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Gradation of mechanical properties in gas diffusion electrode. Part 1: Influence of nano-scale heterogeneity in catalyst layer on interfacial strength between catalyst layer and membrane

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ABSTRACT

Stress and plastic deformation analyses of catalyst layer have been conducted after experimentally investigating its mechanical properties at nano-scale. Interestingly, catalyst layer is found to have varying mechanical properties as a function of depth and therefore it is classified under graded material. Effect of gradation in catalyst layer on interfacial strength between membrane and catalyst layer is explained with the aid of numerical simulations. Stress redistribution near interface line is observed in graded model, while stresses are found to have concentrated at critical locations throughout the discrete model. However, it is outlined from this study that the gradation in catalyst layer leads to greater amount of plastic energy dissipation—an indication of enhanced ductility. An experimental coupled numerical approach is presented to characterize the effect of transitional variations of mechanical properties in catalyst layer on the interfacial line and membrane.

1. Introduction

Graded materials are classes of materials where structural and mechanical properties vary as a function of depth. Some natural examples of these include bamboo, bone and some biological structures [1–3]. Learning from the nature, biological structures self-evolve in developing material layers to protect themselves from the external forces. Imitating the structural integrity principles involved in these structures (focused on material gradation), innovative materials can be made available for engineering applications. In structural applications, graded materials find their major role in sustaining greater amount of stresses and thereby functioning as a damage resistant [4]. This concept can be advantageous in the interfacial contact regions where force transmission takes place, particularly between two dissimilar materials such as gas diffusion layer (GDL) and nafion membrane. However, the choice of gradation in any engineered material must be reasonable. In a PEM fuel cell, catalyst layer (here after it is denoted as CL) work as an interfacial layer between GDL and membrane. It is later found in this study that CL belongs to a class of graded materials. The choice of CL as a graded material was totally unintentional (spray coated on GDL) which raises an important question – whether this gradation is desirable under PEM fuel cell loading/operating conditions or not? External loading and material property varying directions are the two basic parameters to be considered in utilizing the graded material for a desired application (employing a continuously graded material near the interface would suppress the evolution of crack or permanent plastic deformation [5]). Vital information in terms of modulus or stiffness variation from a graded material surface to the bottom level can be helpful in quantifying the stress concentration and related failure mechanisms. If CL acts as a 'smooth transition zone' (caused due to gradation in its composition) between GDL and membrane, it will reduce the crack driving force throughout the interface by maintaining a good interfacial bond. Gradation can be defined over a single layer and/or when its definition is applied to the whole system, it will be referred as a 'graded system'. MEA (membrane electrode assembly) is one perfect example for a 'graded system', where an individual-layer has a different modulus and yield/failure limits and its values are expected to decrease in an exponential or stepwise (absence of smooth gradation) manner. However, it is too early to comment further on its effect on the structural integrity of the fuel cell system without being studied about the interfacial CL. Hence, in our current study we deal with a thorough investigation on mechanical property variation in CL from its surface to the bottom.

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On the other hand, from a macroscopic perspective, degradation of fuel cell parts largely depends upon the fabrication and operating conditions as well as on the individual-layer material properties. Structural durability of MEA is one of the areas where morphological defects do exist [6,7] and may lead to severe mechanical failure modes. It is believed that fuel cell working conditions such as varying temperature, humidity and external compressive load are the primary factors for 'mechanical degradation' in the interfacial region between membrane and CL. Studying the structural response of MEA through numerical simulation under the cell operating conditions will give much knowledge about actual underlying principles of failure. Numerical simulation of cracks in bulk CL and delaminations between the cell layers (membrane and CL) becomes more challenging given the nature of complexity in assigning the material properties for CL. Lack of understandings about mechanical characterization of CL certainly hinders the simulation capabilities to predict the failure. Recent developments related to structural analyses can be found elsewhere [8–11]. All of the structural simulations done to date have assumed CL and gas diffusion layer as a one single layer referred as gas diffusion electrode (GDE) due to the unknown mechanical properties of CL.

Nafion and Pt/C black are the major constituents of CL. In general, distribution of pores and networks depends on these constituents' distribution and fabrication process. Studies [12,13] show that performance of cathode electrode is directly influenced by the distribution of nafion content (multilayered catalyst coating) and better results are expected when nafion content is higher toward membrane than toward GDL. In other words, CL is said to have 'graded', when there is a non-uniform distribution of nafion content. However, like in our case, when a single CL is coated over GDL, nafion distribution would be uniform. Hence, on mechanical perspective, it is presumed in our study that nafion is a binder material and Pt/C particles are spatially distributed. From now on, the CL would be classified as a 'graded' or 'uniform' based on the Pt/C particle distribution and not by the binder material.

For our experimental investigation, instrumented indentation, also referred as 'nanoindentation' is opted for mechanical characterization of CL. Nanoindentation is commonly used for measuring nano- or microscale mechanical properties of thin films. However its application is not only limited to films. This technique has become ubiquitous in characterizing the mechanical properties of materials whose properties are size or small volume dependent. Recently, nanoindentation has been applied to characterize the mechanical properties of nanowires [14,15], CNTs [16], amorphous carbon films [17], nanobelts [18], biological tissues [19,20], and nanocomposites [21]. The obtained values of load and displacement as a function of depth or time are used to calculate the hardness and elastic modulus. It is also possible to establish a relation between contact stiffness and displacement and from this, material under investigation can be classified as a graded or uniform one. Sensing its capability to characterize the individual constituents within the heterogeneous sample, it can well be adopted in obtaining the mechanical parameters of CL.

Experimental data obtained from indentation is used in combination with the FEA (finite element analysis) to evaluate the yield strength and resulting stresses in catalyst layer. Indentation behavior of combined CL and membrane (in our present investigation it will be referred as a dual-layer system) is also studied numerically. Discrete and graded models with two different layers (membrane and CL) having the same material model (elastic–plastic) are opted for our present study. It will be interesting to see on how these mechanical gradations affect the indentation behavior of discrete CL as well as on dual-layer models.

2. Experimental

In the following, procedure adopted in preparing CL is explained. The carbon slurry was prepared by mixing carbon black (Vulcan XC72, Cabot) vigorously with the distilled water. Then this mixture was heated to 90 °C. The pH of the slurry was adjusted to the basic using NaOH. The chloroplatinic acid (H_2PtCl_6, Aldrich) solution, prepared by dissolving into the distilled water, was added to the carbon slurry and the pH of the slurry was again adjusted to the basic. Reducing agent was then introduced into the slurry for in situ liquid phase reduction. The Pt/C mixture was filtered, washed, and then dried at 90 °C. From now on 20 wt% Pt/C catalyst referred as Pt/C-1. Catalyst ink was prepared by dispersing Pt/C catalyst in a mixed solution of ethanol and nafion. Prepared catalyst ink was coated on GDL (Carbon paper, Toray) using spray technique. Pt loading was 0.15 mg cm^{-2}. Same procedure is followed in preparing the 20 wt% Johnson–Matthey based catalyst layer (here after it is referred as J–M).

For mechanical characterization, samples (Pt/C-1 and J–M) of 0.5 cm^2 were carefully cut and subjected to indentation testing. Nano indenter G200 (MTS corp.) with Berkovich diamond indenter tip was used for our experimental investigations. Samples were mounted on sample disk, which was initially heated using heating element to appropriate temperature in order to bond the sample and disk using small amount of crystalbond.

3. Analytical

In general, contact on graded material can be typified as elastic or plastic. Corresponding numerical modeling also follows the same material models. In the elastic graded material, either modulus increases or decreases from a surface level to the bottom, linearly or nonlinearly. In contrast to homogeneous material, graded model must involve these gradations as a function of material thickness. Quantifying a material for its contact stiffness can be very informative in predicting its strength as a function of depth. It is now understandable that modulus and hardness are dependable on material stiffness throughout the material thickness. On the other hand, indentation modeling of graded material under plastic material model requires an estimation of the yield strength. Further, the yield strength of a graded material varies as a function of depth and thus numerical modeling becomes even more challenging than the elastic case.

Fig. 1(a) shows the schematic diagram of indentation on graded material (non-uniform particle distribution). Generalizing the results obtained in the literature [1,21] one can predict the contact stiffness response of graded material to be nonlinear for an increasing indentation depth. This gives information related to the particle distributions in a material. Initial increase in contact stiffness for a small indentation depth is attributed to the densely packed particles on a surface level. Fig. 1(a) is a typical case where slope of the stiffness curve decreases, indicating a decreasing modulus of the material. If the slope increases upon indentation depth, material is possessed to have an exactly opposite behavior (increasing gradation). Fig. 1(b) shows a schematic representation of indentation on uniform material. Corresponding response of contact stiffness as a function of indentation depth is linear. Fig. 1(c) depicts a typical indentation curve for loading and unloading response of a material as a function of indenter displacement. This curve is used to obtain important mechanical parameters such as modulus and hardness. Contact stiffness, S, can be obtained from the slope of the initial part (straight line) of the unloading curve that can then be used to calculate the reduced modulus using a following