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Contradictory concepts in tortuosity determination in porous media in electrochemical devices

Bernhard Tjaden [a], Donal P. Finegan [a], Jonathan Lane [b], Dan J.L. Brett [a], Paul R. Shearing [a,*]

[a] Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, WC1E 7JE, UK
[b] Praxair, Inc., 175 E. Park Dr., Tonawanda, NY 14150, USA

HIGHLIGHTS

- Microstructural analysis of oxygen transport membrane porous supports.
- Correlative tortuosity determinations via X-ray tomography and diffusion cell experiments.
- Evaluation of the effect of tortuosity, porosity and sample thickness on diffusion resistance.
- Visible differences between different tortuosity calculation approaches are encountered.
- Diffusion cell experiments yield the highest and geometric image quantification results in the lowest tortuosity values.

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ABSTRACT

Porous media are a vital component in almost every electrochemical device in the form of electrode, support or gas diffusion layers. Microstructural parameters of porous layers such as tortuosity, porosity and pore size diameter are of high importance and crucial for diffusive mass transport calculations. Among these parameters, the tortuosity remains ill-defined in the field of electrochemistry, resulting in a wide range of different calculation approaches. Here, we present a systematic approach of calculating the tortuosity of different porous samples using image and diffusion cell experimental-based methods. Image-based analyses include a selection of geometric and flux-based tortuosity calculation algorithms. Differences between the image and diffusion cell-based results are encountered and attributed to the small pore diameters and thereby induced Knudsen effects within the samples which govern the diffusion flux.

1. Introduction

The rate limiting step at high fuel utilisation ratios of oxygen transport membranes (OTMs) and fuel cells is dominated by mass transport limitations through porous layers (*cf.* concentration losses in fuel cells) (Virkar et al., 2000; Wilson and Barnett, 2008; Shearing et al., 2013a). Here, microstructural characteristics of porous structures including tortuosity, porosity and pore size diameter, play a vital role in quantifying gaseous mass transport (Kast and Hohenthanner, 2000; Bertei et al., 2013; Yuan and Sundén, 2014).

At the same time, the mechanical stability of electrochemical devices during operation is ensured by porous support layers, commonly placed on the anode side. Such porous support layers can be several orders of magnitude thicker compared to the functional electrode and electrolyte layers (Tsai and Schmidt, 2011). Their mechanical strength is adjusted by altering either the microstructural properties, such as the porosity (Chen et al., 2015; Kaiser et al., 2016), or the thickness of the support layer. However, modifying these parameters can influence the mass transport behaviour and hence, the performance of the device.

The aforementioned microstructural characteristics are interrelated in a complicated manner (Robertson et al., 2010; Shearing et al., 2010), where tortuosity remains notoriously difficult to calculate (Tjaden et al.). In electrochemistry, the tortuosity is commonly used to quantify the resistance of a structure towards a flux.

Geometrically, tortuosity is defined as the shortest path length through a porous structure divided by its thickness. Yet, in combination with porosity, the tortuosity is also used to relate the bulk diffusion of a gas in empty space to the effective diffusion coefficient of a gas migrating through a porous membrane as shown in Eq. (1) (Epstein, 1989). The easiest approach to estimate tortuosity is by using porosity-tortuosity relationships (Shen and Chen, 2007), such as the widely applied Bruggeman equation (Bruggeman, 1935; Tjaden et al., 2016a), which estimate a tortuos-

* Corresponding author.
E-mail address: p.shearing@ucl.ac.uk (P.R. Shearing).

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Nomenclature

ε	porosity (–)
μ	dynamic viscosity (kg m^{-1} s^{-1})
τ	tortuosity (–)
B_O	viscous flow parameter (m^2)
c_i	molar concentration (mol m^{-3})
D_{bulk}	bulk diffusion coefficient (m^2 s^{-1})
D_{eff}	effective diffusion coefficient (m^2 s^{-1})
$D_{i,K,eff}$	effective Knudsen diffusion coefficients (m^2 s^{-1})
$D_{i,Kn}$	Knudsen diffusion coefficient (m^2 s^{-1})
$D_{ij,eff}$	effective binary diffusion coefficient (m^2 s^{-1})
d_P	mean pore diameter (m)
$d_{P,2D}$	2D pore diameter
$J_{i,D}$	diffusion flux (mol m^{-2}s^{-1})
M_i	molar mass (kg mol^{-1})
p	pressure (Pa)
R	ideal gas constant (J mol^{-1} K^{-1})
S_v	2D interface area between the two phases
T	temperature (K)
V_P	2D pore volume fraction
y_i and y_j	molar fractions (–)

ity and thus, an effective transport property value based solely on the porosity of the structure. However, such correlations are only valid for a small number of ideal microstructures (Chung et al., 2013), which makes them invalid for the microstructures analysed here (Tjaden et al., 2016b).

$$D_{eff} = \frac{\varepsilon}{\tau^2} D_{bulk} \quad (1)$$

Due to the difficulty in determining the tortuosity of a porous membrane, a wide range of different methods have been developed in the field of electrochemistry (Tjaden et al.). Recently, improved access to tomography techniques, such as lab-based X-ray computed tomography has increased the amount of microstructural data extractable for a single sample (Izzo et al., 2008; Shearing et al., 2013b; Taiwo et al., 2016a) and has provided new ways to calculate tortuosity. However, there is a lack of standardisation across the different calculation approaches. Studies have shown that differences between imaging, simulation and experimental-based calculation methods can amount to more than a factor of two (Tjaden et al., 2016b) and might only achieve agreement under certain conditions (*e.g.* at high concentration losses Brus et al., 2014). One reason for this may be that image-based techniques typically do not consider all of the transport phenomena during diffusive mass transport such as Knudsen effects and are inherently limited by the imaging resolution (Finegan et al., 2016).

Here, we present a systematic study comparing a range of tortuosity calculation algorithms of OTM porous support layers. Previously, published work by the authors (Tjaden et al., 2016b) focused on quantifying the tortuosity of OTMs through planar diffusion cell experiments at ambient temperatures. As a consequence, diffusion cell experiments are carried out at temperatures of up to 600 °C, which is close to the operating temperature of OTMs and solid oxide fuel cells (Singhal and Kendall, 2003; Delbos et al., 2010). In addition, lab-based X-ray nano computed tomography is used to capture and reconstruct the OTM microstructure in 3D for image-based calculations. The tortuosity values calculated via diffusion cell experiments of the tubular, yttria partially-stabilized zirconia (YSZ) porous support membranes are then compared with image-based simulation approaches. The effect of tortuosity, porosity and thickness of the sample structure on the membrane's resistance to diffusive mass transport is evaluated via this correlative approach and the disparity of measurements between methods is elucidated.

2. Experimental

2.1. Description of samples

For diffusion cell experiments, four tubular YSZ porous support samples were provided by Praxair, Inc. (Tonawanda, NY, USA), which differed in porosity and wall thickness. The differences in porosities were achieved by varying the sintering temperature of the samples: Table 1 shows the different tubular samples and their respective parameters, where porosity values lay between 22.6% and 30.0% and wall thicknesses between 1.0 mm and 1.3 mm. The tubular samples were cut to equal lengths of 110 mm for the diffusion cell experiments.

The porosity values for each sample were calculated by comparing the gravimetrically determined apparent density of the sample to the density of the material. The sample names indicate the porosity and thickness of each membrane. Finally, the samples were capped off on one end to fit with the tubular diffusion cell test rig, as explained in the next section.

2.2. Diffusion cell experiments

The diffusion cell test rig layout was similar to the one used previously (Tjaden et al., 2016b), which was extended by a tubular furnace, housing the tubular diffusion cell. Fig. 1A and B illustrate the components used and the operating principle of the diffusion cell for the tubular porous support samples, respectively. The samples were mounted via a standard 1/4″ Swagelok Ultra-Torr vacuum fitting to ensure gastight sealing. A high temperature O-ring (BS012P330B, Polymax Ltd.) was inserted for experiments below 300 °C. For temperatures above 300 °C, a ceramic adhesive (Ceramabond 685-N, Aremco Products, Inc.) combined with layers of Thermiculite 866 (Flexitallic Ltd.) was applied around the 1/4″ fitting. The furnace was capable of reaching temperatures above 1000 °C, however, the highest temperature during experiments was set to 600 °C due to the maximum operating temperature of stainless steel components of the tubular diffusion cell.

The tubular samples were sealed on one end to fit into the cell configuration shown in Fig. 1: fuel gases were injected into the tubular sample by a 1/8″ tube, which reached as close to the sealed end of the tubular sample as possible. The injected fuel gas was thus forced to travel back towards the 1/4″ along the inside of the porous sample. The whole cell was operated inside an impervious aluminous porcelain work tube with an inner diameter of 38 mm, mounted in a tubular furnace (EST 12/300B, Carbolite Ltd.). The void between the porous support sample and the work tube was swept with pure nitrogen, flowing counter-currently to the fuel gas on the inside of the porous membrane. The diffusion cell layout presented here is comparable to the reactor used by Delbos et al. (2010), where the performance of a tubular OTM for CH_4 reforming was evaluated.

Diffusive mass transport across the porous membrane was induced by injecting pure N_2 on the outside and a pure fuel gas on the inside of the porous support layer. Fuel gases considered