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Analysis of representative elementary volume and through-plane regional characteristics of carbon-fiber papers: diffusivity, permeability and electrical/thermal conductivity

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ABSTRACT

Understanding the transport processes that occur in carbon-fiber papers (CFPs) used in fuel cells, electrolyzers, and metal-air/redox flow batteries is necessary to help predict cell performance and durability, optimize materials and diagnose problems. The most common technique used to model these thin, heterogeneous, anisotropic porous media is the volume-averaged approximation based on the existence of a representative elementary volume (REV). However, the applicability of the continuum hypothesis to these materials has been questioned many times, and the error incurred in the predictions is yet to be quantified. In this work, the existence of a REV in CFPs is assessed in terms of dry effective transport properties: mass diffusivity, permeability and electrical/thermal conductivity. Multiple sub-samples with different widths and thicknesses are examined by combining the lattice Boltzmann method with X-ray tomography images of four uncompressed CFPs. The results show that a meaningful length scale can be defined in the material plane in the order of 1–2 mm, which is comparable to the rib/channel width used in the aforementioned devices. As for the through-plane direction, no distinctive length scale smaller than the thickness can be identified due to the lack of a well-defined separation between pore and volume-averaged scales in these inherently thin heterogeneous materials. The results also show that the highly porous surface region (amounting up to 20% of the thickness) significantly reduces the through-plane electrical/thermal conductivity. Overall, good agreement is found with previous experimental data of virtually uncompressed CFPs when approximately the full thickness is considered.

1. Introduction

Carbon-fiber papers (CFPs) are an integral component of numerous energy conversion and storage technologies, including gas diffusion layers (GDLs) in polymer electrolyte membrane fuel cells (PEM fuel cells) [1–10], cathode GDLs in PEM electrolyzers [11,12] and metal-air batteries (MABs) [13,14], and electrodes in redox flow batteries (RFBs) [15–17]. CFPs must fulfill several critical functions such as providing adequate mechanical support to the membrane electrode assembly (MEA), a transport pathway for reactants/products through its pore volume, and electrical and thermal conductivity through its solid fibrous structure [10,18–20]. In RFBs, they have the added functionality of providing a reactive surface area [17,21–23]. On the way to broad commercialization, a thorough understanding of the mass, charge and heat transport properties of these materials is crucial to achieving improved performance and durability [2,18,19].

CFPs are thin, highly porous composite materials made of polyacrylonitrile (PAN)-based carbon fibers (diameter ∼6–12 μm), usually connected by a carbonaceous binder. If necessary, a hydrophobic polytetrafluoroethylene (PTFE) coating can also be added to enhance removal of product liquid water [10,20]. A

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Nomenclature

Symbols

A	cross-sectional area [m^2]
C	mass concentration [mol m^{-3}], temperature [K], electronic potential [V]
$\boldsymbol{c}$	lattice velocity [m s^{-1}]
c_s	lattice speed of sound [m s^{-1}]
D	mass diffusivity [m^2 s^{-1}]
d	diameter [m]
f	particle distribution function, normalized effective gas-phase diffusivity [–]
f_{solid}	normalized effective solid-phase conductivity [–]
h	mute variable
$\boldsymbol{j}$	diffusive flux [mol m^{-2} s^{-1}], conductive flux [J m^{-2} s^{-1}], current density vector [C m^{-2} s^{-1}]
K	permeability [m^2]
k	thermal conductivity [W m^{-1} K^{-1}]
L	length [m]
l	chord length [m]
p	pressure [Pa]
R_e	Reynolds number [–]
s	water saturation [–]
t	time [s]
$\boldsymbol{u}$	velocity [m s^{-1}]
x	in-plane coordinate [m]
$\boldsymbol{x}_{\mathrm{i}}$	node position [m]
y	secondary in-plane coordinate [m]
z	through-plane coordinate [m]

Greek letters

α	index
Δ	increment
δ_{ft}	full thickness [m]
ε	porosity [–]
ε_{i}	area-averaged porosity in i-direction [–]
υ	kinematic viscosity [m^2 s^{-1}]
ρ	density [kg m^{-3}]
σ	electrical conductivity [S m^{-1}]
τ	dimensionless relaxation time [–]

Subscripts

f	carbon fiber
g	gas phase
gr	graphite
i	direction of interest
ip	in-plane direction
p	pore
tp	through-plane direction

Superscripts

avg	average
bulk	bulk property
eff	effective property
eq	equilibrium

Abbreviations & acronyms

CFP	carbon-fiber paper
CR	core region
FT	full thickness
GDL	gas diffusion layer
IP	in-plane
LBM	lattice Boltzmann method
MAB	metal-air battery
MEA	membrane electrode assembly
MPL	micro-porous layer
PEM	polymer electrolyte membrane
PNM	pore-network model
PTFE	polytetrafluoroethylene
REA	representative elementary area
REV	representative elementary volume
RFB	redox flow battery
SR	surface region
TP	through-plane
X-CT	X-ray computed tomography

variety of manufacturers produce CFPs, including Toray Industries, SGL Carbon Group, Freudenberg and Mitsubishi Rayon Corporation [24]. The porosities and thicknesses of commercial CFPs are in the range of 0.6–0.9 and 100–400 µm, with a mean pore radius in the order of tens of micrometers [19,20]. CFPs typically show high anisotropy between the in-plane (IP) and through-plane (TP) directions due to the predominant arrangement of carbon fibers in the material plane. Moreover, properties can vary within the material plane, where the machine and cross-machine directions can be distinguished due to the preferential orientation of fibers that arise from the manufacturing process [10,25,26].

Modeling the various coupled transport processes that occur in CFPs is one of the key tools used to design novel materials and optimize operation of the above-mentioned devices [2,27,28]. However, there are several approaches to achieve this modeling. The traditional technique is to invoke the macro-homogeneous continuum approximation, which treats the porous medium as a homogeneous domain with effective transport properties [2,29]. Examples of effective properties are the permeability used in Darcy's law, the tortuosity factor used to correct Fick's law of diffusion, or the effective electrical and thermal conductivities used in Ohm's and Fourier's laws [2,18,19,30,31]. Continuum formulations are derived upon the assumption of a representative elementary volume (REV) [32,33]. A REV is defined as the smallest subset of a material that shows similar volume-averaged properties as larger subsets. A REV must therefore satisfy two requirements: (i) it has to be large enough to be a meaningful volumetric average of the discrete microstructure; and (ii) it has to be small enough to not be affected by any large-scale heterogeneity of the porous medium. In addition, a REV should be significantly smaller than any characteristic length of the problem at hand to ensure that its boundary region is small compared to the size of the modeled domain. The above requisites should be satisfied for all volume-averaged quantities of interest (e.g., porosity, saturation and effective properties) to be confident that the scenario under study can be rigorously described using the continuum approach.

The continuum hypothesis is generally valid for geological applications in pseudo-infinite domains, such as flow in rocks and soils [32,33]. Researchers in these disciplines are concerned that sub-samples used for testing are not too small, being several orders of magnitude smaller than the geologic formation, and that they represent meaningful volumetric averages. If necessary, spatially-varying transport properties can also be incorporated to account for any macroscopic heterogeneity above the REV scale. However, CFPs represent the opposite limit: being so thin allows one to test and model the entire domain (at least in the TP direction), but the question then arises whether the microstructural randomness of the material allows for a definition of a REV within