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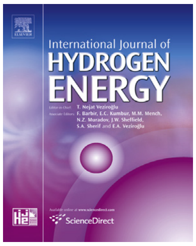

Influence of compressive stress on the pore structure of carbon cloth based gas diffusion layer investigated by capillary flow porometry

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ABSTRACT

Gas diffusion layer (GDL) is subjected to compressive stress at high temperature along with polymer electrolyte membrane in the fabrication process and in assembling the fuel cell stacks. Compressive stress decreases the thickness of GDL, electrical conductivity, permeability, and affects the pores. Carbon cloth based GDL withstands higher strain level when compared to carbon paper and the pore structure is also disrupted to a greater extent in cloth based GDL. In the present paper, we have addressed the effects of stress on pore structure of cloth based GDL. An optimum GDL must offer low mass transport resistance in an operating PEM fuel cell. The pore size analysis of pristine GDL and GDLs pressed at different pressure levels (200, 600 & 1000 kg cm^{-2}) and their characteristics are evaluated using capillary flow porometry. The compressive stress affects the three types of pores in GDL called *bubble point pore*, *mean flow pore* and *smallest pore*. The change in electrical resistance, wetting behavior and surface morphology is also examined as a function of compressive stress. The fuel cell performances using these GDLs pressed at different compressive stresses are also evaluated and presented. The highest PEMFC performance is achieved at a compressive stress of 200 kg cm^{-2}, which could be attributed to the combined effect of reduced ohmic resistance and optimized pore structure. The order of increasing performance in terms of current density is observed to be $j_{200} > j_{Pristine} > j_{600} > j_{1000}$ at 0.15 V. The thicknesses and pore sizes of custom made GDL for optimum fuel cell performance are recommended.

1. Introduction

Gas diffusion layer (GDL) is one of the key components in membrane electrode assembly (MEA) of Proton exchange membrane fuel cell (PEMFC). The performance of an operating fuel cell is typically characterized by three polarization regimes viz. Activation, ohmic and mass transport regions. A key performance limiting factor in higher current densities is due to the mass transport loss, which originates from liquid water transport and resulting flooding phenomena in the constituent components. Performance in the mass transport region depends on pore structure and permeability of the GDL.

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GDL structure consists of a substrate (carbon cloth) coated with carbon powder, hydrophobic agent, and pore formers, limits current in the mass transport region. Different pore sizes and their distribution in the GDL help with reactant transport and water retention to hydrate ionomer [1]. It has been suggested through several modeling and experimental studies that in order to achieve the optimum pore structure characteristics, it is necessary to have composite diffusion layers which include a micro porous layer (MPL) [2–7]. Micro porous layer adds smaller pores or micro pores which could be easily filled by-product water and condensed water from humidified reactant. However, the pores must be unoccupied for the reactant transport to reach catalytically active sites. MPL is coated on macro-porous substrate (Carbon cloth) in order to build a graded porous structure. MPLs are prepared according to the operating conditions of PEM fuel cell with various loadings of hydrophobic agent and carbon content in a graded porous GDL. This has better water management capability and provides better mating between the layers to reduce contact resistance in an operating PEM fuel cell. MPL also acts as a physical support for catalyst layer, thus it helps in preventing the precious catalyst from dropping into the GDL, thereby reducing loss of catalyst. MPL also decreases the contact resistance of catalyst layer with GDL by acting as an inter layer between the catalyst layer and carbon substrate [8]. At high current densities, MPL allows an additional diffusion path for electrons. Larger pores or macro pores are less prone to flooding; hence will not hinder the flow of reactants. Small pores are considered as water reservoirs and therefore built close to the membrane for hydration.

GDLs are subjected to compressive stress during MEA fabrication, which affects the pore size, pore structure, and its distribution. The fuel cell performance in the high current density regions depends mainly on the pore structure, thickness, and the permeability of GDL. The pore structure dominates the polarization loss in addition to activation and ohmic losses in the mass transport region. It is necessary to connect the performance characteristics with a comprehensive evaluation of porosity of the GDL. The optimum porosity of the gas diffusion electrode for low and high temperature PEMFCs depends on limiting current, air stoichiometry, and hydrogen utilization [9–14]. The knowledge of optimum porosity helps to balance the mass transport and catalyst utilization for high performing fuel cell electrodes. Su et al. [15] carried out a numerical analysis of compressed, uncompressed, and nonhomogeneously compressed GDL on the fuel cell performance. Higher limiting current density was observed for uncompressed GDL than nonhomogeneously compressed and compressed GDL. Similarly, two phase model of GDL (near the ribs and channel) was studied by Chippar et al. [16]. Their investigations revealed that local variation in current density due to the compression of GDL induces significant ohmic and concentration polarization as a result of deformed pores. Park et al. [17] investigated the optimum pore structure for paper and cloth based GDL using mercury intrusion porosimetry (MIP). Micro porous layer with increased pore volume for oxygen transport towards the catalyst layer was found to be effective due to efficient water removal from catalyst layer to gas flow channel. In addition, it was observed that the liquid phase water management in GDL with a hydrophobic micro porous layer improves the overall performance by repelling water from the GDL. The optimum pore structure for better performance depends on the hydrophobic content and the thickness of the micro porous layer [18].

The capillary flow porometry evaluates the pore size characteristics of porous materials. Accurate detection of intruded mercury in MIP has some limitations, especially in GDLs with smaller pore volume due to the back streaming of extruded mercury in some samples which leads to inaccurate estimation of pore volume [19]. Jena and Gupta [20] studied the effects of compression on the pore sizes of thin fibrous battery separator through a capillary flow porometer. The capillary flow porometry is often the preferred method of GDL characterization, due to its relatively faster and non-destructive nature [21]. It measures three types of pores in the GDL, based on the flow rates of fluid. In wet samples, the pressure corresponding to the flow of gas through the *largest pore* is called bubble point pressure. The plot of pressure versus flow rate is referred to as '*wet curve*' and after emptying the pores the same plot is recorded on the dry sample which corresponds to the '*dry curve*'. The *smallest pore* is determined by the intersection of the wet and dry curve. The '*half dry curve*' is calculated simultaneously at a given pressure which corresponds to half of flow rate observed in the dry curve. The *mean flow pore* size and the pressure at which it opens are determined from the intersection point of wet and half dry curve [22,22]. Since carbon cloth based GDL withstands higher compressive stress, it is informative to explore the pore structure of carbon cloth based GDL with the applied compressive stresses. A study of this kind also helps in choosing better GDL for the electrodes of PEM fuel cells, especially the pore structure and porosity of cathode which is fairly thicker than anode. Commercialization of this technology necessarily requires the undertaking of systematic studies on the functionality of representative materials and components that possess known and controllable structures and functionalities. In the present paper, GDLs are compressed to create a varied pore structure comprising of micro and macro pores, the effects of compressive stress on the GDL thickness and porosity are studied using the capillary flow porometry. The trend in pore structure, permeability, electrical conductivity, compression ratio is determined and its dependence on the applied pressure is studied. Their morphology is examined using scanning electron microscopy and the overall fuel cell performance and electrochemical impedance of MEAs using compressed GDLs are evaluated and presented.

2. Experimental

Carbon cloth was wet proofed with poly tetra fluoro ethylene (PTFE) solution. Then a mixture comprising of Vulcan XC 72 carbon and PTFE was coated onto the carbon cloth, dried in a series of temperatures ranging from 50 °C to 400 °C. The process details can be found elsewhere [23]. The finished GDLs were compressed using a hydraulic press from M/s. Carver, USA at various pressures ranging from 200 to 1000 kg cm^{-2}. GDL's thickness was measured using micrometer with a 0.01 mm least count. The compressive forces were selected in such a way to have a notable compression ratio of the GDL