Multiscale relationship of electronic and ionic conduction efficiency in a PEMFC catalyst layer

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The three-dimensional structure and composition of a PEMFC catalyst layer (CL) define this component as a random heterogeneous material. During the manufacturing process of CLs, agglomerates form composed of primary components plus a number of pores of a variety of sizes. These structural features of the CL allow us to define internal substructures at different scale levels, and with that, we can establish a scaling strategy for numerical simulation. This work presents an analytical scaling method to determine electronic and ionic conduction efficiency in a whole PEMFC catalyst layer defined by internal substructures at three scale levels. The effective conductive area and effective conductive length of a subdomain are used to estimate a conduction efficiency of an element formed by subdomains of smaller scales. The effect of porosity and ionomer load over conduction efficiency can be quantified. The case study presented in this work shows that the ionic conduction efficiency increases, while the electronic conduction efficiency diminishes, both in an exponential fashion, when ionomer load increases. Furthermore, both electronic and ionic conduction efficiency decreases linearly with the porosity. Finally, the scaling method not only reduces computer-processing time but also allows a detailed study of the CL at the nanoscale level.

Introduction

Fuel Cells (FCs) are going to play a key role in the current transition to the hydrogen-based energetic system [1]. FCs are stationary state reactors, where the reagents are dosed and the products are extracted at continuous flow. One of its advantages consist of using pure hydrogen as fuel produces inverse hydrolysis, which gives water and heat as by-products, without generating any toxic product, as it converts chemical energy to electrical energy directly [2].

The Proton Exchange Membrane Fuel Cell (PEMFC), with its low-temperature, durability and its versatility to the energy request can be used in a wide range of applications: from transport systems to residential energy systems as well as substitutes of portable batteries.

During the PEMFC operation, fuel is injected to the anode, where it is oxidized; then, the protons travel through the
electrolytic membrane and the electrons flow through the external circuit (electrical charge). Both, (electron and proton) travel to the cathode. In this section, oxygen is injected, which promotes the water reduction, together with the electro-catalyst, the electrons and the protons. Fig. 1, shows a graphical representation of the components, reagents, products and by-products of a typical PEMFC.

From this point of view, the operation of a PEMFC seems very simple. However, the mass and energy transport phenomena, which happen into the cell, are complex processes that intrinsically affect the FC electrical performance. Among the most important points, which describe this complexity, are found:

1) Reactant gases are introduced to the flow field of the bipolar plates, causing a distribution of concentration and pressure on the surface of the Gas Diffusion Layer (GDL). As well, it is important to mention that reactant gases reach the catalytic sites by convection and diffusion processes through the GDL and catalytic layer pores.

2) Protons are carried from the anode, where they are produced, to the cathode, where they combine with oxygen and electrons to produce water.

3) Depending on the thermodynamic conditions, water inside of the cell can be either liquid or gas. Then, water is carried through the pores at catalyst layer (CL) and the diffuser, once it arrives at the flow field, water is expelled from the cell. Water, might also be carried by diffusion or by electro-osmotic dragging through the electrolyte present on the CL and through the membrane. The electro-osmotic dragging refers to drag water molecules by the protons movement.

4) Heat, produced in the cell, is removed mainly by conduction, through the bipolar plate and by convection in the flow field and the cell borders to the environment. Heat production at a PEMFC is caused by the exothermic reactions that occur at CL’s (oxidation at the anode and reduction at the cathode) as well, it is originated by the ohmic resistivity of the materials (electronic and ionic).

5) The catalytic layers should be well-designed to make easier the transport of protons, electrons and reactant gases, as well to promote the efficient use of water, which is produced at the cathode and introduced by the gases.

It is important to emphasize that all the mentioned species and phenomena are present at the PEMFC CL. Therefore, CL is a critical component for the operation of the PEMFC. CL provides the active sites for the desired catalytic reactions. Furthermore, structure of CL determines the PEMFC general performance.
The aim of present work is theoretical study of the structure of a PEMFC CL. The charge transport continuity equation is used to determine a conduction efficiency in a CL defined by internal substructures at three scale levels. Results of each scale and the scaling effect within the CL are discussed in the article. The phenomenology and definition of CL structural model is detailed in the Sections PEMFC catalyst layer and CL Scales.

**PEMFC catalyst layer**

The electrochemical reactions are carried out at the CL, these reactions promote the production of electrical energy of the cell. It is worth mentioning that PEMFC, have two CL’s (anode and cathode) with similar characteristics. In literature, there are wide range of these components with different physical and electrochemical properties [3–5]. However, the most common electrocatalyst is platinum (Pt), the support material is carbon (C) and the dispersed electrolyte (ionomer) is the Nafion® polymer.

The reactant is ideally carried from the CL border with the GDL to the catalytic sites through the empty space (pores). The electrocatalyst has the function to promote the electrochemical reaction, whilst the carbon carries the electrons and the ionomer carries the protons produced or consumed by the reaction, anodic or cathodic, respectively.

The effectiveness of the physical and electrochemical properties (i.e. effective transport coefficient and active catalytic sites) of this component depends on the microstructure, significantly. From a structural point of view, two aspects are the most important: 1) the transfer path of mass, electrons and protons should not be interrupted and avoiding full of bends path. 2) The electrocatalyst should be in direct contact with the electronic conductor (support material) and the ionomer; this connection of materials is known as the “three-phases union” (U3F), which is necessary to activate the electrocatalyst. Then, it is important to stress that if one of those materials is not present, the catalyst will not be active. Fig. 2 shows a scheme of the U3F, stating when the catalyst (Pt) is active or inactive.

Experimental data at microscale have shown that CL is formed by macro-agglomerates in a matrix with a wide-range of pore sizes [6]. The concept of macro-agglomerates have been developed from a while ago in electrochemical systems and it has been also wide used in PEMFC [7–10].

The manufacture technique of thin electrodes is one of the most popular in the preparation of CL’s in PEMFC’s because it has an efficient performance [11]. There are several variants of this technique, however most of them coincide in mixing the Pt/C and the ionomer in a liquid solution by continuous stirring; the resulting mixture (catalytic ink) is deposited over a substrate. It is worth mentioning the concentration and composition of the catalytic ink and/or substrate has not a specific effect, as the primary components are distributed randomly and their properties remain unchanged.

Using the statistical techniques of structural description [12] and experimental techniques, the resulting microstructure of the CL can be characterized after the manufacture and afterwards, it can be rebuilt stochastically [13–15].

Properties of materials can be identified before manufacturing the CL. These materials are known as main elements: platinum synthesized over carbon (Pt/C) and Nafion®. These elements describe the microstructure based on the hypothesis that structure, size and physical properties do not change when the electrodes are manufactured. This hypothesis is valid when the composite is made using physical techniques, in other words, there are not chemical reactions that change the composition of the main component. In this work, the studied structures lie fulfill this hypothesis.

The typical design relations used and controlled before manufacturing the FCs are: (1) the platinum load (γPt), which
has the following units mg Pt/cm². (2) The ionomer load (θ_N), which is a weight relation between the Nafion® content and the total CL weight. (3) The percentage of platinum deposited over carbon (θ_Pt), which is characteristic of the electro-catalytical material synthesis. As it will be shown, these design relations and properties of the component elements (density), allow calculating the volumetric fraction of each phase constituent of the CL.

It is known that volume of a solid phase (V_S) of any mixture equals to the sum of the mass (m) over the density (ρ) of each component i, as it is shown in Equation (1).

\[ V_s = \sum m_i/\rho_i \] (1)

Substitution of the designed relationships (\( \theta_Pt \), \( \beta_N \), \( \theta_Pt \)) in Equation (3) provides the volume occupied for each primary elements of the CL solid phase. Equations (2), (3) and (4) are used to calculate the occupied volume by the platinum (V_Pt), the carbon (V_C) and the Nafion® (V_N), respectively.

\[ V_Pt = \frac{V_s}{\frac{\rho_C(1-\theta_Pt)}{\rho_{Pt} \rho_C} + \frac{1}{\rho_C} + \frac{1}{\rho_N} \rho_{Pt}} \] (2)

\[ V_C = \left( \frac{1}{\rho_C/\rho_Pt} \right) (V_Pt \rho_Pt) \] (3)

\[ V_N = \left( \frac{\delta_N}{\delta_Pt \rho_Pt} \right) \left( \frac{V_Pt \rho_Pt}{1 + \theta_Pt} \right) \theta_Pt \] (4)

where, \( \rho_{Pt} \), \( \rho_C \), \( \rho_N \) corresponds to the platinum, carbon and Nafion®, respectively. On the other hand, Equation (5) relates the total porosity of the CL (\( \Theta_{(Pt;T)} \)) with V_S and the total CL volume (V_T).

\[ \Theta_{(Pt;T)} = 1 - \frac{V_S}{V_T} = 1 - \left( \sum m_i/\rho_i \right) / V_T \] (5)

These relationships allow to define the volumetric fractions for each one of the existing phases in a domain which characterizes all the CL. However, looking at the experimental data, the global microstructure of the CL can be categorized at different scales, which can also be related using the previous equations. Below, a scaling-up strategy is described. This strategy is based on the volumetric fractions of the void phase.

**CL scales**

Due to the nature of the used materials during the manufacture of the CL, there are structures at nanometric scales that has a significant influence over the global behavior of the PEMFCs (i.e. the primary elements: Pt/C, Nafion, nanopores). On the other hand, the experimental data suggest that CL’s are formed by macro-agglomerates (formed by a mixture of primary elements) and micropores (with a wide range of pore sizes) [15–19].

A way to explain these structural changes is considering an observer getting closer to the CL center coming from the infinite. When the window aperture is ~50,000 nm, it is observed a homogeneous structure with a mesopores dispersion. When the window aperture is ~500 nm, focusing in the zone where there are not mesopores, the structure is defined by macro-agglomerates and micropores. Finally, when the window aperture is ~500 nm, the observer focuses on a macro-agglomerate, where it is distinguished a structure composed by a random distribution of Pt/C, ionomer and maybe nanopores. This last proposition constitutes a hypothesis, because the experimental information at this scale is restricted. However, it seems a more realistic hypothesis that the one commonly accepted that establishes that macro-agglomerates are basically spheres which contain Pt/C in the inside, with a thin layer of ionomer surrounding the sphere [7–10]. The different internal elements which are distinguished in every scale, from now onwards will be known as representative elements. Fig. 3 shows a representation of the scales described previously in a PEMFC CL.

Fig. 3a refers to the “mesopores” scale in a domain of 50,000 nm. Fig. 3b consists of macro-agglomerates and micropores scale in a domain of 5000 nm. Finally, Fig. 3c represents the internal macro-agglomerate scale in a domain of ~500 nm, where it is distinguished the primary elements: Pt (~5 nm), carbon conglomerate (~50 nm), ionomer and pores which cover specific sizes at this scale.

The scaling number and the sample size, for a representative electrode, depend on the structure and individual size of the components of the CL. It mainly depends on the distribution of the pore sizes, agglomerates, the minor element (typically platinum 2–4 nm), carbon conglomerate (20–100 nm) and the theoretical position of Nafion®. The complete scale, the scale that simulates the completely CL,
encloses the properties of the subsequent scale samples with lower metric scales, with the aim to keep the coherence among the design relations. In some cases, where there are islands at the real micrometric CL structure, it is important to add an extra scale between the micro and milimetric scale.

The structural changes cause different relative porosities at every scale. For example, if half of the electrode porosity contains mesopores with pore sizes that overflow the nano-metric scale, it is necessary to adjust the porosity of the other scales to fulfill with the desired total porosity. Defining as relative porosity the volumetric proportion exclusively occupied by the empty phase, without considering the pseudosolid phase also contains some porosity.

The solid-phase volume fractions found at every scale can be mathematically related using the Equation (6),

\[
\Phi(S,T) = \prod \Phi(S,r)
\]

where \(\Phi(S,T)\) is the “total” volume fraction of the CL solid-phase and \(\Phi(S,r)\) is the relative volume fraction of solid-phase of each scale. Substituting Equation (5) into (6), it is obtained a mathematical relation that calculates the total porosity of the CL and the relative porosities of every sample (Equation (7)),

\[
\Phi(P,T) = 1 - \prod \left(1 - \Phi(P,r)\right)
\]

where, \(\Phi(P,T)\) represents the total porosity of the CL and \(\Phi(P,r)\) the individual relative porosity of every sample.

This work considers that the sample with the lowest scale is the only one that contains the main elements. The ascending scale samples will contain the inferior sample plus the specific porosity at that scale. This hypothesis is accepted if the lower scale sample fulfill the design parameters. There is a chance to modify the design standards for the structure, where it is necessary to add solid elements in the upper scales, so it is necessary to reorganize the individual proportions of the electrode. As an example, consider the case of an electrode composed by agglomerates of different volume fractions. However, the structure and size of the agglomerates do not affect the volume fractions.

This “inter-scales” relation between the solid-phase and the vacuum can be applied to determine the efficient transport coefficients in a global domain of the CL, but considering independent internal samples.

**Analytical scaling method to ETC**

Effective Transport Coefficients (ETCs) are generally relationships of significant microstructure properties, which involve complex iterations among the components of the material. The macroscopic properties of a random heterogeneous material (RHM) depend on the constituent individual properties \(\Gamma\), the composition volume fraction \(\Phi\) and by the structure of such phases \(\Omega\) (Equation (8)).

\[
R_{\text{eff}} = f (\Gamma_1, \Gamma_2, ..., \Gamma_n; \Phi_1, \Phi_2, ..., \Phi_n; \Omega)
\]

where the subscript indicates the phase, \(\Gamma\) is the phase proportionality constant, \(\Phi\) is the phase volume fraction and \(\Omega\) represents the microstructural information of the whole medium [12].

Additionally, the effective conduction properties (which can be adapted to the general equation for transport by simple diffusion) are defined by a linear relationship between the average local flow generalized \(J\) and the average of the local potential generalized \(E\).

\[
J \propto R_{\text{eff}} \cdot E
\]

Considering the effectiveness of the charge conduction (electronic or ionic) as an example, Ohm’s law states that the electric current \(J\) of an ohmic material is directly proportional to the applied potential difference \(\Delta\Phi E\), as showed in the Equation (10).

\[
J = \Gamma A (\Delta\Phi E) / L
\]

where \(\Gamma\) is the proportionality coefficient known as conductivity, which is a property of the material, \(A\) is the area and \(L\) the length of the charge transportation. By applying the continuity equation in a discretized medium by finite control
volume (FCVs), the charge conservation transport equation in a non-reactive system, can be expressed by Equation (11):
\[ \nabla (I_{\Delta \phi}E) = 0 \]  

Solving the charge conservation transport equation directly in the structural mesh, it is possible to obtain the flow average of the local currents generated by the potential applied. Returning to the Ohm’s law (Equation (10)), and substituting the current local flows generated, it is possible to separate the ratio of the length and conduction effective area. This method allows the structure scaling [14].

The effective conductance \( (K_{eff}) \) of a heterogeneous material, composed by a conductive phase and one or more insulating phases, is a function of the conductivity \( (\Gamma_{\phi}) \), its effective area \( (A_{eff}) \) and its effective conduction length \( (L_{eff}) \) of the material conductor, as described by Equation (12),
\[ K_{eff} = \frac{\Gamma_{\phi} A_{eff}}{L_{eff}} \]  

From another point of view, the \( K_{eff} \) can also be calculated as a function of the effective conductivity \( (\Gamma_{eff}) \), the area \( (A_{M}) \) and conduction length \( (L_{M}) \) of a sample domain, as showed in the Equation (13),
\[ K_{eff} = \frac{\Gamma_{eff} A_{M}}{L_{M}} \]  

Using Equations (12) and (13), \( \Gamma_{eff} \) can be obtained; this relates the effective conductivity of the entire sample with the “effective” characteristic parameters forming the conductive phase microstructure: conductivity of the phase, and length and effective area of conduction (Equation (14)).
\[ \Gamma_{eff} = \frac{\Gamma_{\phi} (A_{eff}/L_{eff}) (A_{M}/L_{M})}{\Gamma_{eff} A_{eff}/L_{eff}} \]  

As the effective conductivity characterizes the RHM, is an intensive property, this can be extended to find the resistance of any continuous structure formed by the same material. Equation (14) can be generalized to find conductivity of an element consisting of sub-domains of smaller scales (Equation (15)).
\[ \Gamma_{(\text{eff,} \text{M1})} = \Gamma_{\phi} \prod A_{\text{eff,} \text{M1}}/L_{\text{eff,} \text{M1}} \prod L_{\text{M1}/A_{\text{M1}}} \]  

where \( \Gamma_{(\text{eff,} \text{M1})} \) is the effective conductivity of the global domain consisting of several sub-domains \( i \); \( L_{\text{eff,} \text{M1}} \) and \( A_{\text{eff,} \text{M1}} \) are the intrinsic length and area of conduction, respectively, of the intrinsic materials forming each one of the sub-domains; \( L_{\text{M1}} \) and \( A_{\text{M1}} \) are the lengths and global areas of the sub-domains, respectively.

With the aim to standardize and generalize the results, in this work, the conductivity found are used to calculate the conduction efficiency \( (\eta_{\phi}) \). According to the second law of thermodynamics, \( \eta_{\phi} \) is calculated by comparing the effective conductivity with the intrinsic conductivity of the phase studied, as shown by Equation (16). By substituting Equation (15) into Equation (16), we can obtain a relation that provides the conduction efficiency of the global domain \( (\eta_{(\text{eff,} \text{M1})}) \) formed by several sub-domains of smaller scales (Equation (17)).
\[ \eta_{\phi} = \frac{\Gamma_{\phi}}{\Gamma_{\phi}} \]  
\[ \eta_{(\text{eff,} \text{M1})} = \prod A_{\text{eff,} \text{M1}}/L_{\text{eff,} \text{M1}} \prod L_{\text{M1}/A_{\text{M1}}} \]  

Table 1 – Conditions of simulated structures: ionomer CL load \( (\beta_n) \), CL porosity \( (\Phi_{(P,M1)}) \), M1 scale porosity \( (\Phi_{(P,M2)}) \) and M2 scale porosity \( (\Phi_{(P,M2)}) \), and FCVs \((\delta x, \delta y \) and \( \delta z)\) for each of

<table>
<thead>
<tr>
<th>S</th>
<th>( \Phi_{(P,T)} )</th>
<th>( \Phi_{(P,M1)} )</th>
<th>( \Phi_{(P,M2)} )</th>
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<tbody>
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<td>80</td>
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the scales (M). The orders of magnitude of the selected values are based on the average diameters of the representative elements.

For this analysis, three scales are considered then the conductivity efficiency can be obtained according to Equation (18):

$$h(G, T) = h(G, M_1)h(G, M_2)h(G, M_3)$$

In this work, the sample that simulates the inside of agglomerate is the only one that contains the primary elements, while samples of ascending scale contain only the sample of the immediately smaller scale and its corresponding porosity. Fig. 4 plots ionic and electronic conduction efficiency versus ionomer load ($\beta_N$) of the M3 scale (interior of a macro-agglomerate).

In Fig. 4, it can be observed that the proton conduction efficiency increases, while the electronic conduction efficiency diminishes, both in an exponential fashion, when $\beta_N$ increases. On the other hand, if we analyze an horizontal behavior, it should be noticed that $h(G, M_3)$ value is similar for electronic and ionic conduction efficiency. There are four interesting points: i) $h(G, M_3) = 56.54\%$ for electronic behavior at $\beta_N = 20\%$ and $h(G, M_3) = 59.57\%$ for ionic behavior at $\beta_N = 80\%$. ii) $h(G, M_3) = 27.24\%$ for electronic behavior at $\beta_N = 40\%$ and $h(G, M_3) = 27.90\%$ for ionic behavior at $\beta_N = 60\%$. iii) $h(G, M_3) = 10.94\%$ for electronic behavior at $\beta_N = 60\%$ and $h(G, M_3) = 8.67\%$ for ionic behavior at $\beta_N = 40\%$. iv) $h(G, M_3) = 3.52\%$ for electronic behavior at $\beta_N = 20\%$ and $h(G, M_3) = 1.00\%$ for ionic behavior at $\beta_N = 80\%$. This behavior is caused by two structural conditions. The first is the fact that when $\beta_N$ grows what really increases is the volume fraction of the ionomer phase while the electronic conduction phase decreases inversely. Thus, it is expected that ionic conduction efficiency increase and electronic conduction efficiency diminishes. However, it is not expected that exponential growth and decay occur. ii) In this work, the individual relative porosity ($\phi_{(P,3)}$) of M3 scale is zero and the density of Carbon and Nafion® are similar, this setting causes the sum of $\beta_N$ and the volume fraction of the Carbon ($\beta_C$) is around the unity ($\beta_N + \beta_C = 1$). Thus, this condition makes that $h(G, M_3)$ for electronic behavior at $\beta_N = \lambda$ was similar of $h(G, M_3)$ for ionic behavior at $\beta_N = (1-\lambda)$, where $\lambda$ is any $\beta_N$ value.

In Fig. 5 we show results obtained for conduction efficiency versus total porosity in M2 scale ($h(G, M_2)$, Fig. 5a) and M1 scale ($h(G, M_1)$, Fig. 5b). Each curve represents a different $\beta_N$ and it can be noted that $h(G, M_3)$ decrease almost linearly when the CL’s porosity increases. This trend is caused by the smaller volume proportion of solid component in each scale when the porosity increases, which clearly affects the effective conductivity of the heterogeneous material. Also it should be noticed that the slope for the M2 scale is different from that for the M1 scale and it can be noticed that the $\beta_N$ affect the $h(G, M_1)$ mainly in M1 scale.

### Table 2 — Dimensions of the domain and control volume for the studied scales.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nx</th>
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<tbody>
<tr>
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</tr>
<tr>
<td>M2</td>
<td>5000</td>
<td>50</td>
</tr>
<tr>
<td>M1</td>
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</table>

Fig. 4 — Effect of ionomer load ($\beta_N$) on ionic and electronic conduction efficiency of the M3 scale (interior of a macro-agglomerate).

Fig. 5 — Conduction efficiencies versus total porosity ($\phi_{(P, T)}$) in the M2 scale (a, $h(G, M_2)$) and M1 scale (b, $h(G, M_1)$).
Table 3 presents the slope \( m \) and the constant term \( b \) of equations. The results show that the M2 scale is affected by the change of \( \phi_{(P,T)} \) (total porosity) and less affected by \( \beta_N \) (ionomer load). Conversely, M1 scale is more affected for \( \beta_N \) than \( \phi_{(P,T)} \).

Fig. 6 shows the obtained results for the ionic conduction efficiency (Fig. 5a) and electronic conduction efficiency (Fig. 5b), versus different total porosity \( \phi_{(P,T)} \) of the whole CL. The results for 20, 40, 60 and 80% the ionomer loading \( (\beta_N) \) are presented.

![Table 3](image)

### Table 3

<table>
<thead>
<tr>
<th>( \beta_N )</th>
<th>M1</th>
<th>M2</th>
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<tr>
<td>20.00</td>
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![Fig. 6](image)

Fig. 6a and b shows that both ionic and electronic conduction efficiency decreases almost in a linear behavior when the CL porosity increases. This observation also can be explained by the decrease of the volume proportion of the solid elements (electronic and ionic) when the porosity increases, affecting the efficient conductivity of the heterogeneous material. It is also observed that the decay rate depends on the \( \beta_N \) value. Fig. 5a, shows that the slope is greater for lower \( \beta_N \) while in Fig. 5b shows the opposite, the slope is greater for higher \( \beta_N \). Table 4 briefs the coefficients of the straight lines according with Fig. 5.

The slope of the trend lines \( (m) \) gives a velocity of change, while the coefficient of intersection \( (b) \) determines the point at which the line crosses the y-axis \( (\phi_{(P,T)} = 0) \). It is relevant to point out that the value \( b \) corresponds to the ionic conduction and electronic conduction efficiency of the M3 scale \( (\eta_{(G,M3)}(\beta)) \). An example of this behavior is seen in Fig. 4 when \( \beta_N = 80 \), ionic \( \eta_{(G,M3)} = 59.6\% \) and electronic \( \eta_{(G,M3)} = 3.5\% \), this results are consistent with the first line of Table 4. This is an expected behavior of the scaling approach: when the porosity is zero, ionic and electronic conduction efficiency of the whole CL is the same that the ionic and electronic conduction efficiency of the inside of agglomerate.

In this article, the finite control volume technique was applied to solve the charge transport continuity equation in the structural mesh in order to obtain the average local flows generated by simulating electric potential. Ionic an electric conductivity efficiency are determined by solving the conservation transport equation directly in the 3D structural mesh of a reconstructed CL in three scales. Although in this work, the effective ohmic conductivity was the unique property determined, the scaling approach can be applied to determine other effective transport parameters of heterogeneous structures in CL’s, such as thermal conductivity and diffusion coefficient, can be determined using the same approach.

### Conclusions

A scaling method to determine effective transport properties has been proposed like a tool to design PEMFC CL’s. The reconstructed CL was conducted in three scales: 1) the M3 scale simulates an interior of a macro-agglomerate, 2) the M2 scale simulates a structure composed for a macro-agglomerates and micropores, and 3) the M1 scale take account the mesopores. It is interesting to observe that the multiscale relationship of the whole CL microstructure are sustained by the results of each independent scale. The case study presented in this work

![Fig. 6](image)

![Table 4](image)

### Table 4

<table>
<thead>
<tr>
<th>( \beta_N )</th>
<th>Electronic</th>
<th>Ionic</th>
</tr>
</thead>
<tbody>
<tr>
<td>80.00</td>
<td>0.05</td>
<td>3.19</td>
</tr>
<tr>
<td>60.00</td>
<td>0.16</td>
<td>10.09</td>
</tr>
<tr>
<td>40.00</td>
<td>0.40</td>
<td>24.95</td>
</tr>
<tr>
<td>20.00</td>
<td>0.82</td>
<td>51.46</td>
</tr>
</tbody>
</table>
shows that the $\eta_{(G,T)}$ is the same than $\eta_{(G,M3)}$ when $\varnothing_{(P,T)} = 0$. Finally, the techniques presented in this work can be applied to study already existent CL microstructures as well as to propose new and more efficient CL’s.

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REFERENCES