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A method for measuring relative in-plane diffusivity of thin and partially saturated porous media: An application to fuel cell gas diffusion layers

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ABSTRACT

A new experimental technique, extended from similar work on dry materials, is presented for measuring the in-plane components of the relative diffusivity tensor for partially saturated porous media. The method utilizes a custom-built holder and measures the transient response to oxygen concentration changes at the boundaries of a porous sample placed between two plates surrounded by a cooling block. The apparatus is kept close to the freezing temperature of water to ensure stable saturation throughout the experiment. Fick's second law is used to fit the transient change in concentration to a numerical solution to obtain the diffusion coefficient for samples of differing saturation. As expected the effective gas diffusivity is found to decrease with increasing water saturation of the media as the porosity is reduced and the tortuosity of the diffusion pathways increased. After extensive validation, this new technique is used to determine the relative in-plane diffusivity of some common fuel cell gas diffusion layer materials. The results are found to follow a power-law function dependent on the saturation consistent with previous modelling work. Samples without hydrophobic treatment are found to have lower relative gas diffusivity, compared with treated samples for the same average saturation.

1. Introduction

Transport in thin, partially saturated porous media is of interest to fuel cell engineers due to the use of thin porous materials known as gas diffusion layers (GDL) in polymer electrolyte fuel cells (PEFC). Water produced by the reaction on the cathode side of the PEFC can form liquid which percolates throughout the GDL, blocking reactant gases and reducing performance through mass transport limitations [1]. The GDL has been intensively studied to date, but mostly with respect to single-phase transport properties [2–9]. To reduce stack costs, cell manufacturers aim to increase power density, which in turn increases water production within the cell. Under these conditions, the GDL can become partially filled with liquid water owing to the condensation of water vapour if the relative humidity exceeds the saturation point. If ameliorating mechanisms are not in place, such as purging or heating, the reactant diffusion through the media becomes significantly hindered compared to dry conditions. An understanding of the *relative* diffusivity, i.e. how gases diffuse through the partially water-filled porous media, is essential for understanding and improving the performance of the fuel cell.

The typical material used as GDLs is a carbon fibre paper which exhibits anisotropic transport characteristics. Fibres have a high degree of in-plane (IP) alignment, increasing transport in this direction compared with through-plane (TP). The TP direction tends to be the focus of studies, as this is the principal direction for transport from the gas channels to the reaction sites. However, IP transport is also important for distributing gases beneath the flow-field ribs, facilitating a more uniform current-density across the cell, and increased durability [7,10]. Channel design and implications are reviewed by Hamilton & Pollet [11]. To make the GDLs more hydrophobic and therefore improve water management they are often treated with PTFE. Flückiger et al. showed that PTFE treatments reduce diffusive transport by occupying and blocking the pore pathways [4], but this reduction is a worthwhile trade-off since it prevents liquid water from spreading within the GDL where it would completely block gas diffusion.

A review of the experimental and modelling techniques used to characterize the diffusive transport in PEFC materials is presented by Ismail et al. [12]. Numerous techniques have been employed to measure the dry diffusivity in both IP and TP directions. Büchi and co-workers used electrochemical impedance spectroscopy (EIS) to

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measure the ionic transport in an electrolyte soaked GDL, and by analogy diffusive transport [5,13,14]. This technique is not readily adaptable to partially saturated porous media, due to problems establishing a two-phase liquid-liquid solution. However, numerous in-situ techniques can be applied to diagnose mass transfer in running fuel cells, such as EIS and limiting current measurements [15] employing measurements coupled with models to extract the contributions of each component to mass transfer limitations. However, with in-situ techniques, knowledge and/or control of the water saturation becomes more difficult, and setups must also be combined with expensive visualisation techniques such as X-ray radiography [16]. Another method is the Loschmidt cell, which measures the transient concentrations of a mixture within two chambers separated by a porous sample and/or controllable barrier [17,18]. This method has not been applied in the IP direction, although the approach presented by Rashapov et al. [19] is similar; a step change in concentration boundary conditions is applied and the transient concentration of oxygen is measured.

To date, only a few studies have succeeded in measuring the diffusivity in GDLs under conditions of variable water saturation [20–22]. These studies all focused on the TP direction, but to fully understand transport within the GDL it is also necessary to measure the IP component(s) of the diffusivity tensor. These methods are unsuitable for IP measurements, however, since they require the use of a reactive layer on one face of the GDL to consume the transferring species resulting in a TP diffusive flux. Numerous studies have approached the problem by modelling transport using direct numerical simulation on images of the GDL microstructure. Becker et al. obtained tomographic images of dry GDLs, then simulated water invasion using morphological image opening, followed by diffusion calculations in the remaining gas space [23]. The problem with this approach is that simulating water invasion in mixed wettability, fibrous, anisotropic media is not trivial. Garcia-Salaberri et al. performed Lattice-Boltzmann simulations on tomographic images with water injected during imaging, hence providing realistic invasion patterns [24]. A key finding of that work and the subsequent work [25] was that global average water saturation was not a good indicator of diffusive resistance. The presence of saturation gradients undermined any attempts to extract generalized trends about relative diffusivity. Garcia-Salaberri et al. also recommend that diffusion measurements are made under conditions of uniform saturation profile.

The aim of the present paper is to demonstrate an experimental methodology, which could be applied to any thin porous media, to evaluate the relative IP diffusive transport in the presence of water-filled pores. The method utilizes an oxygen sensor placed inside a custom-built sample holder that enables the control of temperature and oxygen concentrations at the outer boundaries of the samples. Saturation is carefully controlled and regulated by keeping the water in a state close to freezing. The transient response to a step-change in oxygen concentration at the boundaries is used to calculate diffusivity using Fick's second law. The present study is the first to experimentally examine the in-plane diffusive transport through the GDL as a function of water saturation.

2. Scientific approach

2.1. Theoretical background

2.1.1. Relations for dry material

The general conservation of mass equation for a species in a fluid passing through porous media, neglecting sources since no reactions or phase changes are taking place and assuming incompressible flow, is given as:

$$\frac{\partial(\phi C)}{\partial t} = -\nabla \cdot (C\boldsymbol{u_s} - \boldsymbol{D_{EFF}}\nabla C) \tag{1}$$

where ϕ is the porosity of the medium, $\boldsymbol{u_s}$ is the superficial velocity ($\boldsymbol{u_s} = \phi\boldsymbol{u}$), C is the concentration or volumetric fraction in the fluid phase (mol m^{-3}), and $\boldsymbol{D_{EFF}}$ is a general effective diffusion-dispersion tensor defined as:

$$\boldsymbol{D_{EFF}} = \phi D_{AB}\boldsymbol{I} \tag{2}$$

where I is the identity tensor, D_{AB} is the molecular diffusion coefficient of species A through stagnant species B and is assumed to be spatially constant, as the sample holder temperature is held constant. The GDL is assumed to be isotropic in the cross-sectional plane normal to diffusion. We also assume a zero pressure gradient across the sample and attribute all motion to diffusion so that Eq. (2) becomes a scalar: $D_{EFF} = \phi D_{AB}$. Combining Eq. (2) into Eq. (1), and also simplifying to its one dimensional form, known as Fick's 2nd Law of Diffusion, we have:

$$\frac{\partial(C)}{\partial t} = D_{AB}\nabla^2 C \tag{3}$$

Note that ϕ has now disappeared because the impact of the reduction in pore volume on the time-dependent accumulation term (LHS) and the reduction in flux of species in D_{EFF} (RHS) cancel each other. Shen and Chen [26] warn that cancelling of the porosity term leads to identical concentrations at a given point in space and time regardless of the material's porosity, an incorrect result. This implies that the effective diffusion coefficient must also scale inversely with tortuosity like:

$$D_{EFF} = D_{AB}\frac{\phi}{\tau_\phi} \tag{4}$$

where tortuosity, τ_ϕ, represents the increase in diffusion path length in the presence of obstacles in the form of the solid phase and is defined here as:

$$\tau_\phi = \left(\frac{\Delta l}{\Delta x}\right)^2 \tag{5}$$

where Δl is the diffusion path length and Δx is the physical length of the medium. Using the effective diffusion coefficient, Eq. (3) becomes:

$$\frac{\partial(C)}{\partial t} = \frac{D_{AB}}{\tau_\phi}\nabla^2 C = D'\nabla^2 C \tag{6}$$

Here the notation D' is used to represent a reduced diffusion coefficient, dependent only on tortuosity. There is much confusion surrounding the definition of tortuosity, owing to the inconsistent mathematical treatments throughout the literature, as documented by Epstein [27]. It is common in fuel cell literature to express the normalized effective diffusivity of dry materials purely in terms of porosity, such as:

$$\frac{D_{EFF}}{D_{AB}} = f(\phi) = \frac{\phi}{\tau_\phi} \tag{7}$$

since the tortuosity is some function of porosity. A common expression for τ_ϕ is $\phi^{-0.5}$ leading to: $f(\phi) = \phi^{1.5}$. Other common expressions for $f(\phi)$ are presented by Shen and Chen [26] and Hwang and Weber [20].

2.1.2. Extension to partially saturated material

When considering a partially saturated domain, liquid can be treated in a similar fashion to the solid phase, with the effect of both reducing the pore volume and increasing the tortuosity. So if saturation, S, is the fraction of the pore volume occupied by water, then all the ϕ terms can be multiplied by $(1 - S)$ and the effective diffusivity can be formulated as follows: