Nano composite membrane-electrode assembly formation for fuel cell – modeling aspects

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Abstract. Long term stability is an essential requirement for fuel cell applications in automobile and stationary energy systems. In these systems the agglomeration of the catalyst nanoparticles is a well-known phenomenon which cannot be easily overcome or compensated for by re-designing the system. A direct result of this occurrence is the irreversible decrease of the electrochemical performance. Irregularities in electric field distribution are one root cause for migration and subsequent agglomeration of the catalyst nanoparticle. In this work, the impact of the electrode mechanical deformation on electric field distribution was studied using a computer modeling approach. Model of a Proton Exchange Membrane (PEM) fuel cell with interdigitated flow field from Comsol Chemical Engineering/Electrochemical Engineering Module library was used for simulations. It was established that by minimizing the backing layer deformation it is possible to achieve some improvement in current distribution.

1. Introduction

Fuel cells are one of the main candidates for clean energy power production in future cars. A fuel cell is an electrochemical device similar to a battery, but differing from the latter in that it is designed for continuous replenishment of the reactants consumed. In a fuel cell-powered engine, the fuel is converted to electrical energy through electrochemical reactions instead of combustion. The benefits inherent to the use of a fuel cell are the combination of high energy conversion efficiency and the potential to significantly reduce power source emissions. In such applications as transportation and portable power, fast start-up at low temperatures is essential. For energy applications hydrogen and methanol are considered as promising fuel replacements. Currently, hydrogen as an energy carrier can not compete with grid electricity (which can be used to re-charge an electric vehicle), and such a trend will most likely remain unchanged in the near future. Introducing hydrogen is a comprehensive task and a new complete energy chain should be created reaching from hydrogen production to hydrogen end use. Methanol can be used as a fuel for Direct Methanol Fuel Cell (DMFC), and can be easily adapted to the existing infrastructure [1]. Theoretically, methanol has a superior specific energy density (6000 Wh/kg) in comparison with the best rechargeable battery, lithium polymer and lithium ion polymer (600 Wh/kg) systems. Another significant advantage of methanol over the rechargeable battery is its potential for instantaneous refueling [2-3]. Long term stability is required for automobile and stationary energy system applications and about 0.1 percent power decrease per 1000 hrs is generally accepted for stationary applications. Power decrease is usually caused by fuel cell aging, and there are a number of reasons for this. Agglomeration of the platinum catalyst particles is a well-known phenomenon in these systems, and currently there is no feasible method to compensate for the problem. In addition, it leads to an irreversible decrease of the electrochemical performance. For supported catalysts
the effect is more pronounced when the metal loading on the carbon support is relatively high. For this reason DMFC systems are ideally suited for the investigation of these phenomena, where the catalyst loading is higher. However, from the point of view of long term stability the same problem should also be investigated for hydrogen fuel cells [3]. It was shown by Zhai et al [4] that the Pt particle size in the cathode increased from 4.0 to 8.3 nm in 300 h at 150°C in H3PO4/PBI PEMFC, which resulted in 55% loss of power. Better understood is the temperature influence on catalyst particle agglomeration. In general, small metal particles grow on a support via two possible mechanisms: the coalescence growth and the Ostwald ripening process. High humidification and especially a liquid phase enhance the platinum agglomeration significantly [5-7]. It has been suggested to use various substrates or a multi-alloy approach (including Nb) in order to prevent the Pt agglomeration [8]. Jiang et al [9] studied platinum agglomeration in a direct methanol fuel cell, and found that the improved life time for cell performance is attributed to a better contact between the catalyst layer and the electrolyte membrane. Liu et al [10] observed the increase of particle size of the Pt/C catalysts in the anode and cathode from 3.72 to 7.40 and 8.39 nm (phosphoric acid doped polybenzimidazole membrane, 600h, 150°C). In this work, we investigated the potential impact of geometrical factor and formation of local electrical field on catalyst agglomeration by using computer modeling.

2. Experimental
The distribution of the electric field was calculated with the Comsol Multiphysics 3.3 software. In this work, the Model of a Proton Exchange Membrane (PEM) fuel cell is used. The Model is included in Comsol Chemical Engineering/Electrochemical Engineering Module library and detailed description of underlying physics is available on Comsol website [11]. The model uses current balances, mass balances and momentum balances to simulate the PEM fuel cell behavior. Both feed gases (humified hydrogen and humidified air) are treated as ideal and they are transported through diffusion and convection. The electrodes are treated as homogeneous porous media with uniform morphological properties such as porosity and permeability. The general goal of this work is to investigate the existing physical model and only the geometry of the membrane-electrode assembly was varied.

3. Results and discussions
Computer modeling is used to optimize the design of durable and efficient fuel cell; to visualize the current density and the flow of fuel and air through cell stacks in order to improve the efficiency of design. Typical cell components within a stack include:

* The ion exchange membrane
* An electrically conductive porous backing layer
* An electro-catalyst (the electrodes) at the interface between the backing layer and the membrane
* Cell interconnects and flow plates that deliver the fuel and oxidant to reactive sites via flow channels and electrically connect the cells (Figure 1). Interdigitated flow field is used for this model.

An approach for sealing the cell with flat gaskets is accompanied with applying pressure. In an ideal case, it is assumed that fuel cell components are not deformed during assembly (Figure 1c). However, during the fuel cell assembly the surface of the backing layer (e.g. carbon cloth) is deformed (Figure 1b), because the backing layer material is typically softer, compared to the material of current collector (metal or graphite). The impact depends
on carbon cloth quality. In this case, some decrease of the backing layer porosity and geometrical dimensions of the flow channel will occur. Humidified gases (hydrogen, air) are supplied to the inlet channels of the anode and cathode. The humidification, which is used to provide high proton conductivity for ion conducting phases (membrane, proton conducting component in the catalyst composition), is also a cause for the mechanical deformations. At the same time, it can cause the backing layer and catalyst layer to swell. This is a negative side effect and it results in the partly filling of the gas flow channels. The swelling effect is clearly observed in DMFC, because most polymer materials can easily swell in methanol, and it will lead to an increase in the porosity and will cause changes in flow channel geometry. In this work, the impact of the changes in flow channel geometry on the fuel cell performance is studied by computer modeling. In order to simplify the task and to obtain the preliminary insight the porosity was accepted as a constant value.

Different backing layer materials are used for PEM and DMFC fuel cells. The backing layers, one next to the anode and the other next to the cathode, are usually made of a porous carbon paper or carbon cloth (for example, from SGL Carbon [12], E-Tek [13], Lydall, Inc. [14]). The selection of material is typically based on physical properties of the material as well as the cost. The backing layer also helps in managing water in the fuel cell. Too little or too much water can cause the cell to stop operating. Powdered Teflon® (registered trademark of E. I. du Pont de Nemours and Co) is often added to give the carbon material a hydrophobic property, which improves functionality as an electrode backing material. This will ensure that at least some of the pores in the backing layer do not become clogged with water. Different companies are offering high variety of low price materials for backing layers. However, in most cases the stability of those materials in hot water or methanol solution is low and lead to backing layer deformation. Mechanical stability of the Teflon treated carbon paper (e.g., Toray Carbon paper [15]) is much higher and it is widely used in most high performance PEM’s and DMFC’s. However, it is very expensive. For this reason, we wanted to simulate the impact of mechanical deformations and mark the limits for tolerable deformations, thus establishing a working range for various cost effective alternative backing layer materials.

The electric field distribution in the PEM fuel cell is depicted in Figure 2. There are significant electric field spikes present at the corners of the current collectors and it is clear that the interface between the catalyst layer and the membrane is highly inhomogeneous from the point view of electric field distribution. The metal nanoparticle is attached to electronically conductive carbon substrate and it is immersed in an ion-conducting electrolyte, which covers the surface of the substrate. In order to prevent the particle agglomeration, the electric field gradient should be minimized.

In order to evaluate the electric field gradient, the current density is plotted along the surface of the electrode (Figure 3, for anode). Single surface segment according to the image in Figure 2 was analyzed. The current density is uneven and the highest density arises close to the air inlet. This means that the oxygen-reduction rate in the cathode determines the current density distribution. For this reason, it is understandable that the impact of the anode backing layer geometry on current distribution is negligible (Figure 3). In the case of the cathode, the geometry change is leading to a reasonable increase in the current density close to the hydrogen inlet. This might be related to the higher gas flow, because of decreased mechanical deformation of the flow channel.

Conclusions.
Mechanical deformation, which is caused by the fuel cell assembly and exposure to water and/or methanol, will produce irregularities in electric field distribution. It was demonstrated, using computer modeling, that the cathode deformation has a higher impact on fuel cell performance as compared to anode deformation. It is proposed that these irregularities are playing a role in stimulating the catalyst nanoparticle agglomeration. By minimizing the backing layer deformation, it is possible to achieve
some improvement in even current distribution. However, the electric field gradient is very high because of the fuel feed gradient. Experimental evidence is needed to show that the catalyst agglomeration might be slowed down by improving uniformity of the electrical field. If this is the case, it is very likely that better fuel cell design is needed which allows uniform feed and prevents formation of the concentration gradients. The modeling approach used is suitable for fuel cell engineering, providing design for long term applications.

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