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Effective transport coefficients in PEM fuel cell catalyst and gas diffusion layers: Beyond Bruggeman approximation

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A B S T R A C T

The Bruggeman approximation has widely been used for estimating the effective conductivity and diffusivity of both the catalyst and gas diffusion layers of polymer electrolyte membrane (PEM) fuel cells. This approximation is based on the Bruggeman's Effective Medium Theory [Bruggeman D. Berechnung verschiedener physikalischer konstanten von heterogenen substanzen. Ann Phys (Leipzig) 1935;24:636–79], which provides empirical correlation for the effective properties of a composite system. Since it is an empirical correlation, a unique correlation based on the Bruggeman approximation does not always hold for the PEM fuel cell effective properties. Rather, the Bruggeman correlation is a cell specific and experiment dependent correlation that depends on structure, phase composition, water saturation, experimental parameters, etc. Further, this correlation needs to be combined with other correlations to estimate the effective diffusivities. In this article, a set of mathematical formulations has been proposed for the effective transport properties in both the catalyst and gas diffusion layers of a PEM fuel cell. The effective conductivity and diffusivity expressions are derived from the mathematical formulations of the Hashin Coated Sphere model [Hashin Z. The elastic moduli of heterogeneous materials. J Appl Mech 1962;29:143–50], which provides an identical mathematical foundation for each of these effective properties rather than an empirical correlation and avoid to use of multiple correlations together. The present model formulations agree well with the results available in literature for the limiting case. Hence, the proposed formulations for the effective transport properties will be a useful estimating tool in the numerical modeling of PEM fuel cells.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are considered as most promising candidate for the next generation power sources for portable, mobile, and stationary co-generation applications due to its high power density, low operating temperature, quick start-up, and fast dynamic response. Hence, there has been immense interest to the numerical modeling and simulation of PEM fuel cells to gain better understanding of the fundamental processes and to optimize engineering design parameters. The numerical modeling/simulation of a PEM fuel cell is always based on the conservation of mass, momentum, energy, and species. Expression for the effective properties in these conservation equations are needed for the closure of formulation. Further, an accurate estimation of the effective properties in PEM fuel cells, e.g. effective conductivities and diffusivities in the catalyst layers (CLs) and gas diffusion layers (GDLs), is crucial for accurately predicting the fuel cell performance and optimizing design parameters in the numerical modeling/simulation.

Over the last century, there has been immense interest in calculating the effective physical properties for composite systems [1–11] (e.g. effective dielectric constants, effective thermal conductivities, effective electric conductivities, effective elastic constants, effective magnetic permeabilities, etc.). There are varieties of techniques available, including approximate methods, rigorous bounding techniques, and numerical methods [1,2,12,13]. Among these techniques, the Effective Medium Theory (EMT) is considered as the most powerful approach to estimate the effective properties for the composite systems, such as cosmic dusts, aerosols, and porous media. One of the oldest and most popular EMT is the Maxwell-Garnett (MG) mixing rule that was developed for optical properties of a medium [2]. Another popular EMT is the Bruggeman approximation (BA) that was developed for the effective electrical properties of a composite system [1]. The MG mixing rule only holds for the dilute composite media, while the BA has a wider applicability. The BA was initially founded from intuition that the total polarization of an electric field is zero throughout the homogenized composite medium. So far, many other approaches and predictive

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Nomenclature

A	area (m^2)
d	dimensionality of the system
D	diffusivity $(m^2\ s^{-1})$
f	volume fraction; surface coverage
HS	Hashin–Shtrikman bound
r	radius (m)
s	liquid saturation
V	volume (m^3)
W	Wiener bound

Greek letters

α	empirical constant
δ	thickness (m)
ϵ	porosity
ϵ_p	percolation threshold
ε	dielectric constant
λ	geometry factor
ϕ	bulk property
ρ	density $(kg\ m^{-3})$
σ	conductivity $(S\ m^{-1})$

Superscripts

eff	effective value
m	Bruggeman exponent
n	saturation exponent

Subscripts

12	composite made of phases 1 and 2
123	composite made of phases 1, 2, and 3
b	bulk value
C	carbon
CL	catalyst layer
eff	effective value
g	gas phase
GDL	gas diffusion layer
i	the ith phase $(i = 1, 2, 3, 4, \ldots)$
l	liquid phase; lower limit
m	membrane phase
max	maximum value
n	number of particle
Pt	platinum
s	solid phase
θ	surface coverage
u	upper limit
v	void space

Abbreviations

BA	Bruggeman approximation
CL	catalyst layer
EMT	Effective Medium Theory
GDL	gas diffusion layer
HS	Hashin–Shtrikman
MG	Maxwell-Garnett
PEM	polymer electrolyte membrane

schemes have been proposed based on the EMT in various fields of science and engineering [3–11].

Generally, for a two-phase flow in a porous medium such as in CLs or GDLs of a PEM fuel cell, the effective physical property can be expressed as:

$$\phi_{\text{eff}} = \phi_b f(\epsilon) f(s) \tag{1}$$

where ϕ_b represents the bulk property, ϵ is the porosity, and s is the liquid saturation in a porous medium. Several empirical correlations for Eq. (1) have been proposed in literature. The most prominent formulation used for the PEM fuel cells is Bruggeman's approximation that is based on the EMT [1]. According to the EMT, the bulk effective property for a composite system of a two-phase flow in a porous medium satisfies:

$$f_1 \frac{\phi_1 - \phi_{\text{eff}}}{\phi_1 + (d-1)\phi_{\text{eff}}} + f_2 \frac{\phi_2 - \phi_{\text{eff}}}{\phi_2 + (d-1)\phi_{\text{eff}}} = 0 \tag{2}$$

where ϕ_{eff} represents the effective property in a two-phase composite system, and $\phi_1$and ϕ_2 are the bulk properties of phases 1 and 2, respectively. The terms f_1 and f_2 represent the volume fractions of phases 1 and 2 in the two-phase composite system, respectively, and d is the dimensionality of the system. Later, Böttcher [4] provided a formulation by considering the electric field inside a spherical particle. Although both the Bruggeman's equation and the Böttcher's formulation have different origins and forms, it was observed that both formulations give approximately the same result [5].

For the effective diffusivity in a composite system, Tomadakis and Sotirchos [14] suggested a percolation type correlation for random fibrous porous media as:

$$D_{\text{eff}} = D_b \epsilon \left(\frac{\epsilon - \epsilon_p}{1 - \epsilon_p} \right)^{\alpha} \tag{3}$$

where ϵ is the porosity, ϵ_p is a percolation threshold, and α is an empirical constant. Recently, Mezedur et al. [11] used a two-dimensional ordered and random lattice network model to predict the effective diffusivity of reactants and products for catalytic converter and proposed the following relation:

$$D_{\text{eff}} = D_b (1 - (1 - \epsilon)^{0.46}) \tag{4}$$

This formulation is the heat-transfer analog that is given in Ref. [15]. The effect of liquid saturation on the gas diffusion has also been modeled numerically using the most commonly used function that is given as:

$$f(s) = (1 - s)^m \tag{5}$$

where m is an empirical constant. Nam and Kaviany [16] later extended the work of Tomadakis and Sotirchos [14] using a network model for anisotropic solid structure and liquid water distribution. Both of these expressions are identical to what is commonly used in literature as the BA, which is expressed as:

$$D_{\text{eff}} = D_b f(\epsilon) f(s) = D_b \epsilon^m (1 - s)^n \tag{6}$$

where the Bruggeman exponent, m, has been widely used as 1.5 and the saturation exponent, n, is considered the same as m, assuming the pore structure does not change with water saturation. It is also worthwhile to note that Neale and Nader [17] proposed formulation for the isotropic porous medium composed of spherical particles as:

$$D_{\text{eff}} = D_b \frac{2\epsilon}{3 - \epsilon} \tag{7}$$

In terms of the effective property bounds, the most widely used bounds are the Wiener bounds [18] and the Hashin–Shtrikman (HS) bounds [10]. The Wiener bounds were derived by assuming that the phases in a composite system are lumped in either series or parallel layers. The effective properties for these cases can be found using the analogy of an equivalent electrical circuit using a series model for the lower limit and a parallel model for the upper limit. Hence, the Wiener bounds can be written as [18,19]:

$$W_l = \left(\frac{f_1}{\phi_1} + \frac{f_2}{\phi_2}\right)^{-1} \tag{8}$$

$$W_u = f_1\phi_1 + f_2\phi_2 \tag{9}$$

where W_l and W_u are the lower and upper limits of Wiener bounds, respectively. Conversely, the HS bounds are [10,20]:

$$\mathrm{HS}_l = \phi_2 + \frac{3f_1\phi_2(\phi_1 - \phi_2)}{3\phi_2 + f_2(\phi_1 - \phi_2)} \tag{10}$$

$$\mathrm{HS}_u = \phi_1 + \frac{3f_2\phi_1(\phi_2 - \phi_1)}{3\phi_1 + f_1(\phi_2 - \phi_1)} \tag{11}$$

where HS_l and HS_u are the lower and upper limits of HS bounds, respectively.

In the PEM fuel cell literature, the Bruggeman approximation has been widely used for the effective conductivities and diffusivities. In several instances both the Wiener bounds and Bruggeman approximation were used together for estimating the effective properties [21–26]. The average of Wiener bounds has also been recommended for the effective thermal conductivity [27]. Previous studies, however, have not used or attempted to implement the HS bounds. It was further observed that the results reported in literature lack information on several physical and electro-chemical parameters. In some cases, it has been found that replicating published results is very difficult because of the missing information or parameter values [21,24]. Further, the effective properties of composite systems depend on the internal microstructure; and no such straightforward method exists to consider the effect of microstructure. Even formulations for the effective properties discussed earlier did not agree with each other. As shown in Fig. 1, while comparing several correlations with the Bruggeman correlation, all the correlations are underestimating the effective diffusivity compared to the Bruggeman correlation. Clearly, each of these correlations has different estimates and it is not reasonable to argue which correlation is a better fit for the numerical modeling of PEM fuel cells. The differences observed in this comparison (Fig. 1) could be that these correlations are empirically fitted to certain experimental results and none of these experiments used similar geometrical and physical parameter values. The formulations available in literature for the effective transport properties were developed for different porous media, for example, fibrous porous media [14], spherical shell porous media [17], sand [28], rock [29], shaly sandstone [30], etc. None of them is specifically developed for the CLs and GDLs of PEM fuel cells. Furthermore, the GDLs of PEM fuel cells are made of hydrophilic carbon cloth and hydrophobic PTFE (Teflon). Hence, the wettability and composition of these materials in GDLs not only change the effective transport properties but also influence the water flooding that can further change the effective properties. Therefore, it is crucial to provide a better mathematical expression for the effective properties of a PEM fuel cell that has fundamental mathematical proof rather than empirical verification, which would be more useful in the numerical modeling of PEM fuel cells. Numerical approaches, like finite volume, finite element, and lattice Boltzmann methods [31,32], can also be used in estimating the effective properties for the PEM fuel cells. These methods, however, require complicated numerical modeling, sophisticated programming knowledge and time-consuming calculation. Hence, there is a significant need to develop a simple correlation for the effective properties that can be easily implemented in PEM fuel cell modeling/simulation.

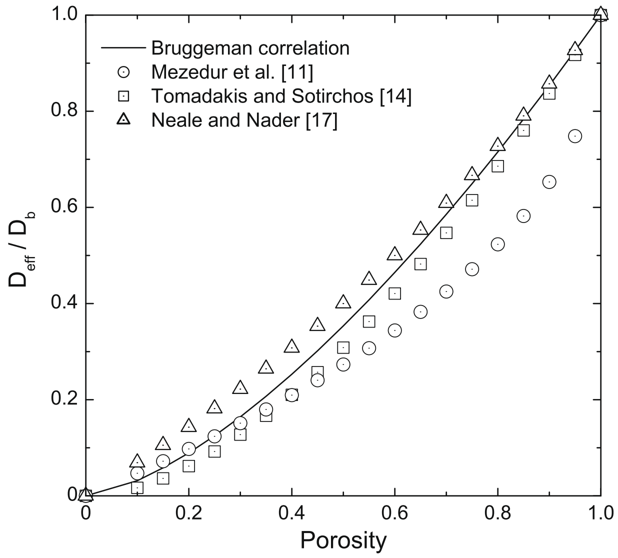

Fig. 1. Comparison of effective diffusivities using the expressions available in literature with the Bruggeman correlation.

In this article, we report a consistent and systematic approach for calculating the effective transport properties in the CLs and GDLs of a PEM fuel cell. The effect of pore size distribution in the porous composite has been neglected as the effect of pore size can be incorporated correcting the bulk effective diffusivity with the Knudsen effect coefficient [16]. The formulations provided in this article are based on the Hashin Coated Sphere model and the HS bounds [10,33]. Through several comparisons with various model results available in literature, we showed the predictive capabilities of the expressions proposed for the effective transport properties in PEM fuel cells. It is worthwhile to mention that no experimental results are available in open literature for these effective transport properties in PEM fuel cells. Here, the mathematical formulations are derived from a well-established model; hence, this type of formulation would be useful for estimating the effective transport properties for the numerical modeling/simulation of PEM fuel cells.

2. Formulation

2.1. Hashin–Shtrikman Model

Using the effective bulk modulus formulation developed by Hashin [33], Hashin and Shtrikman [10] showed an exact expression for the effective conductivity of a coated sphere assemblage. A schematic representation of both the Hashin coated sphere and coated sphere assemblage are shown in two parts of Fig. 2. Here, the coated sphere in a coated sphere assemblage represents a two-phase spherical particle, where phase 1 can be coated by phase 2 (or vice versa) that is shown in Fig. 2a. Each coated sphere in the coated sphere assemblage, shown in Fig. 2b, was considered as a scaled version of the original prototype coated sphere. Practically, it might be impossible to build a macro-homogenous layer using an infinite number of coated spheres. However, considering a composite system with large number of coated spheres that can fill more than 90% of the total volume or higher, it can be shown that the effective property of the composite system will obey the following relation [20]:

$$\phi_1 + \frac{3f_2\phi_1(\phi_2 - \phi_1)}{3\phi_1 + f_1(\phi_2 - \phi_1)} \geqslant \phi_{\mathrm{eff}} \geqslant \phi_2 + \frac{3f_1\phi_2(\phi_1 - \phi_2)}{3\phi_2 + f_2(\phi_1 - \phi_2)} \tag{12}$$

where ϕ_{eff} represents the effective property of the coated sphere assemblage, ϕ_1 and ϕ_2 are the bulk properties, and f_1 and f_2 are the volume fractions of phases 1 and 2 in the coated sphere, respectively. It was also assumed that phases have been labeled, such that $\phi_1 > \phi_2$. Using Eq. (12), we derive the expressions for the effective transport properties in the CLs and GDLs of a PEM fuel cell that are given in the following section.

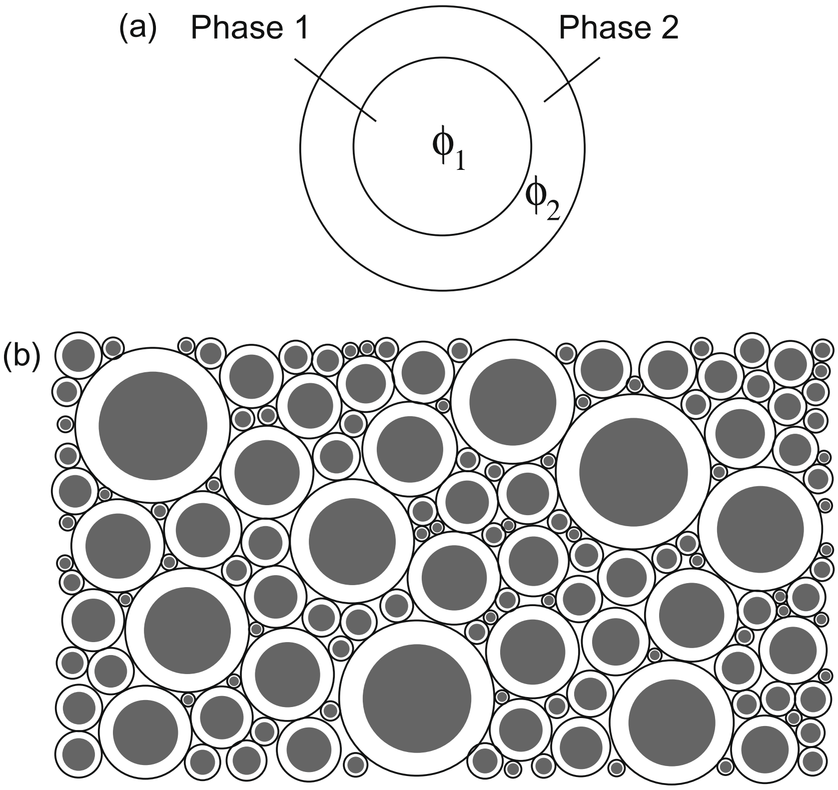

Fig. 2. Schematic representation of: (a) the Hashin coated sphere, and (b) cross section of the Hashin coated sphere assemblage. Each coated sphere in part (b) is a scaled version of the coated sphere shown in part (a) [20].

2.2. Effective conductivity

The microstructure of a PEM fuel cell catalyst layer consists of a matrix of catalyst particles, electrolyte membrane (also known as ionomer), and void space. Ideally, the platinum (Pt) particles supported on a large carbon particle surrounded by ionomer membrane form a catalyst agglomerate, or several carbon particles combine together that is surrounded by ionomer membrane form a large agglomerate. Such a catalyst is also known as platinum supported on carbon or simply referred as Pt/C particle. Fig. 3 shows a schematic representation of the idealized structure of catalyst agglomerate with single carbon particle in part (a) and idealized structure of a large catalyst agglomerate formed by multiple carbon particles in part (b). Part (c) of Fig. 3 illustrates an idealized microstructure of catalyst layer made of such small and large agglomerates with negligible void region, and a simplified structure of catalyst agglomerate is shown in part (d). Here, each of these agglomerates is a scaled version of the original single-carbon agglomerate (Fig. 3a) or multi-carbon agglomerate (Fig. 3b). Generally, the size of the Pt-particles is much smaller than the carbon particles; hence, both the platinum and carbon particles can be considered as one solid phase. Therefore, the catalyst agglomerate can be simplified as a two-phase coated sphere that has a solid core (phase 1) coated with ionomer membrane (phase 2) as shown in Fig. 3d, which is identical to the Hashin coated sphere shown in Fig. 2a. The volume fraction occupied by phase 1 in the coated sphere is represented by:

$$f_1 = \frac{r_1^3}{r_2^3} = 1 - f_2 \tag{13}$$

where f_2 is the volume fraction of phase 2, and r_1 and r_2 are the radii of the inner core (phase 1) and the outer coating (phase 2), respectively. The outer radius of the simplified agglomerate (Fig. 3d) is identical to the radius of the original agglomerates (Fig. 3a), whereas the inner radius needs to be calculated from the volume occupied by the platinum particles and carbon particles that is defined as:

$$r_1^3 = n_C r_C^3 + n_{Pt} r_{Pt}^3 \tag{14}$$

where r_C and r_{Pt} are the radii of carbon and platinum particles, and n_C and n_{Pt} are the numbers of carbon and platinum particles in a catalyst agglomerate, respectively. Using the simplified catalyst agglomerate shown in Fig. 3d, it is possible to re-build a macro-homogenous layer with negligible void space fraction that would be identical to the catalyst layer shown in Fig. 3c. For instance, if the fraction of void space in the CL is 0.1, then 90% of the total CL volume needs to be filled with ionomer membrane coated Pt/C spheres. Practically, this can be attainable. Further, it has been observed that the electrolyte membrane forms a layer on the surface of Pt/C agglomerate when the paste method is used for the fabrication of catalyst layer [34], which is almost identical to the coated sphere assemblage shown in Fig. 3c. Hence, the catalyst layer made of such simplified agglomerates can be compared with the Hashin's two-phase coated sphere assemblage [20], where the Pt/C particle can be treated as phase 1 and the ionomer membrane as phase 2. Therefore, the effective conductivity of the catalyst layer can be estimated from the upper bound of HS formula:

$$\left(\sigma_{12}^{\text{eff}}\right)_u = \sigma_1 + \frac{3f_2\sigma_1(\sigma_2 - \sigma_1)}{3\sigma_1 + f_1(\sigma_2 - \sigma_1)} \tag{15}$$

and the lower bound formula:

$$\left(\sigma_{12}^{\text{eff}}\right)_l = \sigma_2 + \frac{3f_1\sigma_2(\sigma_1 - \sigma_2)}{3\sigma_2 + f_2(\sigma_1 - \sigma_2)} \tag{16}$$

where $\sigma_1 > \sigma_2$, and σ_1 and σ_2 are the conductivities of inner core (i.e., Pt/C for the PEM fuel cell catalyst layer) and outer coating

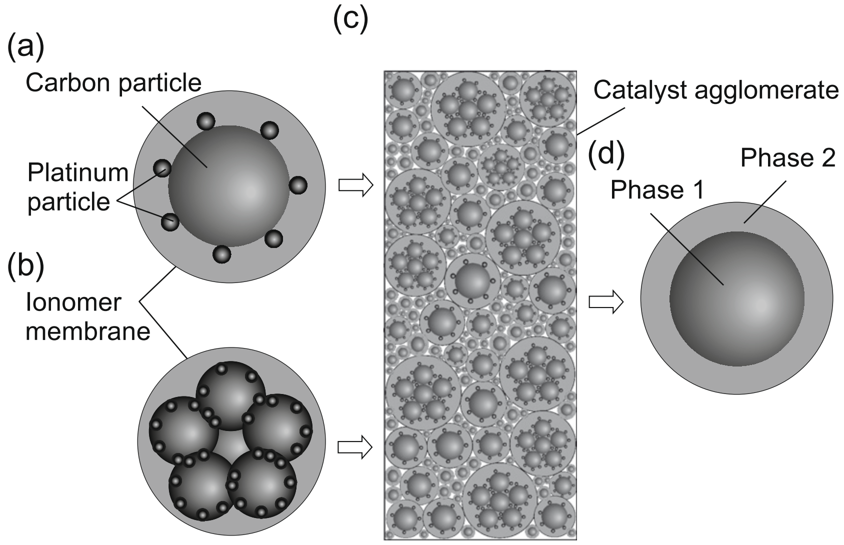

Fig. 3. Schematic representation of: (a) the idealized structure of a small catalyst agglomerate with platinum catalyst particles and single carbon particle, (b) idealized structure of a large catalyst agglomerate formed by multiple carbon particles, (c) idealized microstructure of catalyst layer made of small and large agglomerates with negligible void region, and (d) simplified structure of a catalyst agglomerate.

(i.e., electrolyte membrane for the PEM fuel cell catalyst layer), respectively. The term f represents the volume fraction for different phases as denoted by subscripts.

2.2.1. Proton transport

For proton transport in the catalyst layer shown in Fig. 3c, the inner core of the coated sphere does not transport protons, protons can only be transported through the electrolyte membrane or the outer coating of the coated sphere, i.e., $\sigma_1 < \sigma_2$. Hence, the HS bounds need to be modified for $\sigma_1 < \sigma_2$ as:

$$\sigma_2 + \frac{3f_1\sigma_2(\sigma_1 - \sigma_2)}{3\sigma_2 + f_2(\sigma_1 - \sigma_2)} \geqslant \sigma_{12}^{\text{eff}} \geqslant \sigma_1 + \frac{3f_2\sigma_1(\sigma_2 - \sigma_1)}{3\sigma_1 + f_1(\sigma_2 - \sigma_1)} \tag{17}$$

After re-arranging, Eq. (17) yields:

$$\sigma_2 + \frac{3(1 - f_2)\sigma_2}{f_2 - \frac{3\sigma_2}{\sigma_2 - \sigma_1}} \geqslant \sigma_{12}^{\text{eff}} \geqslant \sigma_1 + \frac{3(1 - f_1)\sigma_1}{f_1 - \frac{3\sigma_1}{\sigma_1 - \sigma_2}} \tag{18}$$

where σ_{12}^{eff} is the effective protonic conductivity of the composite system of phases 1 and 2. Since the inner core is inactive for proton transport, i.e., $\sigma_1 = 0$. For the outer phase, we have $\sigma_2 = \sigma_m$, where σ_m is the bulk protonic conductivity of membrane phase. Hence, the effective conductivity for membrane phase (or the effective protonic conductivity) can be written as:

$$\sigma_m - \frac{3f_s\sigma_m}{3 - f_m} \geqslant \sigma_m^{\text{eff}} \geqslant 0 \tag{19}$$

where σ_m^{eff} is the effective conductivity of membrane phase, and f_s and f_m are the volume fractions of solid Pt/C and ionomer membrane in the catalyst layer, respectively. Practically, the effective protonic conductivity cannot be zero; in such case, there will be no proton transport from the anode side to the cathode side of a PEM fuel cell. For an operating fuel cell that seems impossible too. The lowest possible protonic conductivity has always to be higher than zero; therefore, the lower bound in Eq. (19) cannot exist so that Eq. (19) becomes:

$$\sigma_m - \frac{3f_s\sigma_m}{3 - f_m} \geqslant \sigma_m^{\text{eff}} > 0 \tag{20}$$

Eq. (20) also implies that the highest possible effective protonic conductivity would be:

$$\sigma_{m,\max}^{\text{eff}} = \sigma_m - \frac{3(1 - f_m)\sigma_m}{3 - f_m} \equiv \sigma_m^{\text{eff}} \tag{21}$$

The lower limit of Eq. (20) can be extracted from Eq. (21) when $f_m \to 0$. Further, Eq. (21) is valid for a composite layer composed of solid Pt/C and ionomer membrane with negligible fraction of void space, i.e., for $(f_s + f_m) \to 1$. In such situation, the diffusion of reactant gases in the catalyst layer of a PEM fuel cell will be almost "completely" hindered due to the significantly smaller diffusion coefficient of the reactant in the membrane. Therefore, it would be worthwhile to consider a certain fraction of void space over the ionomer membrane phase, which can be considered as doubly coated sphere as shown in Fig. 4. Here, the solid Pt/C is represented by phase 1, the ionomer membrane is represented by phase 2, and void space is by phase 3. Practically, the void spaces are randomly distributed over the entire catalyst layer. To simplify the problem, it has been assumed that the void space is uniformly distributed over the catalyst agglomerate as shown in Fig. 4, where the outer radius of doubly coated sphere can be estimated for the same equivalent volume:

$$\sum \left(\frac{4}{3}\Pi r_3^3 - \frac{4}{3}\Pi r_2^3 \right) = f_3 V \tag{22}$$

where r_3 is the outer radius of doubly coated sphere and r_2 is the outer radius of phase 2. The term f_3 represents the volume fraction

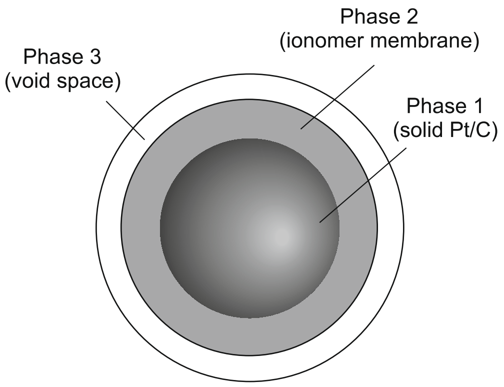

Fig. 4. Schematic representation of a doubly coated sphere.

of phase 3 that is equivalent to the total volume fraction of void space in the catalyst layer and V is the total volume of the catalyst layer. In a doubly coated sphere assemblage, proton conductivity through the void space would be smaller (or even no proton transport) than the effective proton conductivity of solid Pt/C and ionomer membrane coated sphere, i.e., $\sigma_{12}^{\mathrm{eff}} > \sigma_3$. The expression for the doubly coated sphere assemblage can also be derived from the above-mentioned simplified coated sphere formulation. Using the similar approach, it can be shown for a doubly coated sphere assemblage ($\sigma_{12}^{\mathrm{eff}} > \sigma_3$) as:

$$\sigma_{12}^{\mathrm{eff}} + \frac{3(1-f_{12})\sigma_{12}^{\mathrm{eff}}}{f_{12} - \frac{3\sigma_{12}^{\mathrm{eff}}}{\sigma_{12}^{\mathrm{eff}} - \sigma_2}} \geqslant \sigma_{123}^{\mathrm{eff}} \geqslant \sigma_3 + \frac{3(1-f_3)\sigma_3}{f_3 - \frac{3\sigma_3}{\sigma_3 - \sigma_{12}^{\mathrm{eff}}}} \tag{23}$$

where $\sigma_{123}^{\mathrm{eff}}$ is the effective conductivity of a three-phase composite system made of doubly coated spheres as shown in Fig. 4. For the CL of a PEM fuel cell, Eq. (23) finally yields:

$$\left(\sigma_m^{\mathrm{eff}}\right)_{\mathrm{CL}} = \sigma_m^{\mathrm{eff}} + \frac{3(1-f_s-f_m)\sigma_m^{\mathrm{eff}}}{(f_s+f_m) - \frac{3\sigma_m^{\mathrm{eff}}}{\sigma_m^{\mathrm{eff}} - \sigma_v}} \tag{24}$$

where σ_v is the protonic conductivity of void space, and σ_m^{eff} is the effective protonic conductivity when only solid Pt/C and ionomer membrane phases are considered (given in Eq. (21)). For an unflooded CL, the void spaces are filled with the reactant gases only; hence, the protonic conductivity of void space is zero. Conversely, for a flooded case, liquid water in the pore can act as a liquid electrolyte and participate in proton transportation. However, such transportation will be negligible compared to the proton transport through the ionomer membrane. In addition, liquid water needs free acidic group to be an electrolyte. Assuming the ionomer membrane was fully saturated before being assembled in the membrane electrolyte assembly of a PEM fuel cell, then there will be no such free acidic group for the liquid water to be an electrolyte. Therefore, it is justifiable to neglect the protonic conductivity of void spaces even under the flooding situation. Hence, Eq. (24) simplifies to:

$$\left(\sigma_m^{\mathrm{eff}}\right)_{\mathrm{CL}} = \sigma_m - \frac{3(1-f_m)\sigma_m}{3-f_m} - \frac{3f_v\left(\sigma_m - \frac{3(1-f_m)\sigma_m}{3-f_m}\right)}{2+f_v} \tag{25}$$

where f_v is the volume fraction of void space in the catalyst layer, which is simply the catalyst layer porosity. For the practical scenarios, the protonic conductivity will be even lower, i.e.,

$$\left(\sigma_m^{\mathrm{eff}}\right)_{\mathrm{CL}} = \sigma_m - \frac{3\lambda_m(1-f_m)\sigma_m}{3-f_m} - \frac{3\lambda_m f_v\left(\sigma_m - \frac{3(1-f_m)\sigma_m}{3-f_m}\right)}{2+f_v} \tag{26}$$

where λ_m is a multiplying factor which will be relying on the geometrical structure of membrane phase in a catalyst layer, for instance, membrane connectivity in the catalyst layer or shape of the agglomerate. The bounds for λ_m can be written as:

$$\frac{3-f_m}{3(1-f_m)} > \lambda_m \geqslant 1 \quad \text{for } f_m \neq 0 \text{ or } 1 \tag{27}$$

The sum of the volume fractions of void space, ionomer membrane, and solid Pt/C in the catalyst layer should be unity, i.e.,

$$f_v + f_m + f_s = 1 \tag{28}$$

The volume fraction of membrane in the catalyst layer can be related through the Nafion content $\%N$ (defined as the weight percentage of Nafion in the sum of Nafion and solid particles) by [23]:

$$f_m = \frac{\%N}{(1-\%N)\rho_m}\frac{m_{\mathrm{Pt}}}{\%\mathrm{Pt}\cdot\delta_{\mathrm{CL}}} \tag{29}$$

where ρ_N is the density of Nafion, %Pt is the mass percentage of platinum in the combined total mass of platinum and carbon particles, m_{Pt} is the Pt-loading, and δ_{CL} is the catalyst layer thickness. If the catalyst layer surface area (A_{CL}) and carbon weight (W_{C}) are known, %Pt can be calculated from the following relation [23]:

$$\%\mathrm{Pt} = \frac{m_{\mathrm{Pt}}A_{\mathrm{CL}}}{m_{\mathrm{Pt}}A_{\mathrm{CL}} + W_{\mathrm{C}}} \tag{30}$$

The volume fraction of solid Pt/C in the catalyst layer is related to %Pt, catalyst layer thickness, and the densities of platinum and carbon black (ρ_{Pt} and ρ_{C}) as [24]:

$$f_s = \left(\frac{1}{\rho_{\mathrm{Pt}}} + \frac{1-\%\mathrm{Pt}}{\%\mathrm{Pt}\cdot\rho_{\mathrm{C}}}\right)\frac{m_{\mathrm{Pt}}}{\delta_{\mathrm{CL}}} \tag{31}$$

2.2.2. Electron transport

For electron transport in the catalyst layer shown in Fig. 3c, both the membrane phase and the void space act as electric insulators, and only the solid Pt/C phase transports electron. Therefore, both the membrane and void space together can be considered as phase 2. Although the Pt/C particles are considered coated with non-electron conducting phase as shown is Fig. 3d, it is assumed that the Pt/C particles are actually in contact with some small contact area while assembled in the catalyst layer that would not affect the estimate of proton conductivity and mass diffusivity. Further, it is assumed that the contact area is sufficient without impairing electron conductivity since the Pt/C particle has very high electronic conductivity compared to the protonic conductivity. Hence, for the electronic conductivity, we have $\sigma_1 = \sigma_s$ and $\sigma_2 = 0$, and the effective conductivity for the solid phase (or the effective electronic conductivity) can be written as:

$$\sigma_s - \frac{3(1-f_s)\sigma_s}{3-f_s} \geqslant \sigma_s^{\mathrm{eff}} \geqslant 0 \tag{32}$$

where σ_s^{eff} and σ_s are the effective and bulk electronic conductivities in the solid phase of CL, respectively, and f_s is the volume fraction of Pt/C. Similar to the analogy provided for the protonic conductivity, it can be claimed that the effective electronic conductivity cannot be zero. It has to be higher than zero to maintain a properly operating PEM fuel cell. Hence, the effective electronic conductivity should obey the following relation:

$$\sigma_s - \frac{3(1-f_s)\sigma_s}{3-f_s} \geqslant \sigma_s^{\mathrm{eff}} > 0 \tag{33}$$

The above expression also implies that the highest possible value for the effective electronic conductivity would be:

$$\sigma_{s,\max}^{\mathrm{eff}} = \sigma_s - \frac{3(1-f_s)\sigma_s}{3-f_s} \equiv \sigma_s^{\mathrm{eff}} \tag{34}$$

The bulk electronic conductivity is significantly higher than the bulk protonic conductivity in PEM fuel cells; hence, it can easily be presumed that the effective electronic conductivity will be close to its highest value. This statement may not be valid for every composite system; however, this approximation is justifiable for a PEM fuel cell, where the electronic conductivity has much less influence on the cell performance compared to the protonic conductivity. To be more precise, the above equation can be re-written as:

$$\sigma_s^{\mathrm{eff}} = \sigma_s - \lambda_s\frac{3(1-f_s)\sigma_s}{3-f_s} \tag{35}$$

where λ_s is the solid phase geometry factor and the bound is found as:

$$\frac{3-f_s}{3(1-f_s)} > \lambda_s \geqslant 1 \quad \text{for } f_s \neq 0 \text{ or } 1 \tag{36}$$

It is worthwhile to note that the GDL of a PEM fuel cell is composed of solid carbon phase and void space, which is a combination of two phases. Therefore, Eq. (35) is valid for both the CLs and GDLs of a PEM fuel cell.

2.3. Effective diffusivity

For the catalyst layer effective diffusivity, it is required to consider a coated sphere assemblage where both the liquid and gas phases co-exist in the void space. In PEM fuel cells, the formation of liquid water in the cathode catalyst layer is still unknown. It can be film-wise or drop-wise or may be a combination of both. A good approximation would be to consider a uniform mixture of gas and liquid phases in the void space. Such approach, however, will require complicated mathematical approach to derive an expression for the effective diffusivity. Therefore, a random liquid water film over the ionomer membrane surface has been considered as shown in Fig. 5 as phase 3, and this sphere can be referred as a triply coated sphere when phase 2 is completely covered by phase 3. In the following paragraphs, a general formulation is first derived by considering a triply coated sphere, where the solid core (phase 1) is first considered coated by phase 2 and the coated sphere is considered subsequently covered by phase 3, and then simplified for the case when phase 2 is partially covered by phase 3 or liquid water.

As described earlier for a coated sphere assemblage that has two phases (phases 1 and 2 as shown in Fig. 3d), the lower bound of an effective property is:

$$\phi_{12}^{\mathrm{eff}} = \phi_2 + \frac{3(1-f_2)\phi_2}{f_2 - \frac{3\phi_2}{\phi_2-\phi_1}} \tag{37}$$

Therefore, the effective diffusivity for a coated sphere assemblage that has two phases can be written as:

$$D_{12}^{\mathrm{eff}} = D_2 + \frac{3(1-f_2)D_2}{f_2 - \frac{3D_2}{D_2-D_1}} \quad \text{for } D_2 > D_1 \tag{38}$$

where D_1 and D_2 are the bulk diffusivities of phases 1 and 2, respectively, and D_{12}^{eff} is the effective diffusivity of the entire composite system. Since phase 1 for the PEM fuel cell catalyst layer is made of Pt/C particles that do not allow gas to diffuse, the lower bound must be considered for estimating the effective diffusivity. Using the similar approach mentioned above, it can be considered that sphere made of phases 1 and 2 that is coated with phase 3, i.e., the doubly coated sphere assemblage, has the effective diffusivity of

$$D_{123}^{\mathrm{eff}} = D_3 + \frac{3(1-f_3)D_3}{f_3 - \frac{3D_3}{D_3-D_{12}^{\mathrm{eff}}}} \tag{39}$$

where D_{123}^{eff} is the effective diffusivity of a three-phase composite system and D_3 is the bulk diffusivity in phase 3. The terms f_1, f_2, f_3 are the volume fractions of different phases in the coated sphere shown in Fig. 4. Since the solid phase does not allow reactant gas to diffuse through it, the diffusivity of the solid medium is taken to be zero. Hence, the effective diffusivity in a CL made of doubly coated spheres can be simplified as:

$$D_{123}^{\mathrm{eff}} = D_3 + \frac{3(1-f_3)D_3}{f_3 - \frac{3D_3}{D_3 - D_2 - \frac{3(1-f_2)D_2}{f_2-3(1-f_3)}}} \tag{40}$$

Referring to the PEM fuel cell catalyst layer structure shown in Fig. 3b, it is easily recognizable that phase 1 represents the solid Pt/C particles, phase 2 represents the ionomer membrane layer over the Pt/C particles, and phase 3 is the void space over the entire catalyst agglomerate. Since a part of void space in the catalyst layer can also be occupied with liquid water that is produced from the electrochemical reaction, phase 3 shown in Fig. 4 is divided into two phases, phases 3 and 4, to make the doubly coated sphere to a triply coated sphere. For a triply coated sphere assemblage system, the formulation of doubly coated sphere assemblage can further be extended by considering a continuous film of phase 3 over phase 2; hence, the effective diffusivity for such a four-phase coated sphere system becomes:

$$D_{1234}^{\mathrm{eff}} = D_4 + \frac{3(1-f_4)D_4}{f_4 - \frac{3D_4}{D_4-D_{123}^{\mathrm{eff}}}} \tag{41}$$

where D_{123}^{eff} represents the effective diffusivity when the phase 2 is completely covered by phase 3. In the PEM fuel cell catalyst layer, however, phase 2 is partially covered by phase 3 as shown in Fig. 5. Here, a random liquid water film has been considered to specify the geometry explicitly instead of a random distribution for both the liquid water and void spaces. Hence, Eq. (41) is modified for a coated sphere system that is partially covered by phase 3 as:

$$D_{1234}^{\mathrm{eff}} = D_4 + \frac{3(1-f_4)D_4}{f_4 - \frac{3D_4}{D_4-\left(D_{123}^{\mathrm{eff}}\right)_{\mathrm{CL}}}} \tag{42}$$

where $\left(D_{123}^{\mathrm{eff}}\right)_{\mathrm{CL}}$ is defined as a function of the liquid water surface coverage, f_θ, as [18,19]:

$$\left(D_{123}^{\mathrm{eff}}\right)_{\mathrm{CL}} = f_\theta D_{123}^{\mathrm{eff}} + (1-f_\theta)D_{12}^{\mathrm{eff}} \tag{43}$$

Simplifying Eq. (42), the effective diffusivity for a PEM fuel cell catalyst layer is found as:

$$D_{\mathrm{CL}}^{\mathrm{eff}} = D_g - \frac{3(1-f_g)D_g}{\frac{3D_g}{D_g-f_\theta D_A-(1-f_\theta)D_B} - f_g} \tag{44}$$

where

$$D_A = D_l - \frac{3(1-f_l)D_l}{\frac{3D_l}{D_l - D_m - \frac{3(1-f_m)D_m}{f_m-3(1-f_l)}} - f_l} \tag{45}$$

$$D_B = D_m - \frac{3(1-f_m)D_m}{3-f_m} \tag{46}$$

The terms, D_g, D_l, D_m, are the diffusivities in gas phase, liquid water, and ionomer membrane, respectively, and f_g, f_l, f_m are the volume fractions of gas phase, liquid water, and ionomer membrane, respectively. Since the Knudsen effect is dominant in the catalyst layers, the bulk diffusion coefficient must be modified so that the Knudsen effect is counted while using the proposed diffusivity formula in the PEM fuel cell catalyst layers.

Conversely, the GDL is composed of solid carbon and void space only. The void space can also be partially filled with liquid water. In such case, the effective diffusivity for the partially flooded GDL of a PEM fuel cell can be calculated from the relations of flooded-GDL and dry-GDL using the relation given in Eq. (43). The expression for the effective diffusivity in a flooded-GDL can be written as:

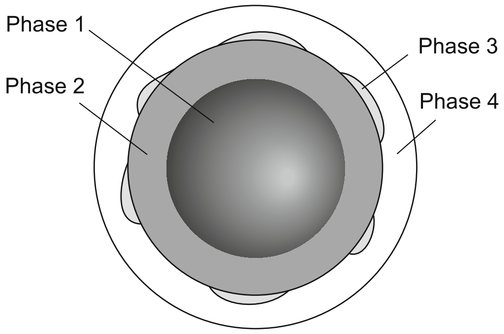

Fig. 5. Schematic representation of a coated sphere with liquid water film (referred as phase 3) in void space (phase 4).

$$D^{\mathrm{eff}}_{\text{flooded-GDL}} = D_g - \frac{3(1-f_g)D_g}{\frac{3D_g}{D_g - D_l - \frac{3(1-f_l)D_l}{f_l - 3(1-f_g)}} - f_g} \qquad (47)$$

where f_g and f_l are the volume fractions of gas phase and liquid water in the GDL, respectively; whereas for a dry electrode, it can be written as:

$$D^{\mathrm{eff}}_{\text{dry-GDL}} = D_g - \frac{3(1-f_g)D_g}{3-f_g} \qquad (48)$$

It should be noted that neither the void space is uniformly distributed nor the solid phase is perfectly spherical in the GDL. Therefore, the second term in Eqs. (44), (47) and (48) needs to be multiplied by a geometrical factor (λ_g). The simplest bounds for λ_g can be obtained from Eq. (48), which can be written as:

$$\frac{3-f_g}{3(1-f_g)} > \lambda_g \geqslant 1 \quad \text{for } f_g \neq 0 \text{ or } 1 \qquad (49)$$

3. Results and discussion

In this section, a set of estimates based on the proposed formulations is provided and compared with the Bruggeman approximation and Weiner model for the effective transport properties in the catalyst and gas diffusion layers of a PEM fuel cell.

3.1. Effective protonic conductivity in catalyst layer

Fig. 6 shows the comparison of the effective protonic conductivities in the CL of a PEM fuel cell as a function of catalyst layer porosity that are calculated using the formulation developed in this study and the Bruggeman approximation. Two different combinations of solid Pt/C particles and ionomer membrane volume fractions in the solid phase of CL, namely, 70% of Pt/C and 30% of membrane, and 60% of Pt/C and 40% of membrane, were considered as indicated in the legend as f_s/f_m ratio. Here, both the lines represent the Bruggeman correlation results, while the symbols depict corresponding results obtained using the expression developed in this study. The effective protonic conductivity of Bruggeman approximation is estimated using the following correlation, referred in Fig. 6 as Bruggeman correlation:

$$\sigma^{\mathrm{eff}}_m = \sigma_m(f_m(1-\epsilon))^{1.5} \qquad (50)$$

All other parameters used in the calculation are taken from Refs. [23,24] that are listed in Table 1. As observed at low porosities ($\epsilon < 0.2$), the present formulation overestimates the effective conductivity compared to what has been estimated using the BA. Whereas for moderate porosities (e.g. $0.2 < \epsilon < 0.4$), the present results show a better agreement, particularly for the case when the fraction of membrane in the CL is higher. For higher porosities (e.g. $\epsilon > 0.5$), an underestimation has been observed for both cases, while the case of lower fraction of membrane provides less discrepancy with the Bruggeman correlation. Hence, this variation can be attributed to the multi-phase effect, which is more prominent in the present formulation than the Bruggeman correlation. For instance, the present model results merging toward the Bruggeman's results when $\epsilon \to 1.0$ and the lower membrane fraction case is merging faster implies that the membrane phase has less effect at higher porosity. Clearly for a range of porosity ($0.2 < \epsilon < 0.6$) that is applicable for PEM fuel cells, the present formulation would be more useful than widely used Bruggeman approximation as the present formulation is directly derived considering the agglomerate geometry. Furthermore, this comparison shows that the proposed formulation is capable of predicting the effective protonic conductivity that can be estimated using the Bruggeman correlation, while the Bruggeman correlation is an empirical correlation and the present expression is derived from the fundamental mathematical formulation.

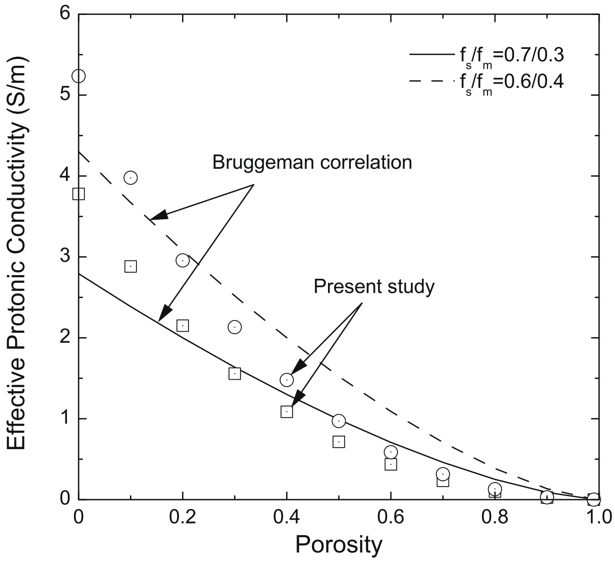

Fig. 6. Comparison of the effective protonic conductivity in the catalyst layer of a PEM fuel cell with the Bruggeman correlation. Both the lines represent the results of Bruggeman correlation, while the symbols depict the present model results for two combinations of Pt/C and ionomer membrane volume fractions.

3.2. Effective electronic conductivity

Fig. 7 depicts a comparison of the effective electronic conductivity in the catalyst layer of a PEM fuel cell with the BA results as a function of catalyst layer porosity. Similar to the effective protonic conductivity, two different combinations of ionomer membrane and solid Pt/C fractions in the catalyst layer were considered as indicated in the legend. Here also an overestimation of the effective electronic conductivity has been observed compared to the Bruggeman's result over the entire range of porosity. No matter what percentages of solid Pt/C and ionomer membrane are present in a catalyst layer, the present formulation provides slightly higher effective electronic conductivity for the catalyst layer of PEM fuel cell. This might be acceptable, as the membrane conductivity is performance-limiting factor for the PEM fuel cells and the electronic conductivity has very little influence on the performance of a cell. Further, the results presented in Fig. 7 for the case when $\lambda_s = 1$, hence the maximum limit for the effective electronic conductivities. However, practically the effective electronic conductivities will be lower than the values shown in Fig. 7 due to irregular

Table 1
Parameter values used in the model calculation.

Parameter	Value
R(J mol^{-1} K^{-1})	8.315
T (K)	323
D_g (cm^2 s^{-1})	2.585×10^{-1}
D_l (cm^2 s^{-1})	3.98×10^{-5}
D_m (cm^2 s^{-1})	3.73×10^{-6}
f_l	0.1
f_s/f_m	0.7/0.3 and 0.6/0.4
f_0	0.5
λ_m	1.0
λ_s	1.0
σ_m (S cm^{-1})	0.17
σ_s (S cm^{-1})	7.27×10^2

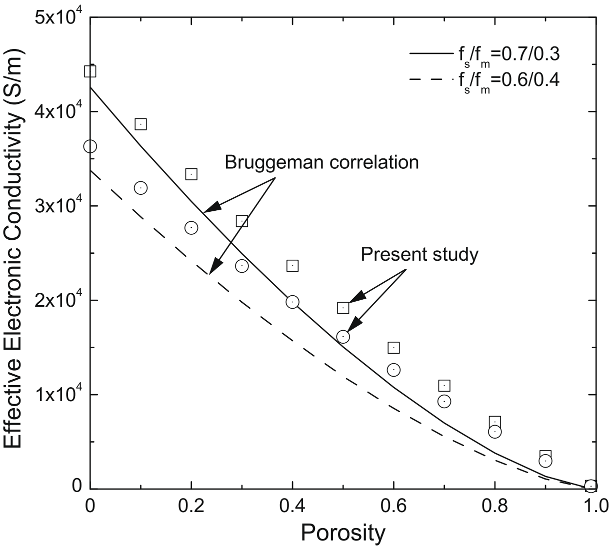

Fig. 7. Comparison of the effective electronic conductivity in the catalyst layer of a PEM fuel cell with the Bruggeman correlation. The lines represent the results of Bruggeman correlation, while the symbols depict the present model results for two combinations of Pt/C and ionomer membrane volume fractions.

solid phase geometry and ionomer layer over the Pt/C phase. Conversely, the effective electronic conductivity in the GDL of a PEM fuel cell shows an excellent agreement with the Bruggeman correlation results as shown in Fig. 8. Clearly, the multi-phase effect is insignificant in a dry-GDL as it has only solid carbon phase. Therefore, both the present formulation and the Bruggeman correlation show identical behavior. However, for higher porosity values ($\epsilon > 0.4$), the present model overpredicts slightly. Here, the overestimation is considerably less than what is observed for the catalyst layer's effective conductivities. This is reasonable as the CL is composed of solid Pt/C particles, ionomer membrane, and void space, while the GDL only consists of solid carbon and void space. For a similar porosity, the GDL consists of more solid carbon phase than the CL, which results in higher electronic conductivity. Therefore, it can be claimed that the effective electronic conductivity formulation provided in this study would be more accurate while we have higher fraction of solid phase in a composite system. Conversely, the effective protonic conductivity formulation will provide more accurate results while the CL consists of higher fraction of ionomer membrane.

3.3. Effective diffusivity in catalyst layer

For the effective diffusivity in the catalyst layer of a PEM fuel cell, several empirical models are available. The most popular and widely used for the individual effective diffusivity is once again Bruggeman's approximation. Here, the individual effective diffusivity represents the diffusion coefficient of a reactant gas in a phase of a multi-phase composite system, for example, effective oxygen diffusivity in ionomer membrane phase of PEM fuel cell catalyst layer. Conversely, the overall effective diffusivity represents the total diffusivity of a reactant gas in a composite layer of PEM fuel cell, for example, effective oxygen diffusivity in the CL or GDL of a PEM fuel cell. If a layer consists of more than one phase then the overall effective diffusivity has contributions from the individual effective diffusivities within that layer. Therefore, the Bruggeman approximation of the individual effective diffusivity needs to be further modified based on the volume fractions of various phases present in a composite (multi-phase) layer using other approaches. Several approaches have been used in literature based on the Wiener's series and parallel models for the composite system. For instance, it can be either a series model [21,35–37] or a parallel model [22,36,37] or a mixed model [23,36,37]. In the following paragraphs, a comprehensive comparison for the effective diffusivity of present model predictions with the above-mentioned models has been provided.

Fig. 9 represents a comparison between the effective oxygen diffusivities in the catalyst layer of a PEM fuel cell that are calculated using the present effective diffusivity expression and a series model [21,35–37]. The solid phase of the catalyst layer is considered as made of 70% of Pt/C and 30% ionomer membrane. All other parameters are listed in Table 1. Here, the line represents the result obtained from the series model, while the symbols show the result estimated using the expression derived in this study. Surprisingly, a complete miss-match has been observed with the series model that is almost several orders of magnitude. This disagreement probably arises due to the assumption usually made in the mathe-

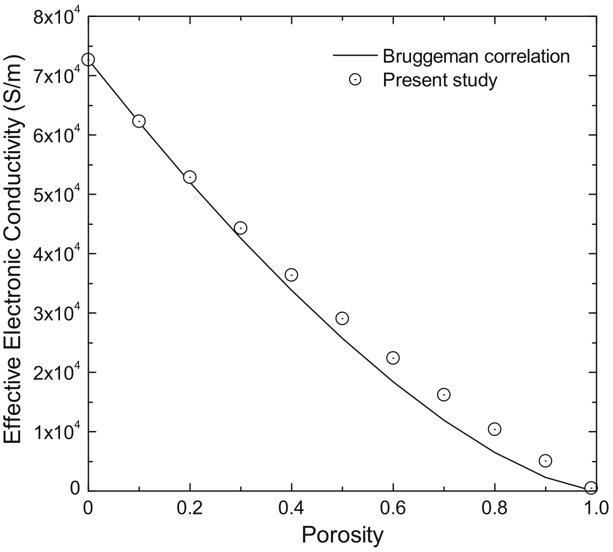

Fig. 8. Comparison of the proposed effective electronic conductivity in the gas diffusion layer of a PEM fuel cell with the Bruggeman correlation.

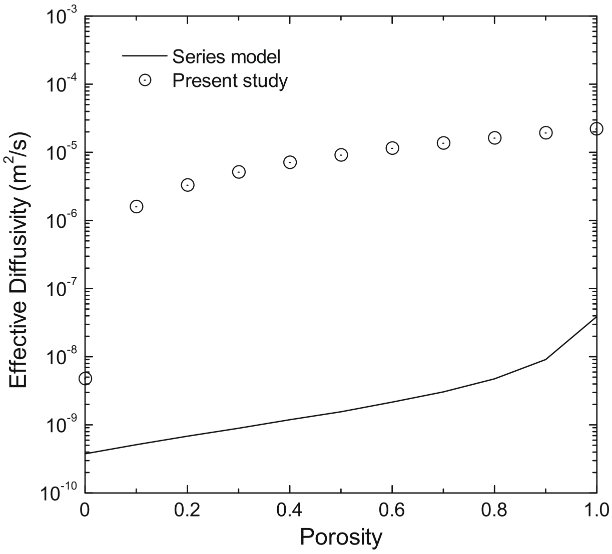

Fig. 9. Comparison of the proposed effective oxygen diffusivity in the catalyst layer of a PEM fuel cell with the series model for 70% of Pt/C and 30% of ionomer membrane in the catalyst layer.

matical formulation of series model that various phases in a composite system were lumped in a layer one after another. For instance, in the cathode catalyst layer of a PEM fuel cell, layers of Pt/C, ionomer membrane, liquid water, and gas phase are lumped in a layer so that each layer of a phase is covered continuously by another phase. Therefore, neither the Pt/C layer nor the ionomer membrane layer has direct contact with the gas diffusion layer, while the present model does not have such continuous film of liquid water. Since both layers are separated from void spaces by the liquid water film in a series model, the reactant gas needs to be dissolved in liquid water to come contact with Pt/C and ionomer membrane. The solubility of oxygen in liquid water is very low, which gives diffusivity of oxygen in liquid water several orders of magnitude lower than that of the void space. Hence, the series model formulation predicts the effective oxygen diffusivity in the order of oxygen diffusivity in liquid water that is about 3–4 orders lower than the oxygen diffusivity in gas phase inside the void space. Nonetheless, this disagreement can easily be attributed to the Weiner series model used in Refs. [21,35–37] and 100% surface coverage for the liquid water used in Ref. [21]. Conversely, the surface coverage of the liquid water has been considered less than unity in the proposed formulation. Therefore, the gas phase has direct contact with the membrane phase that allows faster reactant diffusion than the Weiner series model.

Although several orders of magnitude differences have been observed between the present model predictions and the results of a series model, an excellent agreement has been found with a parallel model formulation [22,36,37] as shown in Fig. 10. Here, a comparison between the effective oxygen diffusivities in the catalyst layer of a PEM fuel cell is shown that are estimated using the expression developed in this study and from a parallel model for 70% of Pt/C and 30% ionomer membrane in the solid phase of a catalyst layer. In this figure, the line represents the parallel model result, while the symbols depict the prediction of proposed model. For high porosity values ($\epsilon > 0.7$), the present results show very good agreement, although for intermediate porosity values (e.g. $0.2 < \epsilon < 0.7$) some differences between the predictions have been observed. It should also be noted that in the parallel model, the effective diffusivity is calculated by applying Wiener's parallel model followed by the Bruggeman approximation [22]; while in the series model, the effective diffusivity is calculated using the Bruggeman approximation followed by Wiener's series model [21]. Hence, it seems that the Wiener parallel model is better than the Wiener series model for the effective diffusivities in PEM fuel cells. Like the effective conductivity formulation, comparison in Fig. 10 nonetheless shows the predictive abilities of the proposed effective diffusivity formulation.

A comparison between the effective oxygen diffusivities that are calculated using the proposed formulation and a mixed model [23,36,37] is shown in Fig. 11. Like the comparison with the parallel model, the present model results also show a good agreement with the mixed model results, particularly for higher porosity values. At low porosities, however, a slight overestimation has been observed. Nonetheless, this comparison one again provides a clear idea of how well the present formulation can predict the effective properties. It should also be noted that the mixed model formulation is a combination of both the Bruggeman approximation and Wiener's mixed model that is based on the empirical correlation, whereas the present model is entirely a mathematical formulation.

3.4. Effective diffusivity in gas diffusion layer

Fig. 12 shows a comparison of the effective oxygen diffusivity in the GDL of a PEM fuel cell with Du et al. [38] as a function of GDL porosity. Here, the line represents the result that is estimated using the following correlation [38]:

$$D_{\mathrm{GDL}}^{\mathrm{eff}} = D_b \epsilon^{1.5} \tag{51}$$

The symbols depict the result of proposed expression that is given for a dry-GDL in Eq. (48). The effective oxygen diffusivity in a GDL estimated using the proposed expression shows an excellent agreement with the results of Du et al. [38], particularly at high porosities values. However, at low porosity values ($\epsilon < 0.5$), the present model overpredicts slightly. This comparison once again established the predictive abilities of the expression proposed for the effective transport properties in a PEM fuel cell.

In the previous sections, we have provided a comprehensive comparison of the result estimated using the proposed formulations for effective protonic conductivity, electronic conductivity, and oxygen diffusivity in both the CLs and GDLs of a PEM fuel cell with the results available in literature. It has been observed that the proposed formulations are capable of estimating effective

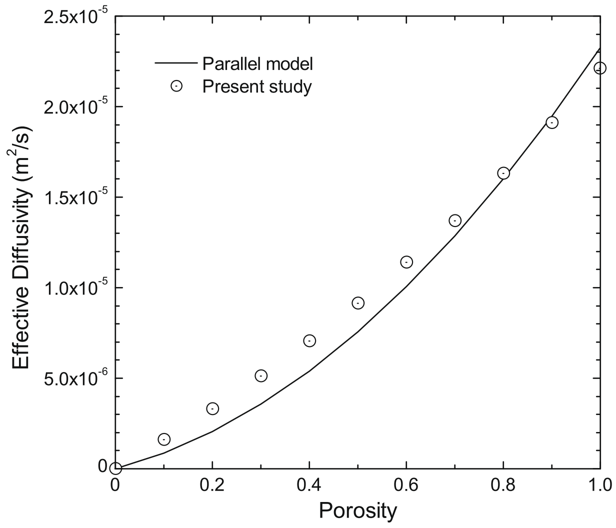

Fig. 10. Comparison of the proposed effective oxygen diffusivity in the catalyst layer of a PEM fuel cell with the parallel model for the composition of 70% of Pt/C and 30% of ionomer membrane.

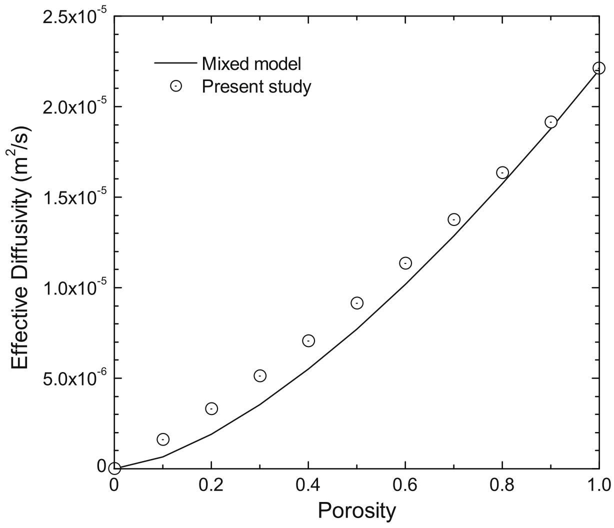

Fig. 11. Comparison of the effective oxygen diffusivity in the catalyst layer of a PEM fuel cell with the mixed model prediction for the composition of 70% of Pt/C and 30% of ionomer membrane.

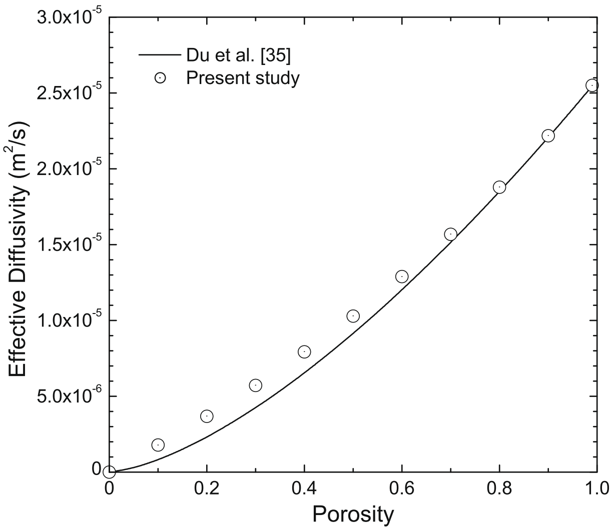

Fig. 12. Comparison of the effective oxygen diffusivity estimated using the proposed expression with the results of Du et al. [38] in the GDL of a PEM fuel cell.

properties as estimated by various methods. Although the real microstructures of GDL and CL are not perfect sphere-based geometry, the comparisons shown in this study proved that the sphere-based approximation is a good approximation to predict these effective properties theoretically. For the effective protonic and electronic conductivities, the Bruggeman approximation has been widely used with an exponent of 1.5 in the correlation, which was obtained by fitting a limited and specialized experimental data [1]. In reality, the exponent can vary between the range from 1.2 to 4 [28,39]. It was observed while validating numerical model with the experimental results, the effective parameters along with other physical and electrochemical parameters have been manipulated to produce comparable results. This type of approach in the numerical modeling can produce inconsistent results as well. Hence, our attempt was to provide a set of unique expressions for the effective properties in PEM fuel cells that would be useful for the numerical models for consistent and reproducible results. It is worthwhile to note that the relative humidity and liquid water saturation in the catalyst layers of a PEM fuel cell can influence the effective protonic conductivity; this study, however, can be considered as a first attempt based on the geometry alone by considering fully humidified membrane. Conversely, the effective diffusivity used in literature varies with each other depending upon how the Wiener model and the Bruggeman approximation have been implemented (comparing Fig. 9 with Figs. 10 and 11). While the present mathematical formulations avoid such contradiction and capable of producing unique results, which are comparable with the results available in literature. For the effective protonic and electronic conductivities, it seems more appropriate to use a theoretical model while numerically model fuel cell performance instead of Bruggeman's empirical correlation. Since the GDL of a PEM fuel is usually fabricated with either carbon cloth or carbon paper, the present formulation, however, would be more appropriate for the carbon paper GDL than the carbon fiber GDL. Also one can avoid complicated combinations of the Wiener model and the Bruggeman approximation to estimate the effective diffusivities by using the proposed mathematical expression. Further, improper combination of Wiener model and Bruggeman approximation can grossly underestimate the effective diffusivity as seen in Fig. 9. The results provided in this study not only show its uniqueness but also its robustness to estimate various effective properties using an identical formulation for each of these effective properties, while neither the Bruggeman approximation nor the Weiner model can independently estimate all these effective properties unless both are combined together. It is worthwhile to note that the present formulation is based on the spherical geometries, where each of the agglomerates is a scaled version of another. Hence, the proposed expressions for the effective properties would be useful in the real engineering problems where the structure of geometry can be simplified or approximated in a spherical-shaped structure, such as PEM fuel cell catalyst layer or underground water transport. The present formulation can also be applicable for the irregular geometries, such as GDL of a PEM fuel cell that is made of carbon cloth or carbon fiber. However, the geometry factors (λ_m, λ_s, and λ_g) for the irregular geometries need to be estimated using appropriate experimental scheme to estimate the effective properties more precisely. Nonetheless, the present formulation can provide preliminary estimates of the effective properties for the irregular-shaped geometries without the help of complex numerical schemes or experimental measurements [31,32,40]. Although a wide range of comparisons provided in this study, we were unable to compare the proposed model results with the experimental results as no such experimentally measured effective transport property values are available in open literature.

4. Concluding remarks

The aim of this study was to provide a unique set of expressions for the effective protonic conductivity, electronic conductivity, and oxygen diffusivity in both the catalyst and gas diffusion layers of a PEM fuel cell that has similar mathematical formulation. Here, a set of mathematical expressions has been proposed for the effective transport properties in a PEM fuel cell and compared with results available in literature. It has been found that the proposed mathematical expressions for the effective transport properties are quite capable of predicting reasonably accurate and comparable results. Further, for the effective electronic conductivity, the higher the volume fraction of Pt/C in a catalyst layer, the better the model's prediction has been found. Similar statement can be given for the effective protonic conductivity; a higher membrane fraction will provide better model predictions. Conversely, if the catalyst layer has high porosity with less water saturation, the present model is found to be in better agreement with the models that used both the Bruggeman and Weiner type of correlations together for the effective diffusivity. While the Bruggeman correlation is purely an empirical correlation, the proposed formulation has its physical and mathematical origins. Furthermore, the complexities involved in using the Bruggeman approximation and Weiner models together can be avoided by employing the proposed effective diffusivity formulation. Hence, the present expressions are recommended for the numerical modeling of PEM fuel cells. Although these expressions are derived focusing on the PEM fuel cells, the present formulations for the effective transport properties are equally applicable for other hydrogen fuel cells, porous media flow, and multi-phase composite systems.

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