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Performance investigation of Passive Direct Methanol Fuel Cell in different structural configurations

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ABSTRACT

The aim of the present work is to systematically investigate the performance of a Passive Direct Methanol Fuel Cell (PDMFC) with different structural configurations.

The PDMFCs are an attractive option for powering advanced electronic devices in the future due to the high power densities, easy fuel storage, low operating temperature, low noise level and simple design. The cell is completely passive, without external pumps and auxiliary devices; it takes oxygen from the surrounding air and the methanol solution is stored in a built-in tank in contact with the active area.

We used a commercial hot-pressed Membrane Electrode Assembly with an active surface of 5 cm^2 composed of a Nafion 117 membrane and two Gas Diffusion Layers with catalyst loadings of 4 mg/cm^2 Pt–Ru on the anode side and 4 mg/cm^2 PtBlack on the cathode side. The supporting external case was manufactured in polymethylmethacrylate; the electrodes consist of two stainless steel SS316 plates and the gaskets are made of PTFE and silicone.

The performance of the cell with three different assembly configurations and two different current collector geometry was investigated changing methanol molar concentration (ranging between 1 M and 4 M).

1. Introduction

In the field of renewable energy sources, from stationary applications to portable ones, significant efforts are being made to reduce environmental impact of technologies by improving their efficiencies. The present economy based on fossil fuel represents a serious risk due to the continuous increase in demand of oil, the depletion of non-renewable resources and the dependency on politically unstable oil producing countries. In order to reduce waste of energy with not-renewable sources and to increase the efficiency of renewable systems, energy should rationally be used and efficiently stored. Fuel cells and energy vectors, such as hydrogen and methanol, may play an important role (Pettersson et al., 2006). Fuel cells can generate energy on demand using them during periods of elevated supply of renewable sources and they can provide power supply either for stationary (Di Carlo et al., 2013; Pirkandi et al., 2012) or for portable applications, as explained by Kamarudin et al. (2009) in which micro-DMFC, in passive configuration, have been considered as possible replacement for conventional battery. In the field of mobility General Motors and other automobile brands announced the release of an electric car where electric energy is generated onboard by hydrogen fuel cells in 2015 (Matthey, 2012).

Hydrogen is the most widespread fuel for fuel cell powering, nevertheless hydrogen has some drawbacks such as low density and high flammability. Methanol storage, due to the high density (liquid) at standard pressure and temperature, is more easy and its handling is more safe (Riaz et al., 2013). Currently, the greater part of the methanol production comes from reforming of syn-gas (CO and H_2) obtained by fossil fuel.

Recycle of CO_2, from natural or industrial sources, including fossil fuel-burning power plants, cement plants and eventually from the atmosphere itself, is a good way for zero emission cycle and methanol generation by reforming. The hydrogen required for this process can be generated from water using the surplus of energy from power plants, when the demand is low, coupling them with methanol reforming systems and avoiding energy waste. It allows also a safe storing and easy transportation as shown by Van-Dal and Bouallou (2013). The chemical recycling of CO_2 would also help to mitigate or eliminate the major human activity cause of

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climate change due, in a significant part, to excessive burning of fossil fuels.

Methanol is an excellent fuel in its own; even neat methanol can be used in today's internal combustion engines with only minor modifications. Methanol can also be efficiently used to generate electricity in fuel cells.

Direct Methanol Fuel Cells (DMFCs) can be made in either an active or a passive configuration. While the former has to be fed by auxiliary devices, such as pumps and fans, the latter functions independently of electronic devices and consists simply of a fuel storage which keeps the reaction mixture and the anode catalysts in contact. The cathode side feeding uses a simple air-breathing mechanism.

Electricity is generally a good way to transport energy over relatively short distances where a suitable grid exists. It is, however, very difficult to store electricity on a large scale.

In the field of portable applications, batteries are still inefficient, expensive and bulky. Passive Direct Methanol Fuel Cells (PDMFCs) seem to represent the most promising candidate to replace them for laptops, mobile phones and all electronic devices with low power supply as Shimizu et al. (2004) have shown.

The easy storing and refuelling and low working temperature (60 °C) (Li and Faghri, 2013) make PDMFCs more suitable for portable applications. The fuel in the PDMFC is supplied by a small tank filled with a homogeneous solution of water and methanol that permanently wets the diffusion layer. The reactions that occur in the cathode and anode are shown in (1) and (2).

$$\textit{ANODE}\ CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6\,e^- \quad (1)$$

$$\textit{CATHODE}\ 6H^+ + 6\,e^- + 3/2\,O_2 \rightarrow 3\,H_2O \quad (2)$$

Each reacting mole of methanol yields six electrons that flow through the external electrical circuit and six cations that migrate to the cathode side by crossing the membrane. Ideally, the membrane should allow only for the passage of ions, however, a small quantity of methanol molecules inevitably cross-over by two principle mechanisms: diffusion and drag. The first one is due to the difference in concentration between the anode and the cathode of the Membrane Electrode Assembly (MEA), whereas the latter is due to the movement of ions which drags along water and methanol molecules. The methanol mass flow through the membrane is quantified by the equation (3).

$$J_{met} = D_{met}\frac{(C_{met,as} - C_{met,cs})}{t_m} + x_{met,as}\delta\frac{i}{F} \quad (3)$$

Methanol molecules that reach the cathode can react directly with the surrounding oxygen leading to a decrease in cell voltage. Equation (1) demonstrates that CO_2 is generated at the anode, resulting in the formation of bubbles which must increase in size before detaching from the surface of the Gas Diffusion Layer (GDL). The presence of CO_2 on the GDL surface denies the fuel access to the active area of the anode, thus inhibiting methanol oxidation.

Technical drawbacks such as methanol cross-over and decreased active area due to CO_2 bubble generation have not been overcome yet. Several researchers have studied cross-over behaviour through NAFION 117 in an attempt to analytically model these phenomena; Cruickshank and Scott (1998) compared numerical and experimental data about methanol permeation with the variation of pressure differentials across the membrane. Xu et al. (2010) investigated the effect of a hydrophobic water management layer to evaluate the decrease in methanol and water cross-over. Casalegno et al. (2007) have tried to model the phenomena by matching the results with the experimental data carried out by tests on a GEFC117 membrane; Neves et al. (2010) conducted an experimental analysis of a modified NAFION membrane to evaluate the difference in cross-over amount relative to that of an unmodified one. Lu and Wang (2004) were the first to study the generation of bubbles at the anode and water droplets at the cathode, focusing on the interaction between CO_2 bubbles and the GDL, particularly their detachment from it. Bewer et al. (2004) investigated the non-uniform distribution of methanol upon the GDL due to the CO_2 bubbles generation in the anode channels and its influence on the power of a 600 cm^2 DMFC. Yang et al. (2005) have studied the different two-phase flow regime established in the anode channels varying current density and cell orientation; Burgmann et al. (2012) used a μPIV (Particle Image Velocimetry) to study the movement of the bubbles in the two phase flow, looking for solutions that might decrease their effects.

A preliminary study of methanol distribution and diffusive and convective components of the motion in the water solution has been conducted by means of numerical investigation. A mathematical model, suitable for an active DMFC, has already been made (Borello et al., 2013) with the use of multiphysics software (COMSOL®). The same model can be applied to the PDMFC with some modification. It allows for the determination of the velocity fields of the fluids, the distribution of the reactants on the catalysts' surface and the electric field through the entire assembly. Fig. 1 shows the passive geometry of the cell with the distribution of the reactants on the respective catalyst layers.

The increasing in number and decreasing in size of the holes allows to reduce local concentration gradients of the reactants upon the catalyst surface. In literature there are not so much 3D numerical analysis of different current collector shape due to the difficulty of modelling the behaviour of PDMFC. In order to find a correlation with the numerical model, discussed above, we used the current collectors with the simplest geometry to study. In this work experimental investigation will be presented and discussed. Different configurations of monopolar plates have been assembled on the same MEA and the electrical efficiency with different methanol concentration has been investigated.

2. Material and methods

2.1. Membrane Electrode Assembly

In this study we used a commercial MEA purchased from Fuel Cells ETC with an active area of 5 cm^2. It is a five-layer hot pressed MEA made up of a Nafion 117 perfluorosulfonic acid electrolytic membrane, two catalyst layers (CLs) with a catalyst load of 4 mg/cm^2 PtRu on the anode side and 4 mg/cm^2 of PtBlack on the cathode side and two GDLs made of woven carbon cloth with a Microporous Layer (MPL) with a thickness of 410 μm. The main function of GDLs is to allow the diffusion of the reactants towards the CLs while the membrane has to behave like an electric insulator and ionic conductor.

2.2. Single cell fixture

PDMFC consists of two current collectors, an anode fuel (aqueous methanol solution) tank, a cathode-end frame, a MEA and four gaskets. The MEA is wrapped between the anode and the cathode current collector.

The current collectors were made of stainless steel plates with a thickness of 0.5 mm. They should have two main characteristics: high conductivity and homogeneous electrical characteristics. Furthermore the plate geometry allows the control of the mass flow rate of the reactants through a series of holes machined on the active area of the current collectors. This feature is defined by the