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Impact of manufacturing processes on proton exchange membrane fuel cell performance

Samaneh Shahgaldi, Ibrahim Alaefour, Xianguo Li*

20/20 Laboratory for Fuel Cell and Green Energy RD&D, Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, ON N2L 3G1, Canada

HIGHLIGHTS

- Investigated the membrane electrode assembly (MEA) manufacturing processes.
- Compared three main processes under same preparation and testing conditions.
- Studied the impact of Nafion layer on catalyst layers and membrane.
- Observed different impacts of the hot press on cell performance with various MEAs.
- Observed significant impact of the manufacturing processes under low Pt loading.

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ABSTRACT

Commercial success for proton exchange membrane fuel cell (PEMFC) requires manufacturing of its core component, membrane electrode assembly (MEA), with consistent and reliable performance. In this study, three common methods for the MEA manufacturing are investigated systematically for their impact on the cell performance under consistent preparation and cell test conditions, including catalyst coated substrate (CCS), catalyst coated membrane (CCM), and low temperature decal method (LTDM). The variations in each of these methods studied include applying an extra Nafion layer, hot press, and Pt loading. It is found that MEA manufacturing process has a significant impact on the cell performance, and this impact is significantly affected by the Pt loading. At the high Pt loading of 0.5 mg/cm^2, CCM without hot press involving gas diffusion layers (GDLs), referred to as CCM-Wo, results in the best performance with the maximum power density of 0.95 W/cm^2, although both LTDM and CCS with an extra Nafion layer (hence called N-LTDM and N-CCS) are just slightly less with the maximum power density of 0.91 W/cm^2. Hot press with GDLs is essential for CCS method to achieve a good performance, while it is not the case for CCM and N-LTDM. Applying an extra layer of Nafion on catalyst layers as in N-LTDM and N-CCS methods has a positive impact on the cell performance; whereas it is negative when it is applied on the membrane as in the N-CCM method. When the Pt loading is reduced to 0.125 mg/cm^2 (75% reduction in the Pt loading), cell performance is reduced for all the MEAs made by the three methods, but significant reduction (about 75%) is observed for CCS method, while it is less than 30% for the other two methods. Therefore, care should be taken in the MEA manufacturing for MEAs with low Pt loadings.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are clean electrochemical power sources for mobile and stationery applications, and bear considerable advantages such as high efficiency, high power density, and the ability to operate at low temperatures. After nearly three decades of intensive R&D, PEMFCs have reached the early stage of commercial deployment with the urgent need for advanced manufacturing of quality PEMFC products for practical applications. The main component of PEMFCs is the membrane electrode assembly (MEA), which contains a polymeric membrane, catalyst layers, and gas diffusion layers (GDLs). The electrochemical reactions can occur only with the existence of the three-phase boundary in the catalyst layers, whose performance is directly impacted not only by the MEA fabrication technique but also by other important factors such as the types and amounts of catalysts, ionomer, deposition methods [1–6].

MEA manufacturing process can be in general classified based on the type of substrate used: (i) the most conventional is the catalyst

* Corresponding author.
E-mail address: xianguo.li@uwaterloo.ca (X. Li).

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coated substrate (CCS), it uses a gas diffusion layer (GDL) as the substrate, on which the catalyst layer is deposited and then hot pressed with a membrane. The CCS method is suitable for mass production owing to its simplicity, yet it offers limited interfacial contact between the catalyst layer and membrane [7–12]; (ii) the membrane is used as the substrate, on which the catalyst layer is applied, hence referred to as the catalyst coated membrane (CCM) method. This method has been shown to have a better interfacial contact between the catalyst layer and membrane. However, the expansion accompanying the hydration of the membrane can ruin the catalyst layers during the CCM fabrication process [13–15]; and (iii) an inert decal is used as the substrate, hence called the decal transfer method (DTM). However, it is difficult to have a complete transfer of catalyst from the decal to the membrane; and the conventional solution is to have decal transfer at high temperatures (210–250 °C), but both the ionomer and membrane cannot withstand such high temperatures, leading to many other problems, and hence many variations of this method [16–22].

Therefore for the DTM, considerable efforts have been made to reduce the hot press temperature to less than 130 °C required by the membrane and ionomer involved. Then in order to complete catalyst transfer at this low temperature, a number of techniques have been explored: (i) different chemical reagents such as glycerol, 1–5-pentanediol, and 1-pentanol have been applied, but they cannot be completely evaporated at such a low temperature hot press process, and could thus cause pore blockage and consequent negative effects on fuel cell performance [23–26]; (ii) a breaking layer, composed of carbon or carbon and Nafion, is deposited on the decal substrate prior to catalyst ink deposition; and (iii) a better approach is to apply an extra Nafion layer on top of the catalyst layers (facing the membrane), which can not only achieve the complete catalyst transfer, but also improve the interfacial contact between the catalyst layers and membrane – such a low temperature decal method with an extra Nafion layer has been referred to as the N-LTDM [27–29]. Recently, a new approach is reported through the judicial selection of the ink composition and substrate materials used; however, only 90% catalyst transfer rate is achieved for PTFE cloth and PTFE sheet as the decal substrate, while only 70% for the aluminum foil [30].

The CCM and LTDM (referred to as CCM-DT in [31]) methods have been compared [31] by preparing two MEAs using 19.4% Pt in multi-wall carbon nanotubes. The catalyst layer is deposited by inkjet printing with an active area of 5 cm^2 for the resulting MEA. For the CCM method, the membrane is stuck to a cellulose sheet and placed into the paper tray of the inkjet. After catalyst deposition on both sides of the membrane, the entire MEA is hot pressed together. For the LTDM method, the catalyst layer is deposited on a Teflon sheet and transferred to the membrane via hot press, then the entire MEA is assembled in another hot press process with the GDLs. Maximum power densities of 231.54 mW/cm^2 and 166.9 mW/cm^2 for MEAs prepared by CCM and LTDM, respectively, are reported for hydrogen/oxygen at 60 °C and 1 atm; hence **CCM** is considered a **better** manufacturing method. In another study [32], three manufacturing methods are compared, using the same ink composition (5 wt% Pt-Pd-Vulcan, 1,2-dimethoxyethane, and ethylene glycol). The prepared ink is deposited on the GDL (CCS), Maylar film CCM-DT, and membrane (CCM). For the CCS method, 0.5 ml Nafion solution is applied on top of the catalyst layer and immersed in hot water for the elimination of chemical reagents; then the MEA is hot pressed at 137 °C and 65 kg/cm^2 for 2.5 min. In the decal and CCM methods, the same hot press condition is applied but in a different sequence (or step) during the MEA manufacturing process – in the decal method, hot press is first used to transfer the catalyst layers to the membrane, and then second to form the MEA with the GDLs; but only one hot press process is implemented for the CCM method. Finally, both MEAs are immersed in boiling water. The **best** performance is reported for the **CCM-DT method**, with the maximum power density of 210 mW/cm^2 for the operation with hydrogen/oxygen at the atmospheric pressure, 60 °C and full humidity. An even better performance, associated with DTM and using a breaking layer, is reported by another research group and compared to CCM and LTDM in a direct methanol fuel cell [28].

In a recent study, guided cracks into the catalyst layer are formed on purpose via stretching the CCM to develop passageways in the catalyst layers for the transport of water, and it is shown that the maximum power density of the MEA is increased by 18% in comparison to the conventional MEA [33]. However, it is also reported that MEA distortion results from the stretching process, and is not applicable for large sized MEAs.

For CCS method, ultra-low platinum loading has been achieved via sputtering technique without scarifying the cell performance [34]; however, the durability of the resulting MEAs is not available. Combination of CCS with decal method is also reported in terms of the so-called double cathode catalyst layer [35], where the cathode catalyst layer is composed of an inner layer (faced to the membrane) prepared by the decal method with the Pt loading of 0.3 mg/cm^2, and an outer layer (faced to the gas diffusing layer) fabricated by CCS method with the Pt loading of 0.1 mg/cm^2. The resulting MEA has 13.5% higher power density at the current density of 1.4 A/cm^2 as compared with the MEA made by the conventional decal method.

It is clear that there is a lack of systematic and comprehensive comparison and analysis of the different manufacturing methods under identical/similar manufacturing and testing conditions, including the sensitivity of the MEA performance to such important factors such as Pt loading and number of hot press in the manufacturing process. Therefore, the objective of the present study is to investigate systematically the different MEA manufacturing methods including the CCS, CCM and N-LTDM, and the impact of each manufacturing step on the cell performance under identical manufacturing and testing conditions. The present study also investigates the effect of important factors such as the number of hot press (twice for decal method; CCM with one, two, or no hot press) and different catalyst loadings.

2. Experiment

2.1. Materials

Nafion 211 is used as the electrolyte without any pre-treatment; Nafion solution (5 wt%)–alcohol based with equivalent weight of 1100 as ionomer; Johnson Matthey HiSPEC 9100 (58.8% Pt-C) as the catalyst (hereinafter referred to as 60% Pt/C catalyst); carbon paper (AvCarb) and Isopropyl alcohol (99.9% purity) as the gas diffusion layer and solvent, respectively; fluorinated ethylene propylene (FEP, 200A, DuPont) as the inert decal substrate.

2.2. Ink preparation

The catalyst ink is made by mixing the proper amount of 60% Pt/C with deionized water, followed by adding Nafion and isopropyl alcohol. The ionomer-to-catalyst ratio is 1:3 by weight. The ink is homogenized by placing it in an ultrasonic bath for one hour at room temperature.

2.3. MEA manufacturing method

Membrane electrode assemblies (MEAs), with active area of 45 cm^2, are manufactured using CCS (catalyst coated substrate), CCM (catalyst coated membrane), and N-LTDM (low temperature decal method with an extra layer of Nafion on top of the catalyst layers facing the membrane) [29]. The main difference among these methods is the substrate on which the catalyst layer is deposited and the number of hot presses involved, as illustrated in Fig. 1. It is shown that the catalyst layer is deposited directly on GDL for CCS, on membrane for CCM and on inert decal substrate for DTM; and one hot press process for the CCS and CCM, while two hot press processes for the DTM – first hot press for the transfer of the catalyst layers from the decal substrate to the membrane,