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Microscale characterisation of stochastically reconstructed carbon fiber-based Gas Diffusion Layers; effects of anisotropy and resin content

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HIGHLIGHTS

- We propose a novel algorithm for resin deposition in GDLs.
- We obtain microscale information using X-ray micro-CT measurements.
- We study the transport properties of realistic reconstructed GDLs.
- We focus primarily on the effects of resin content and medium anisotropy.
- Our numerical calculations compare very good with experimental data.

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ABSTRACT

A novel process-based methodology is proposed for the stochastic reconstruction and accurate characterisation of Carbon fiber-based matrices, which are commonly used as Gas Diffusion Layers in Proton Exchange Membrane Fuel Cells. The modeling approach is efficiently complementing standard methods used for the description of the anisotropic deposition of carbon fibers, with a rigorous model simulating the spatial distribution of the graphitized resin that is typically used to enhance the structural properties and thermal/electrical conductivities of the composite Gas Diffusion Layer materials. The model uses as input typical pore and continuum scale properties (average porosity, fiber diameter, resin content and anisotropy) of such composites, which are obtained from X-ray computed microtomography measurements on commercially available carbon papers. This information is then used for the digital reconstruction of realistic composite fibrous matrices. By solving the corresponding conservation equations at the microscale in the obtained digital domains, their effective transport properties, such as Darcy permeabilities, effective diffusivities, thermal/electrical conductivities and void tortuosity, are determined focusing primarily on the effects of medium anisotropy and resin content. The calculated properties are matching very well with those of Toray carbon papers for reasonable values of the model parameters that control the anisotropy of the fibrous skeleton and the materials resin content.

1. Introduction

Proton Exchange Membrane Fuel Cells Fuel Cells (PEMFCs) are compact electrochemical energy conversion devices consisting of stacks of several layers of materials that perform different highly specialized functions (Fig. 1). The reacting gases (typically H_2 and O_2) are introduced into the Membrane Electrode Assembly (MEA), the core of the system, through appropriately designed flow channels (bipolar plates) and diffuse towards the catalytic electrodes, where the electrochemical reactions take place to generate electricity [1]. The diffusion of the reactants from the flow channels to the catalyst layers is facilitated by a highly porous and tortuous, electrical conductive layer, namely the Gas Diffusion Layer (GDL), with a typical thickness of a few hundreds of microns [2]. GDLs are placed between the flow channels and the electrodes (anode and cathode) on both sides of the MEA and their properties related to

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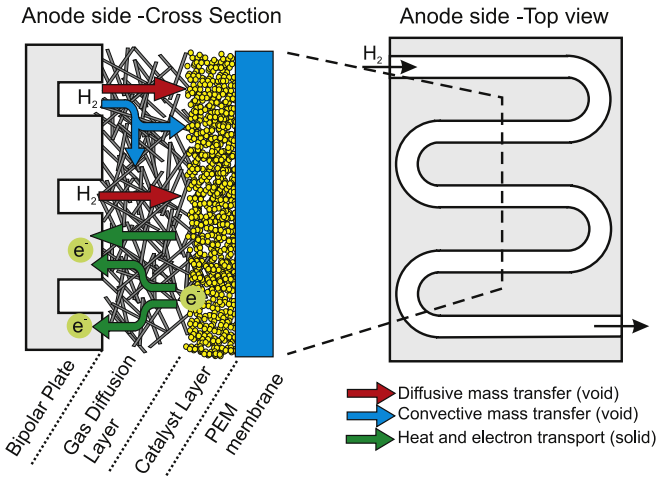

Fig. 1. Schematic of dominant transport mechanisms through the Gas Diffusion Layer at the cross-section of the anode side of a PEM fuel cell. H_2 flows through the channels of the bipolar plane and is transferred towards the catalytic surfaces by diffusion (primarily in the through-plane direction) and convection (primarily in the in-plane direction). The electrical current and heat flow in the opposite direction from the catalyst towards the ribs of the bipolar plate. Higher in-plane conductivities allow for the enhanced collection of electrons and heat from regions of the catalyst surface that are not directly below the ribs.

flow, mass transfer, thermal and electrical conductivity, constitute a crucial parameter for the efficient operation of PEMFC units.

GDLs combine particular transport and structural properties (such as high porosity and permeability to flow) that allow for the efficient flow and mass transport of the reacting species towards the electrodes, even below the ribs of the bipolar plates (that are not in direct contact with the flow channels (Fig. 1)), thus significantly extending their active electrocatalytic surface [2]. GDLs also exhibit excellent electrical and thermal conductivity for the efficient removal of the electrons and heat produced at the catalytic electrodes towards the ribs of the bipolar plates, as well as significant structural strength under compression, which is typically applied to ensure gas-tight conditions [3]. It is thus clear that GDL characteristics are quite essential for the optimization of the PEMFCs' design and the improvement of their performance.

The typical types of materials currently used as GDLs in PEMFCs, include carbon-based materials (such as woven carbon cloths, non-woven carbon papers, carbon foams) or metal-based materials (e.g. meshes, metal foams and other micromachined metal substrates) [4]. The vast majority, however, of GDLs in commercially-available PEMFCs are made of Carbon fiber-based (C-fiber) papers, primarily due to their relative easy and low-cost fabrication from conventional papermaking processes using polyacrilonitrile (PAN) filaments with a typical diameter of 12–14 μm [5]. After carbonizing the filaments at temperatures of 1200–1350 °C, the carbon fibers are chopped into smaller pieces (3–12 mm long) and dispersed into water with polyvinyl alcohol that serves as a binding agent. The film produced after drying is impregnated with a carbonizable, typically thermosetting, resin (e.g. phenolic) that allows for the formation of a fabric-type material at the desired thickness and density. The resin content of this intermediate material typically ranges between 50 and 70% w/w [2]. At the final stage of the production process, heating at temperatures well above 2000°C is applied resulting in the graphitization of the C-fiber-resin composite and significantly enhancing the robustness, but also the transport properties of the finished product. During this step, the material loses approx. 40% of its initial weight, with a greater weight loss originating from the resin component, rather than the already carbonized C-fiber skeleton. While accurate measurements are still lacking in the literature, it may be expected that the resin content of the finished product lies between 10 and 30% w/w. The above production route is currently adopted by manufacturers such as Toray Industries Inc., while other methods are also available (including the use of PTFE powder to bind the material and increase the contact area between fibers, instead of resin impregnation and graphitization) [2].

The accurate determination of the transport properties of such C-fiber/ resin composites is a field of very active research in recent years. A series of studies, both experimental [6–11] and numerical [12,13], have been devoted to the investigation of several important continuum-scale (macroscopic) properties, including permeabilities, thermal and electrical conductivities, also addressing the variation of these features at the in-plane/through-plane directions due to the material's anisotropy. The numerical studies reported so far have focused on the microscale reconstruction of the fibrous matrix for the direct solution of transport equations at the pore scale and the calculation of spatial averages over larger material samples. In this context, different material reconstruction methods have been proposed including pore networks [14,15], Voronoi tesselations [16], but also process-based methods for the representation of the spatial distribution of the individual components of the composite (fibers and resin) [17–20]. The latter, process-based, concept has proven quite successful in reproducing structures that are at least qualitatively similar with the images of the actual material obtained from electron microscopy (e.g. SEM) and/or microtomographic imaging methods (e.g. X-ray μ-CT). The determination of the spatial distribution of the resin component, however, still remains an open challenge, since most of the proposed methods are based on a rather phenomenological approach of morphological opening, that relies on placing spheres of increasing radii in the fibrous skeleton to mimic the wetting behavior of the resin [21,22]. The precise determination of the resin's spatial distribution is in fact a crucial parameter for the accurate calculation of key transport properties of the material, and primarily those related to the through-plane cross-sectional area between fibrous layers, such as thermal and electrical conductivities. However the results of the numerical studies that have attempted so far to address this topic, are quite scattered, and often significantly diverging from experimental data. Those discrepancies have been attributed to the uncertainty related to the bulk phase properties of the two components (resin and fibers), rather than the domain reconstruction method itself [12,19–21].

In the present work we propose a novel process-based methodology for the realistic, stochastic reconstruction of composite carbon fiber/resin matrices, by combining standard algorithms for the anisotropic deposition of carbon fibers [23] with a rigorous resin model hat has significant advantages over conventional approaches, as it allows to obtain realistic, physically meaningful spatial distributions of the graphitized resin based only on very few adjustable parameters. The latter pursues the minimization of the interfacial energy of the system through a stochastic phase redistribution algorithm, which physically describes the wetting process taking place during the impregnation of the fibrous matrix with the resin. In order to be able to arrive to realistic digital domains with this methodology, we first performed X-ray computed microtomography (μ-CT) measurements on commercially available carbon papers to deduce their typical pore and continuum scale properties (average porosity, fiber diameter, resin content, anisotropy). This information is further used for the digital reconstruction of the carbon paper samples, where we solve the corresponding conservation equations at the microscale in order to determine their effective transport properties, such as Darcy permeabilities, effective diffusivities, thermal/electrical conductivities and void