the easy flow of reactants and the products through it and plays an important role in water management thereby controlling the usage of catalyst and cell performance [10].

The heart of the fuel cell is membrane electrode assembly (MEA). It is an assembly of membrane and the electrodes i.e. anode and cathode. Membrane is also called as electrolyte for fuel cells which may be either solid or liquid and it depends on the fuel chosen and the membrane must have reasonably low permeability of fuel in order to prevent the crossover issue in the direct alcohol fuel cells. From a very long time, the membrane being used is the Nafion membrane which is popularly known as polytetrafluorethylene (PTFE or Teflon) in the molecular level with a long chain of sulphonic acid at the end. Membrane is hydrophobic in nature and helps in water management. Other membranes which were investigated in literature are Hyflon and SPEEK, but these tend to have low mechanical stability [11]. MEA can be prepared by two methods i.e. Catalyst coated membrane (CCM) and Catalyst Coated Substrate (CCS) techniques.

In CCM technique, the catalyst ink has to be sprayed on both sides of the membrane either directly or by decal method. In direct method, catalyst ink has to be sprayed on to both sides of membrane and dried at 70 C or 100 C prior to assembling with carbon papers. In decal method, the catalyst ink has to be applied to a Mylar film on both sides and after drying this has to be compressed with membrane at 137 C and 65 kg/cm2 for 2.5 min so that the Mylar film gets peeled away. The obtained coated

membrane has to be immersed in hot water 80 C to remove ethylene glycol and dimethoxyethane if they are used during pretreatment and then dried at 100 C for another 15min. finally, these has to be assembled with GDL by compressing at 137 C and 1000psi for 2.5 min. In CCS technique, the catalyst ink has to be sprayed on both the gas diffusion layers and then assembled with the pretreated membrane at desired temperature and pressure [12, 13 and 14]. The catalyst ink is typically the catalysts like platinum, palladium or bimetallic catalysts on the carbon support mixed with ionomer like nafion solution, isopropanol and DI water.

The electrode design and the materials to be used for making the electrode depends on the electrolyte used. So, fuel cells are classified based on the type of electrolyte used and the operating temperature as alkaline fuel cell, phosphoric acid fuel cell, molten carbonate fuel cell, solid oxide fuel cell and polymer electrolyte membrane fuel cell. The first three cells are liquid-based electrolyte cells and the remaining two are solid based electrolyte cells. The molten carbonate and solid oxide fuel cell can be operated at high temperatures up to 1000°C and the remaining cells at room temperature to 100°C. The polymer electrolyte membrane cells are also called as proton exchange membrane fuel cells and they usually has the advantages of low weight and volume compared to other fuel cells and offers high power density. The polymer electrolyte membrane fuel cells attracted the researchers because of their easy operation at low temperatures upto 80°C. Most of the fuel cells uses fuels like hydrogen, alcohols like methanol and ethanol which are generally called as hydrogen fuel cells and alcohol fuel cells [15].

Direct alcohol fuel cells (DAFC) are the cells that convert the chemical energy stored in alcohols into electrical energy which are being employed in transportation and portable devices. The growing thirst for the usage of portable electronic devices like mobiles, notebooks and other electrical gadgets rises the demand for these fuel cells. Direct alcohol fuel cells are also advantageous than regular polymer electrolyte membrane (PEM) fuel cells which use hydrogen as their fuel [8]. Because DAFC's has comparatively high energy density and these don't face any storage problems. Also, these DAFC's can use electrocatalysts based on palladium, nickel and silver rather than costly platinum which is because of the faster reaction kinetics involving oxygen reduction. The alcohols used in the DAFC's are methanol, ethanol, ethylene glycol and 2-propanol. Among these, methanol and ethanol have attracted researcher's attention because of their superior properties compared to other fuels [16]. Methanol is considered as the simplest alcohol with just one carbon atom and can be oxidized easily. Due to some disadvantages of this fuel like high toxic nature, high flammability and non-renewable nature, this has been replaced with ethanol over time. The reaction kinetics for methanol fuel cells is quite sluggish because of the fuel crossover through the membrane to the oxygen electrode and anode poisoning by intermediates like CO. Also, from various reports energy produced from the direct methanol fuel cells is quite lesser.

Ethanol, a hydrogen rich liquid came into place to overcome these problems of methanol and has many advantages like non-toxicity, higher energy density and easy production from the renewable sources [17, 18]. Ethanol is considered a renewable energy source as it can also be produced from agricultural bioprocesses. And ethanol fuel cells show less crossover through the nafion membrane compared to the methanol fuel

cells [19]. Ethanol fuel cells are generally used in portable devices. For ethanol fuel cells, ethanol in its diluted form has to be supplied to anode of the fuel cell and air is supplied to cathode of the cell. By using the higher concentration ethanol, the crossover problem will be more. So mostly diluted form of ethanol is preferred. Ethanol is oxidized to form protons, electrons and carbondioxide at electrode/electrolyte interface. The protons are allowed through the membrane and the electrons are carried out through the external load. The protons react with the oxygen at cathode/electrolyte interface. The main objective of a direct ethanol fuel cell (DEFC) is to convert ethanol into carbon dioxide through complete oxidation reaction producing 12 electrons in one single reaction which is higher than the direct methanol fuel cell (DMFC) which produces only 6 electrons during the methanol oxidation. The basic layout of an ethanol fuel cell is shown in Figure 1.4. The key reactions involved in the ethanol fuel cell are:

Figure 1.4. Ethanol fuel cell

The major factors that contribute to the performance of the ethanol fuel cell are catalyst activity, membrane performance and the species transport within the cell. The need for highly active catalysts for the ethanol oxidation is one of the main challenges for the development of ethanol fuel cells. Platinum and palladium are taken into consideration for this aspect [20, 21]. But because of the high cost and formation of some intermediates, its applications are limited [22]. Some researchers also found that Pd/C showed higher ethanol oxidation than the Pt/C due to the efficiency of palladium catalyst in cleavage of C-C bond [23]. Palladium has some advantages like low cost, high electron conductivity and proton diffusivity. The performance of the fuel cells depends on nanoparticles have a better effect on the ethanol oxidation [24].

For alcohol fuel cells, crossover has been considered the major factor which can decrease the cell performance. From the literature, the crossover issue is comparatively less for ethanol than methanol fuel cells. The research has been going on to decrease the crossover issues and performance improvement which can be achieved by usage of membranes. Membranes are the heart for the fuel cell playing an important role in separating the reactions at anode and cathode and acts as a barrier by preventing the reaction between fuel and oxidant allowing only protons to flow through it. The membrane requirements for the ethanol fuel cell are low ethanol permeability and high ionic or proton conductivity. These characteristics can be seen in the perfluorinated sulfonic acid electrolyte membrane (Nafion membrane) [25, 26].

This research work is mainly focused on making four different type of ethanol fuel cells i.e. fabrication of the conventional micro ethanol fuel cell with a compact pocket structure eliminating gaskets, fabricating the cell with corrugated structures for the current collectors (also flow field plates) increasing the reaction site with same plane area as that of conventional cell, making a FDM printed cell to improve the sealing and time for fabrication.

The conventional fuel cell contains the endplates, bipolar plates, gaskets, current collectors, gas diffusion layer and the MEA. But in this work, a more compact structure has been developed where gaskets and endplates are avoided by making a pocket structure with acrylic material as backing plate which can accommodate all the parts i.e. current collector, GDL and MEA. This design provides the support and tight sealing without employing any gaskets which in turn decreases the weight of the cell significantly. The conventional cell and the cell with pocket structure are attached in Figures 1.5 and 1.6 below.

Figure 1.5. Conventional cell Figure 1.6. Pocket cell

This research also discusses the new corrugated structures for the membrane which can provide more total surface area for the electrocatalyst coating compared to the conventional structure. The membrane and the carbon cloth gas diffusion layer take the corrugated shape from the current collectors. The corrugated structures have been

modelled in solid works and machined in the workshop on the stainless steel current collectors. The corrugated structures offer nearly 30% area more total surface area compared to the conventional structures. The corrugations provided in this cell increases the reaction site for the electro catalyst enhancing the performance compared to the conventional model of the cell.

This works involves making a cell using FDM, a 3d printing technique. Fused deposition modeling (FDM), a 3D printing technique involves heating a thermoplastic material to its melting point and then deposition on top of or alongside the same material which then allows the material to adhere to itself to form a 3D shape. The 3D printer used is a Prusa I3 M201 purchased from Geetech, utilizing a 0.8mm nozzle tip which is as shown in figure below. FDM is used here to print the end or backing plates for the cell which can help in effective sealing where bolts are not needed and to make the cell in less time compared to conventional CNC machine. The FDM machine is shown below in Figure 1.7 below. The coil used in the FDM is of material Polycaprolactone (PCL).

Figure 1.7. Fused Deposition Modeling Machine

2. MATERIALS FOR CELL FABRICATION

The components of the fuel as discussed earlier are flow field plates for anode and cathode, end plates or backing plates, current collectors for anode and cathode, gas diffusion layer (GDL) and the MEA. From the literature, the materials used for end plates are graphite, stainless steel and some polymers like PMMA and PDMS. For this work, the end plates made of the polymer PMMA (commonly known as acrylic glass) has been chosen with a plain pocket structure on the anode and open-air structure for cathode i.e. fully made of holes as shown in Figure 2.1. The fuel ethanol is supplied through an inlet hole provided in the anode end plate and the oxygen from the cathode side through the holes. The chosen material challenges the conventional materials in the aspect of strength and corrosion [27]. The usage of PMMA provides good mechanical strength, corrosion resistance and good support for the cell. PMMA is strong and light weight material and has a very good impact strength [28]. The size of the end plate is 4cm*4cm for conventional cell and 5cm*5cm for the corrugated cell. PMMA has been purchased from McMaster Carr. These plates were fabricated with CNC machine in workshop.

Figure 2.1. Acrylic end plates

Gas diffusion layer (GDL) acts as a backing material for the membrane electrode assembly (MEA) which is typically a porous material made of carbon fibers. Carbon cloth, carbon paper and graphite felt are being used as the gas diffusion layers. For this research, carbon cloth (ELAT LT2400) of thickness 490µm has been chosen as the gas diffusion layer for conventional and corrugated cells and toray carbon paper of thickness 280µm has been chosen as gas diffusion layer for FDM printed cell and 3d printed cell. The size of GDL is 2.5cm*2.5cm for conventional and FDM printed cells and 3cm*3cm for corrugated cell. The carbon paper and carbon cloth were purchased from fuel cell store.

For conducting the electrons from anode, current collectors have to be placed in between flow field plates and the GDL. In literature different current collectors like gold coated aluminum coated plates, titanium, stainless steel plates and graphite sheets are being used [29]. Graphite being brittle is not a very option for usage as current collector here. By taking into account various factors like cost, corrosion and machinability, easily machinable 303 stainless steel has been employed as the current collector plates. In this work, the stainless steel plates alone acts as both the flow field plates and the current collectors. For this purpose, the serpentine flow channel design is made on anode plate and open-air design with holes all over the surface on cathode plate in order to allow the fuel and the air flow. The current collectors (also flow field plates) were designed in solid works and were machined in the workshop with CNC machine. The total planar area of the conventional current collectors is 2.5cm2 whereas the total surface area of corrugated current collectors is 3.25cm2 which is nearly 30% more than the conventional current collectors both having same planar area. By this corrugated structure, the area of reaction

site has been increased compared to the conventional structures. The conventional and the corrugated structures are shown in Figures 2.2 and 2.3 below.

For MEA, it is comprised of the membrane and the electrodes. Different membranes being in usage are perfluorosulfonic acid membranes like nafion membranes (112, 115, 117 and 211) and Sulfonated poly (ether ether ketone) (SPEEK) membranes [30, 31]. For the ethanol fuel cells, considering the crossover issue, good proton conductivity and mechanical stability nafion membranes has been chosen with grade 115. Nafion membrane was purchased from fuel cell store. Research has been going on the catalysts based on platinum, palladium and ruthenium supported on carbon. Different examples of catalysts are Pt/C, PtNi/C, PtSn/C, Pd/C, PdNi/C, PdSn/C, and PdNiSn/C, PdxRu/C $(x=1, 6, 12)$. Platinum based catalyst is not a good option here because of its high cost and nature of being poisoned by the intermediates formed in the ethanol oxidation like COads. So, by considering the cost issue and the poisoning of platinum catalysts, palladium supported on carbon has been chosen as the catalyst material [32, 33, 34 and 35]. For this work, 10 wt% Pd/C has been used as catalyst for all the cells for both anode and cathode.

3. EXPERIMENTATION DETAILS

Chemicals and materials

Vulcan XC72R and toray carbon paper, carbon cloth and nafion 115 membrane (purchased from fuel cell store); 10 wt % Pd/C (alfa aesar), H2O2, H2SO4, ethanol and 5wt % nafion solution (Sigma Aldrich) and other materials such as isopropanol, deionized water has been used for the experimentation.

3.1. CONVENTIONAL CELL WITH ELECTRO CATALYST INK COATED ON CARBON CLOTH (CELL 1)

Step 1: Membrane Pretreatment

Before the fabrication of electrodes, nafion membrane has to be pretreated to eliminate organic and inorganic contaminants. For this, the membrane has been boiled in 30% (v/v) H2O2 at 80 C for one hour and 8 wt. % H2SO4 at 80 $^{\circ}$ C for one hour and then the membrane has been immersed in deionized water at 80°C for one hour. The membrane has been stored in water until usage i.e. till hot pressing [35].

Step 2: Preparation of catalyst ink

Catalyst ink has been prepared by sonicating the mixture of 200mg of Pd/C catalyst powder with 0.36ml of 5wt % nafion solution and 0.68ml of isopropanol and sufficient amount of deionized water for one hour [36, 37]. This solution was placed in the magnetic stirrer for complete dissolution.

Step 3: Electrode Preparation

Catalyst Coated Substrate (CCS) technique has been chosen for the electrode preparation. The gas diffusion layers (carbon cloth) has been sprayed with the catalyst solution on one side and has been dried. The GDL's with catalyst ink coated over them are shown in Figure 3.1 below. The catalyst coated gas diffusion layers have been hot

pressed by keeping the pretreated membrane in between at a temperature of 135°C for 2 min at a pressure of 1000psi. The hot press machine is shown below in Figure 3.2.

Figure 3.1. Carbon cloths with catalyst ink coated over them.

Figure 3.2. Hot press machine

The hot-pressed membrane and the GDL's with the catalyst ink coated over them for conventional cell is shown in Figure 3.3 below. The hot-pressed membrane with

carbon cloths is then assembled together with the current collectors and the backing plates.

Figure 3.3. MEA hot pressed with GDL (conventional)

3.2. CORRUGATED CELL WITH ELECTRO CATALYST INK COATED ON CARBON CLOTH (CELL 1)

For this cell first two steps are same as in cell 1 except the current collectors are different from the cell 1. Electro catalyst ink has been coated on both the carbon cloths i.e. for anode and cathode and then dried. These catalyst coated carbon cloths are then hot pressed with the pretreated membrane. The corrugated shape is obtained by placing the membrane and GDL's in between the corrugated shaped stainless-steel parts. The corrugated steel parts are removed after the hot pressing is done to see the corrugations over the membrane with gas diffusion layer. The hot-pressed membrane and the GDL's with the catalyst ink coated over them for corrugated cell in the front and top view is shown in Figure 3.4 below.

Figure 3.4. MEA hot pressed with GDL (corrugated)

3.3. CELL FROM FUSED DEPOSITION MODELING (CELL 3)

Carbon paper is used as gas diffusion layer for this cell. All the steps are same as in the first cell, but the backing plates are made from the 3d printing. The hot-pressed membrane with carbon paper is as shown in the Figure 3.5 below.

Figure 3.5. Hot pressed membrane with carbon paper

The 3d design for the required parts is made in solid works and then transferred to the machine in STL format. First the anode backing plate is printed over the bed and then current collector is placed over it and then the hot-pressed membrane is placed over it. Now the cathode current collector is placed over the membrane and then cathode backing plate is printed over it which made the sealing good without using any glue or bolts. The FDM printed cell is shown in Figure 3.6 below.

Figure 3.6. FDM printed cell

4. RESULTS AND DISCUSSION

The micro direct ethanol fuel cell is tested at room temperature. The fuel has been supplied to the cell from the inlet at anode. A diaphragm pump has been used to supply the ethanol fuel at a feed rate of 2ml/min. The diluted ethanol solution has been prepared by mixing 6ml of pure ethanol and 54ml of deionized water. The cathode side has been open to air by which oxygen can be provided from the environment. The terminals of anode and cathode are connected to the battery cycler where the polarization curves are taken.

4.1. POLARIZATION CHARACTERISTICS

Three different cells (cells $1, 2 \& 3$) as indicated above has been tested and polarization curves has been taken to analyze the performance of the cell. For all the cells, the ethanol concentration is same. For polarization testing, the cells have been discharged at small currents for 30 seconds and relaxed them to notice trend of voltage vs current and the polarization plot is shown in Figure 4.1 below.

Figure 4.1. Polarization plot

The cells 1, 2 & 3 generated open circuit potentials of 72mV, 362mV and 68 mV respectively with cell 2 being higher. The polarization curves for conventional cell (cell 1), corrugated cell (cell 2) and FDM based cell (cell 3) are shown below in Figures 4.2 (a), (b) and (c). From the potentials, the power generated has been calculated and the resultant graphs are plotted.

Figure 4.2. Polarization curves for cells (a) conventional (b) corrugated (c) FDM

4.2. POLARIZATION COMPARISION FOR 3 CELLS

The comparison of performance of all three cells at room temperature and flow rate of 2ml/min is indicated by three curves plotted together as shown below in Figure 4.3. For the cells tested under the same conditions, corrugated cell showed better open circuit voltage compared to the conventional cell and FDM printed cell at room temperature. Even after discharging the cell at various current densities, the voltage values for corrugated cell showed better results compared to the remaining two cells. This improvement in the voltage for corrugated cell can be attributed to the increased surface area of MEA. All the cells have same planar area but for the corrugated cell the total surface area is more by approximately 30% enhancing the reaction site thereby improving the performance. The conventional cell and the FDM printed cell almost showed similar performance and this can be attributed to their same planar area. The corrugated cell showed highest open circuit potential of 362mV than the other two cells with values 72mV and 68mV. Also, the corrugated cell showed a peak power of 17.68µW while the other being 1.55µW only. The potential values are quite low compared to the literature values and this can be attributed to various operating conditions like non-uniform supply of oxygen through atmosphere, the variations in the cell temperature as cells are tested on different times, the ineffective removal of byproduct water through the evaporation, insufficient catalyst content in catalyst ink during electrode manufacturing (which is only 10% Pd in carbon). The water produced in all the cells has been seen leaked during testing the cell which usually should have to be evaporated itself in the cell. This water produced has been removed regularly during the testing.

Figure 4.3. Performance analysis of cells 1, 2 & 3

4.3. NORMALIZED POLARIZATION

Polarization curves normalized with respect to the planar area of electrode for conventional and corrugated cells is plotted. The total surface area of conventional electrode is 6.25 sq.cm and for corrugated cell the total surface area is 11.7 sq.cm considering the corrugations. The normalized plots with respect to electrode area are shown in Figure 4.4 below.

Figure 4.4. Normalized plots with respect to electrode area

Polarization curves normalized with respect to the planar area of membrane i.e. area of casing for conventional and corrugated cells is plotted. The total area of conventional cell is 16 sq.cm and for corrugated cell the total area is 25 sq.cm. The normalized polarization plots with respect to membrane area are shown in Figure 4.5 below.

Figure 4.5. Normalized plots with respect to membrane area

4.4. FLOW RATE IMPACT ON PERFORMANCE

Polarization curves were plotted for the cells at an increased flow rate of 3ml/min and this increased the corresponding potentials increasing the power generated. Increasing the flow rate is increasing the amount of the fuel supply i.e. hydrogen supply per minute which will thus generate more amount of electrons improving performance. The voltage drop from open circuit potential for cells at flow rate 3ml/min is quick compared to the cells at 2ml/min. this can be attributed to ethanol crossover with increased flow rate. The polarization curves are shown in Figure 4.6 below.

Figure 4.6. Polarization curves at flow rate 3ml/min

4.5. TEMPERATURE IMPACT ON PERFORMANCE

Polarization curves were plotted for the cells as in Figure 4.7 at an elevated temperature of about 90°C by placing the cells on hot plate. There has been a quite good increase in the open circuit voltage for the cells initially, but the voltage drop is very fast for these cells and this may be accounted for the improper setup used for increasing the temperature which is not very accurate and consistent.

Figure 4.7. Polarization curves at a temperature of 90°C

5. CONCLUSION

The pocket structured conventional cell has been fabricated without employing gaskets which paved a way for more compactness for the cell. The open circuit potential and the voltage values are quite less. New corrugated cell has been developed to increase the reaction site and the polarization curves clearly showed that these structures improved the performance of the cell to a good extent compared to the conventional and FDM structures. Also, fused deposition modeling has been used to 3d print the backing pocket structure for the cell which enhanced the sealing property and bolts has been eliminated. The time taken for fabricating the FDM printed cell is one and half hour which is quite less than the cell prepared from the conventional cell. The performance of the conventional and FDM printed cell is poor compared to the corrugated structured cell because of the less surface area. Also, the overall performance for all the cells is quite less than the literature values which can be due to various reasons like the ineffective water evaporation produced at the cathode side, non-uniform temperature and operating conditions and ineffective supply of air. The water leakage from ineffective evaporation can be solved by using water wicks to remove the water produced. The cell showed improved performance with increased flow rates which can be attributed to increased supply of fuel. Also, the cell performance has been improved at elevated temperature but needs quite improvements in the setup to get more uniform measurements.

REFERENCES

- 1. Dyer, Christopher K. "Fuel cells for portable applications." Fuel Cells Bulletin 2002.3 (2002): 8-9.
- 2. Carrette, L., K. A. Friedrich, and U1 Stimming. "Fuel cells–fundamentals and applications." Fuel cells 1.1 (2001): 5-39.
- 3. Bai, Zhengyu, et al. "Novel Ag@ C nanocables supported Pd anodes and its implication in energy conversion using direct liquid fuel cells." Applied Energy 175 (2016): 429-434.
- 4. Barbaro, Pierluigi, and Claudio Bianchini, eds. Catalysis for sustainable energy production. Weinheim, Germany: Wiley-VCH, 2009.
- 5. Zakaria, Z., Siti Kartom Kamarudin, and S. N. Timmiati. "Membranes for direct ethanol fuel cells: an overview." Applied Energy 163 (2016): 334-342.
- 6. Giddey, Sarb, et al. "A comprehensive review of direct carbon fuel cell technology." Progress in Energy and Combustion Science 38.3 (2012): 360-399.
- 7. Haile, Sossina M. "Fuel cell materials and components." Acta Materialia 51.19 (2003): 5981-6000.
- 8. Mehmood, Asad, et al. "A review on durability issues and restoration techniques in long-term operations of direct methanol fuel cells." Journal of Power Sources 297 (2015): 224-241.
- 9. Li, Xianguo, and Imran Sabir. "Review of bipolar plates in PEM fuel cells: Flow-field designs." International journal of hydrogen energy 30.4 (2005): 359-371.
- 10. Park, Sehkyu, Jong-Won Lee, and Branko N. Popov. "A review of gas diffusion layer in PEM fuel cells: materials and designs." International Journal of Hydrogen Energy 37.7 (2012): 5850-5865.
- 11. Silva, V. S., et al. "Proton electrolyte membrane properties and direct methanol fuel cell performance: I. Characterization of hybrid sulfonated poly (ether ether ketone)/zirconium oxide membranes." Journal of Power Sources 140.1 (2005): 34-40.
- 12. Thanasilp, Sarawalee, and Mali Hunsom. "Effect of MEA fabrication techniques on the cell performance of Pt–Pd/C electrocatalyst for oxygen reduction in PEM fuel cell." Fuel 89.12 (2010): 3847-3852.
- 13. Prasanna, M., et al. "Effects of MEA fabrication method on durability of polymer electrolyte membrane fuel cells." Electrochimica Acta 53.16 (2008): 5434-5441.
- 14. Song, S. Q., et al. "Direct methanol fuel cells: The effect of electrode fabrication procedure on MEAs structural properties and cell performance." Journal of Power Sources 145.2 (2005): 495-501.
- 15. <https://energy.gov/eere/fuelcells/types-fuel-cells>
- 16. Osmieri, Luigi, et al. "Fe-N/C catalysts for oxygen reduction reaction supported on different carbonaceous materials. Performance in acidic and alkaline direct alcohol fuel cells." Applied Catalysis B: Environmental (2017).
- 17. Wang, H., Z. Jusys, and R. J. Behm. "Ethanol electrooxidation on a carbon-supported Pt catalyst: reaction kinetics and product yields." The Journal of Physical Chemistry B 108.50 (2004): 19413-19424.
- 18. Camara, G. A., and T. Iwasita. "Parallel pathways of ethanol oxidation: the effect of ethanol concentration." Journal of Electroanalytical Chemistry 578.2 (2005): 315- 321.
- 19. Ong, B. C., S. K. Kamarudin, and S. Basri. "Direct liquid fuel cells: A review." International Journal of Hydrogen Energy (2017).
- 20. Antolini, Ermete. "Catalysts for direct ethanol fuel cells." Journal of Power Sources 170.1 (2007): 1-12.
- 21. Zhou, Weijiang, et al. "Pt based anode catalysts for direct ethanol fuel cells." Applied Catalysis B: Environmental 46.2 (2003): 273-285.
- 22. Qiao-Hui, G. U. O., Jian-She Huang, and Y. O. U. Tian-Yan. "Electrospun palladium nanoparticle-loaded carbon nanofiber for methanol electro-oxidation." Chinese Journal of Analytical Chemistry 41.2 (2013): 210-214
- 23. Tan, Joshua L., et al. "Preparation and characterization of palladium-nickel on graphene oxide support as anode catalyst for alkaline direct ethanol fuel cell." Applied Catalysis A: General 531 (2017): 29-35.
- 24. Wang, Qiang, et al. "One-pot synthesis of carbon-supported monodisperse palladium nanoparticles as excellent electrocatalyst for ethanol and formic acid oxidation." Journal of Power Sources 292 (2015): 72-77.
- 25. Park, Jun Woo, Ryszard Wycisk, and Peter N. Pintauro. "Nafion/PVDF nanofiber composite membranes for regenerative hydrogen/bromine fuel cells." Journal of Membrane Science 490 (2015):103-112.
- 26. Li, Chennan, et al. "Casting Nafion–sulfonated organosilica nano-composite membranes used in direct methanol fuel cells." Journal of membrane science 272.1 (2006): 50-57.
- 27. Lin, Kaijie, et al. "Surface modification of 316 stainless steel with platinum for the application of bipolar plates in high performance proton exchange membrane fuel cells." International Journal of Hydrogen Energy (2016).
- 28. <http://pslc.ws/macrog/pmma.htm>
- 29. Hentall, Philip L., et al. "New materials for polymer electrolyte membrane fuel cell current collectors." Journal of Power Sources80.1 (1999): 235-241.
- 30. Zhang, Hongwei, and Pei Kang Shen. "Recent development of polymer electrolyte membranes for fuel cells." Chemical reviews112.5 (2012): 2780-2832.
- 31. Maab, Husnul, and Suzana Pereira Nunes. "Modified SPEEK membranes for direct ethanol fuel cell." Journal of Power Sources195.13 (2010): 4036-4042.
- 32. Carrión-Satorre, S., et al. "Performance of carbon-supported palladium and palladium ruthenium catalysts for alkaline membrane direct ethanol fuel cells." International Journal of Hydrogen Energy 41.21 (2016): 8954-8962.
- 33. Moraes, L. P. R., et al. "Synthesis and performance of palladium-based electrocatalysts in alkaline direct ethanol fuel cell." International journal of hydrogen energy 41.15 (2016): 6457-6468.
- 34. Monyoncho, Evans A., et al. "Synergetic effect of palladium–ruthenium nanostructures for ethanol electrooxidation in alkaline media." Journal of Power Sources 287 (2015): 139-149.
- 35. Thanasilp, Sarawalee, and Mali Hunsom. "Effect of MEA fabrication techniques on the cell performance of Pt–Pd/C electrocatalyst for oxygen reduction in PEM fuel cell." Fuel 89.12 (2010): 3847-3852.
- 36. Zadick, Anicet, et al. "Effects of Pd nanoparticle size and solution reducer strength on Pd/C electrocatalyst stability in alkaline electrolyte." Journal of the Electrochemical Society 163.8 (2016): F781-F787.
- 37. Prasanna, M., et al. "Effects of MEA fabrication method on durability of polymer electrolyte membrane fuel cells." Electrochimica Acta 53.16 (2008): 5434-5441.
- 38. Wang, Qiang, et al. "One-pot synthesis of carbon-supported monodisperse palladium nanoparticles as excellent electrocatalyst for ethanol and formic acid oxidation." Journal of Power Sources 292 (2015): 72-77.
- 39. [https://spectrum.ieee.org/computing/software/fuel-cells-poised-to-replace-indias](https://spectrum.ieee.org/computing/software/fuel-cells-poised-to-replace-indias-diesel-generators)[diesel-generators](https://spectrum.ieee.org/computing/software/fuel-cells-poised-to-replace-indias-diesel-generators)

Sindhuja Valluri was born in Tanuku, Andhra Pradesh India. She received her Bachelor of Technology in Mechanical Engineering from R.V.R & J.C College of Engineering, Guntur, India in 2015.

Sindhuja joined in Missouri University of Science and Technology in December 2015 and took up the position of Graduate Research Assistant in the Department of Manufacturing Engineering while working towards her Masters of Science degree at Missouri S & T.

In May 2018, she received her MS degree in Manufacturing Engineering from Missouri University of Science and Technology.