Plasma Activated Fuel Cells

Investigators
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Abstract
Plasma-activated fuel cell operation is examined using dielectric-barrier discharges introduced into the inlet fuel and air streams of laboratory proton exchange membrane (PEM) based devices. We compare the performance of the hydrogen-driven-PEM fuel cell in the presence/absence of the plasma discharge, and under conditions of three different types of membrane electrode assemblies (MEAs). The results of these studies indicate that a conventional Nafion membrane with a catalyst and carbon cloth gas diffusion layer (GDL) show little enhancement under plasma exposure. Removal of just the GDL was also unaffected by the discharge activation, however, operation of the fuel cell with a bare Nafion membrane resulted in an open circuit voltage (OCV) of 1.8V, a nearly 1V increase over the OCV obtained in the standard configuration. No attempt has yet been made to analyze the current-voltage characteristic, as the current is presently limited by the ability to draw away surface charge. The results are nevertheless encouraging, and ongoing studies include the development of a suitable carbon layer to serve as an electrode while providing adequate exposure of the membrane to the adjacent plasma. In parallel, we have developed models of the plasma activated streams, for use in simulating in-situ methane reforming of hydrogen. Experiments are underway in measuring the OCV when operating on methane and dilute methane fuel streams.

Introduction
This research involves the study of the use of non-equilibrium plasma discharges generated in-situ, within the inlet channels of fuel cells, to enhance fuel cell efficiency. While in theory, a fuel cell can have a potentially high thermodynamic efficiency (~ 80 % for a proton exchange membrane (PEM) fuel cell at 100 °C and 1 atm pressure), in practice, fuel cells exhibits a much lower efficiency (~ 40 %) due to three major factors- activation, ohmic and mass transport losses. The activation loss is caused by the inefficiencies at which reactants form ions and electrons at the catalyst surface. Ohmic loss is due to finite ion diffusion rates through an electrolyte. The mass transport loss is primarily a result of the limited rate of ion flux in the gas diffusion layer (GDL). Here, we believe that the use of a non-equilibrium plasma discharge can eliminate/diminish those losses for the following reasons; (i) the non-equilibrium plasma can generate high ion/atom/radical concentrations in low power/volume requirements, which can reduce the activation loss (or may eliminate the need for the catalyst layer altogether), (ii) the presence of higher concentrations of ion/atoms/ radicals in the flow channel should partially alleviate the concentration limit caused by the saturation of mass transport, (iii) the dissociation and the activation of reactants before the GDL due to the presence of the non-equilibrium plasma may improve the diffusion characteristic of the species through the layer.

The exploratory phase of this research is aimed at: (a) carrying out a system level analysis to determine the overall benefits that a plasma discharge can offer to fuel cell systems; (b) designing a preliminary laboratory-scale fuel cell/plasma discharge assembly;
(c) determining the performance of a hydrogen-fueled fuel cell with/without a plasma discharge; (d) investigating the feasibility of in-situ reforming using the non-equilibrium discharge for methane-fueled fuel cell, and; (e) developing a preliminary model of the plasma activated fuel/air stream.

Results

During the past four months, we have focused on investigating tasks (b), (c) and (e) mentioned above. Here, we report on our findings and preliminary results.

Laboratory-Scale Fuel Cell/Plasma Assembly

A photograph of our fabricated plasma activated fuel cell assembly is shown in Fig. 1. Only half of the actual cell is shown in the figure, as this prototype is composed of two identical parts (one for the fuel side and the other for the air side). The overall dimension of the cell is 10 cm in width, 2.5 cm in depth, and 5 cm in height. A membrane electrode assembly (MEA), not shown, is inserted between the parts and uniformly sealed by eight circumferentially located compression fasteners. The seal between the two halves are facilitated by Viton compression o-rings. In each half, there is a 3.8 cm x 1 cm x 1 cm cavity in which fuel and air flows. The dielectric barrier discharges are integrated into the side walls of the cavity, using 90 μm thick copper strips (electrodes for the plasma discharge) and a 520 μm thick glass fiber tape (dielectric barrier). One electrode is exposed to the flowing gases and the other is buried in the dielectric barrier. The resulting discharge (in air) achieved from this configuration is shown in Fig. 2. The overall size of the discharge is 3 mm long, 2 cm wide and the minimum distance from the discharge to the MEA is 2 mm. Using the measured voltage (8 kV peak-to-peak), current (10 mA peak) and frequency (30 kHz), the deposited power is estimated to be approximately 10 W.

Preliminary Performance Measurement of Plasma Activated PEM Fuel Cell

To compare the performance of a fuel cell in the presence/absence of the plasma discharge, open circuit voltages (OCVs) of hydrogen-driven-PEM fuel cells have been characterized with and without the plasma discharge in the inlet chamber, under conditions of three different types of MEAs. The results of these studies are listed in Table 1. The MEAs used here include: (i) a conventional Nafion membrane with a catalyst (Pt particles in a carbon layer) and carbon cloth GDL; (ii) a Nafion membrane with the identical catalyst...
layer in the absence of the GDL, and; (iii) a bare Nafion membrane. For configuration (ii) and (iii), which have no current collecting electrode (which is normally the GDL), two thin copper strips (90 μm thickness) were attached on each side of the MEA to measure the local voltage difference. When the conventional MEA is used, 0.8 V OCV is obtained both with/without the discharge case, which means that the presence of discharge play a negligible role in reducing the activation loss. Similarly, no noticeable gain due to the presence of the discharge is observed when only the GDL is eliminated from the usual MEA (configuration (ii)). With this configuration, we experience the added disadvantage of a lack of a mechanism to draw current from the MEA. When only a bare Nafion membrane is used as an MEA (configuration (iii)), we find that we have a significant increase in the OCV when the discharge is activated (i.e., 1.8 V OCV is measured with the discharge while 0 V is measured without it). Of course, a 0 V OCV (in the absence of a discharge) is expected because of the absence of catalyst layer. However, we are encouraged by the observation of a higher OCV with plasma activation. Indeed, the OCV is even higher than that of an ideal PEM fuel cell (1.2 V). We believe that this fact implies that a significant fraction of hydrogen is excited, ionized, and possibly dissociated by the plasma discharge. However, it is noteworthy that the current we can draw from this configuration, in its present design, is small (~ 10 μA) - similar in magnitude to the current drawn in configuration (ii). As mentioned earlier, this is due to the absence of a mechanism for current collection, such as the addition of a conducting GDL in a conventional fuel cell. At present, the generated current can only be collected at the boundary between the copper strip and the Nafion membrane, which is a very small area in comparison to the entire surface area of the Nafion exposed to the plasma. At present, we are exploring novel ways of drawing current from the bare Nafion surface.

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Table 1. List of OCV for various MEAs

Figure 3. Extent of dissociation of (a) methane and (b) air. Power deposition is 10 W. In (b) blue curve represents N₂ while green represents O₂.
Preliminary modeling of gas dissociation in the presence of non-equilibrium discharge

We have carried out preliminary modeling of the plasma activation process, specifically for the case of fuel cell operation on methane. The rate of gas dissociation due to the presence of a non-equilibrium discharge is simulated using the method described by Penetrante et al. [1]. The method is based on the electron induced collisional fragmentation of parent species. This requires a solution of the Boltzmann equation for the electron energy distribution function (using a commercial package BOLSIG [2]) for a specified reduced electric field (E/n, where E is electric field and n is the number density of parent species). The electron energy distribution function (EEDF) allows us to calculate the dissociation reaction rate and the electron mobility, from which we can determine the fraction of the total dissociated energy that is needed to produce radicals from the parent gases [3]. The extent of dissociated fuel (methane in this example) and air calculated using this procedure is illustrated through the example results given in Figs. 2a and 2b, respectively. For this particular case, the power deposited by the plasma is taken to be 10 W, i.e., the typical value seen in the experiments.

The reactions considered are the direct electron-impact dissociation reactions of methane and air (CH\(_4\) + e \(\rightarrow\) CH\(_3\) + H + e, N\(_2\) + e \(\rightarrow\) N + N + e, O\(_2\) + e \(\rightarrow\) O + O + e) and other secondary dissociation reactions are neglected. Two major observations can be made from the data presented in Fig. 2; first, there exists an optimal reduced electric field to maximize the number of produced radicals by the discharge (~ 220 Td for methane and 400 Td for oxygen in air); and second, the extent of air dissociation is approximately one order of magnitude less than that of methane with identical plasma power deposition. This later observation implies that the power deposition in the plasma located at the air inlet side should be much higher to maintain comparable levels of radical generation to that on the fuel cell side. These calculations continue, and, in particular, we intend to couple these calculations to kinetic simulations of concomitant radical reforming reactions, to determine the extent of conversion of methane to hydrogen, within the inlet fuel channel.

**Future Plans**

*System Level Analysis*

Here, once the measured collected current/voltage characteristics are obtained we will have a more general impression of the overall performance, and will be able to use this data in an analysis of the overall fuel cell benefits, when operating on methane. Experimentally, we will expand the fuel base from hydrogen to various hydrocarbon gases, including methane. To complete the experiments, we must devise a novel way to collect the current from the membrane. At present, we are exploring the possible use of loosely-packed conducting fibres, such as carbon nanotube foams.

*Improved Discharge Cell Design*

We intend to design and fabricate a smaller prototype where the ratio of discharge area to the cavity area can be reduced. The smaller ratio will assist to promote an increasing effect of the discharge on the radical formation. Also, a new type of discharge (ultra short pulsed repetitive discharge, USRD) will be tested for its improvements over the alternating current dielectric barrier discharge, in enhancing the OCV, and overall cell performance. We believe, based on previous uses of USRD in plasma-assisted combustion that this type of plasma generator can lead to higher dissipated power and improved discharge control [4].
Plasma In-situ Reformer

A novel feature of the plasma activation includes the ability to convert (directly) methane to hydrogen, within the inlet fuel channel of the fuel cell. We refer to this as in-situ plasma reforming, which provides the benefit of hydrogen fuel cell operation, with direct methane injection. Our plan is to better understand this in-situ reforming process, by analysis of the post-discharge gas stream using Fourier transform infrared (FTIR) spectroscopy. Of course, FTIR of post-processed gas provides information on stable species only. We will continue to rely on both solution of the Boltzmann equation and initial yield calculations, coupled to kinetics simulations such as CHEMKIN (with GRI MECH 3.0) and PREMIX, to determine the level of active radicals in the post-discharge stream.

References

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