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Gradation of mechanical properties in gas-diffusion electrode. Part 2: Heterogeneous carbon fiber and damage evolution in cell layers

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ABSTRACT

In PEM fuel cell, gas-diffusion electrode (GDE) plays very significant role in force transmission from bipolar plate to the membrane. This paper investigates the effects of geometrical heterogeneities of gas-diffusion electrode layer (gas-diffusion layer (GDL) and catalyst layer (CL)) on mechanical damage evolution and propagation. We present a structural integrity principle of membrane electrode assembly (MEA) based on the interlayer stress transfer capacity and corresponding cell layer material response. Commonly observable damages such as rupture of hydrophobic coating and breakage of carbon fiber in gas-diffusion layer are attributed to the ductile to brittle phase transition within a single carbon fiber. Effect of material inhomogeneity on change in modulus, hardness, contact stiffness, and electrical contact resistance is also discussed. Fracture statistics of carbon fiber and variations in flexural strength of GDL are studied. The damage propagation in CL is perceived to be influenced by the type of gradation and the vicinity from which crack originates. Cohesive zone model has been proposed based on the traction–separation law to investigate the damage propagation throughout the two interfaces (carbon fiber/CL and CL/membrane).

1. Introduction

The commercial success of polymer electrolyte membrane (PEM) fuel cell depends on durability, stability, and reliability issues associated with the cell layers among which mechanical durability is still open for investigation on a much broader class. The power density of PEM fuel cell largely depends upon the coupled electro-chemical and electro-mechanical optimal functioning of the MEA. Many investigations and review articles have been reported recently on the electro-chemical and electro-mechanical durability of cell layers [1–10]. Durability is directly influenced by the degradation mechanism that is different for each layer (membrane, GDL, and CL). For example on a mechanical perspective, membrane, CL, and GDL differ due to their respective material responses of polymer, ductile, and brittle materials. Interplay among these failure modes is the key to understand the structural integrity principle especially near interfacial regions and the mechanical degradation of MEA.

There are number of reasons to study GDL on a mechanical perspective since gas diffusion with optimum flexural stiffness and high structural integrity remains to be the basic mechanical requirements for an ideal GDL [11,12]. One commonly referred problem with the GDL structural integrity is an uneven compression [13–17], which may possibly reduce the cell efficiency by directly affecting its porosity. Further, this will affect the water management ability of the whole cell and is considered as one of the major failure modes in fuel cell [4]. Compression of GDL also leads to carbon fiber breakage and deterioration of hydrophobic coatings as reported by Lin et al. [16] and Bazylak et al. [17]. Further, electrical contact resistance between GDL and bipolar plate (BPP) is considered as one of the major irreversible losses in PEM fuel cell. Researchers have developed various numerical models to predict the contact resistance and the recent advances relative to this field can be found elsewhere [18–24]. Very recently, Wu et al. [18] suggested two models—simplified model and generalized model. Simplified model considers only the elastic deformation near contact asperity, whereas, generalized model considers both the elastic deformation as well as carbon fiber bending. It can well be observed from their results that influence of the elastic deformation is dominative to the electrical resistance indicating the importance of material property responses in BPP as well as carbon fiber. On the other hand, GDL is primarily a carbon–carbon composite [25] where carbon fiber breakage (brittle material) and stress transfer from the broken fiber to intact fiber results in damage accumulation. Volume fraction of the matrix withholding carbon fibers is unknown and is assumed very less as compared to the fiber volume fraction. Further, GDL is a highly porous material (70% porosity) and thus carbon fibers play a key role in force transmission and energy absorption. Although there are experimental evidences suggesting

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the structural failure of GDL, there are no attempts in developing precise numerical models to relate the failure of carbon fiber to GDL. This is because, GDL cannot be treated as a conventional composite material, and hence the classical design principles to define failure modes (e.g., shear failure; flexural strength) of composite material can no longer be applied here directly. In this article, we are presenting a single fiber damage model and flexural strength variation of GDL based on the fiber–bipolar plate (BPP) interaction.

Further, under the BPP land area, carbon fibers of GDL are subjected to compressive loading and under the channel area they are subjected to tensile loading. This nature of the loading followed by a partial unloading caused due to fuel cell operating conditions may cause carbon fiber fracture (tensile or compressive direction), provided the strength of the fiber exceeds its ultimate strength (fracture limit). Further, the 'heterogeneity' of GDL is very well established and it is worth noting that 'heterogeneity' of GDL in all literatures refer to random distribution of carbon fibers which are again compounded by the graded distribution of pores and binder material. However, studying at nano-level, our study predicts that the heterogeneity exists itself in the Teflon® coated carbon fibers which are the building units of GDL and are considered to be a supporting structure against the external compressive forces. As mentioned before, contact resistance is related to the elastic deformation in carbon fiber. Hence, it is highly possible that gradation in carbon fiber properties influences the variation in electrical contact resistance.

This article is broadly classified into two divisions. In the first part, flexural strength of GDL based on fracture toughness of carbon fiber and load transfer limit is investigated. In the second division, damage propagation in GDE is estimated with a special concentration on CL as well as GDL/CL and CL/membrane interfaces. GDL and CL are highly porous structures and hence are capable of absorbing higher amount of energy through a number of energy dissipation mechanisms (chemical or mechanical). It is learnt from our companion paper [26] that CL is a ductile material and it will follow a ductile damage over many loading cycles due to the plastic damage accumulation. Ductility enhancement is associated with the toughness increment in that it is actually related to evolution and motion of dislocations near the vicinity of critical damage. Habitually, ductile fracture is a strain controlled phenomenon unlike brittle fracture which is stress controlled.

Structural integrity principles near interfaces of MEA are explored in this study by evaluating the material response at nano-level. Damage evolution and delaminations are related to the stress transfer mechanism, which is again largely dependent of the cell layer inhomogeneity. Effect of hygrothermal and freeze/thaw cycling can only accelerate this delamination and material degradation. Therefore, justifying the fact that interfacial toughness and geometrical inhomogeneity plays a deciding factor in damage evolution and propagation in a cell layer, a cohesive zone model is developed to understand and investigate the effects of geometrical heterogeneities on the through-plane crack propagation.

2. Analytical models

2.1. Asperity size independent contact resistance model

At first, we define the electrical contact resistance between two conducting bodies as the ratio of change in voltage potential to the current passing through the constricted area. Hence we have

$$R_c = \frac{\Delta V}{I} = \frac{\rho_1 + \rho_2}{Q} \tag{1}$$

In Eq. (1), R_c is the contact resistance, ΔV is the voltage potential difference, I is electrical current. ρ_1, ρ_2, Q are electrical resistivity of carbon fiber, resistivity of BPP asperity and current flux density integrated over the constricted area, respectively. Evaluation of contact resistance between BPP and GDL requires the knowledge of carbon fiber bending and its elastic deformation by a BPP asperity. Elastic deformation is considered dominative and is used in overruling the contribution of fiber bending. Now, we assume that the relative motion at the asperity contact is governed only by the elastic deformation (δ_e); hence, by neglecting the inelastic deformation, relative motion (δ_r) near the contact asperity is equated to the elastic displacement as in the following equation:

$$\delta_r = \delta_e \tag{2}$$

Contact force (F_c) established by the surface asperity of BPP on carbon fiber can be related to fiber's stiffness (K) and the elastic deformation (force–displacement relation) and it is given as

$$F_c = K\delta_e \tag{3}$$

From the elastic-electrical analogy developed by Barber [27], we can have the following equation:

$$K = E_\gamma Q \tag{4}$$

where E_γ is the effective modulus and is expressed in terms of E_{bpp} (BPP modulus) and E_{cf} (carbon fiber modulus) and their Poisson's ratios—υ_1 and υ_2 as in the following equation:

$$E_\gamma = \left(\frac{E_{bpp}}{1-\upsilon_1^2} + \frac{E_{CF}(\delta_e)}{1-\upsilon_2^2} \right) \tag{5}$$

Contact stiffness can be related to Eq. (2) as follows:

$$K = K(\delta_e) \tag{6}$$

Now, electrical contact resistance can be reframed as follows:

$$R_c = \frac{(\rho_1 + \rho_2)E_\gamma}{K} \tag{7}$$

According to Eq. (5) and (6), contact stiffness and elastic modulus are increasing or decreasing function of elastic deformation in the fiber. Above is a simple analogy, which has significant information regarding the mechanical material property variation in single carbon fiber on electrical contact resistance variation. Present model is not restricted to spherical contacts that are commonly assumed in deriving the contact resistance near BPP/GDL interface.

Information regarding contact asperity size can be used in combination with the Eq. (7) to work this model as a contact asperity size dependent.

2.2. Failure model for single carbon fiber

Nanoindentation load–displacement data of single carbon fiber can be used for obtaining the stress–strain response of the fiber. Average stress (σ_c) on a single carbon fiber can be given as load (L) by indentation area (A_p):

$$\sigma_c = \frac{L}{A_p} \tag{8}$$

Strain (ε) estimation must consider the geometrical aspects of the indenter. In our experiment, Berkovich indenter is used and it has a very small radius (around 100 nm) at its tip. In case of spherical indenter, indenter strain is given by

$$\varepsilon \approx \frac{a}{R} \tag{9}$$

where R is the indenter radius and a is the radius of contact area at indentation (see Fig. 1(a)). It is noted from Eq. (9) and Fig. 1(a) that the above ratio is small and contact depth (h_c) is less than the maximum contact depth ($d_{\max}$).