



A simple analytical approach to simulate the electrochemical impedance response of flooded agglomerates in polymer fuel cells



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ABSTRACT

The development of physical based models of electrochemical impedance spectroscopy has shown the potentiality to separate Ohm kinetic and mass transport losses occurring in the catalyst layer of polymer electrolyte fuel cells. Unfortunately, the simulation of impedance spectra becomes complex when dealing with the impedance response of the flooded agglomerate model: a cumbersome analytical solution is available in the literature when considering simple 1D spherical and planar agglomerate geometry only. The known alternative is the numerical integration of the agglomerate AC problem, which increases significantly the computational time and restricts the application to simple models. In this work, an innovative and simple approach for the simulation of the impedance response of flooded agglomerate model is demonstrated starting from conservation equations, regardless of the agglomerate geometry. The innovative method is easy to implement and it requires analytical like computational cost. The validity of the basis hypothesis behind the method is demonstrated against agglomerate data from literature, indicating that the approach is widely usable. Since the innovative method requires the knowledge of the steady state effectiveness factor only, it is of interest if any complex agglomerate configuration is considered.

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1. Introduction

The physics of polymer electrolyte fuel cell (PEMFC) cathode has been successfully represented by a set of differential equations based on the *pseudo* homogeneous continuum approximation [1,2]. The conventional approach consists in solving mass conservation equations across the catalyst layer (CL) for oxygen (Eq. (1)) and proton (Eq. (2)) along with phenomenological equations for closure, e.g. Ohm's law (Eq. (3)) and Fick's law of diffusion (Eq. (4)). The set of differential equations is reported for general catalyst layer 3D geometry:

$$\nabla \cdot \underline{j} = Q_H - C_{DL} \frac{\partial \eta}{\partial t} \quad (1)$$

$$\nabla \cdot \underline{\Phi}_O = Q_O - \frac{\varphi_{CL}}{RT} \frac{\partial p_{O_2}}{\partial t} \quad (2)$$

$$\nabla \eta = -\frac{j}{\sigma_{CL}} \quad (3)$$

$$\underline{\Phi}_O = -D_{CL} \frac{\nabla p_{O_2}}{RT} \quad (4)$$

In which \underline{j} is the local current density vector, $\underline{\Phi}_O$ is the local oxygen molar flux, η is the overpotential of oxygen reduction reaction (ORR) and some properties of the CL are employed: the electrolyte conductivity (σ_{CL}), the double layer capacitance (C_{DL}), the effective diffusion coefficient of oxygen (D_{CL}), which accounts for molecular diffusion and Knudsen diffusion across CL secondary pores, and the secondary porosity (φ_{CL}) that is the volume of the void between agglomerates divided by total CL volume [3].

In addition to Eqs. (1)–(4), other phenomena have to be considered in the CL, e.g. water transport/flooding, that will either introduce additional equations or modify the reported ones.

Proton (Q_H) and oxygen (Q_O) sinks in Eqs. (1) and (2) are proportional to the volume averaged catalyst layer reaction rate, which is affected by sluggish mass transfer in the primary pores of the catalyst agglomerates that are partially/totally flooded by the electrolyte. Several approaches have been proposed to model the mass transport in the micro/meso pores of the catalyst layer agglomerates [3,4], but the most common alternatives are the macro-homogeneous model (MHM) and the flooded agglomerate model (FAM). While MHM neglects mass transport inside Platinum

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catalyst/Carbon support pellets where it postulates homogeneous concentration of reactants, FAM identifies an additional mass transport resistance inside the catalyst layer microstructure and for this reason is considered as the evolution of the MHM. Nevertheless, in the literature there is still debate regarding the validity of continuum based FAM [5], partially due to the difficulty in the estimation of the FAM parameters: agglomerate size and electrolyte fraction are generally calibrated on experimental polarization curves and as a consequence, microstructural parameters are roughly estimated, as reviewed by Dobson et al. [6]. Advanced *ex situ* experiments are a possible way to overcome this controversy, by directly estimating FAM parameters: recent works [7,8] adopted Nano-scale computed tomography imaging to estimate agglomerate relevant parameters.

An alternative and additional way to strengthen model validation [9] and to improve parameter estimation [10] deals with information provided by the electrochemical impedance spectroscopy (EIS). The development of physical based models of EIS has shown the potentiality to separate Ohm kinetic and mass transport polarizations with reasonable computational power, if any Fourier transform based solution method is used [9–14]. Unfortunately, when dealing with the impedance response of the agglomerate, a cumbersome analytical solution is obtained for simple 1D spherical [12] and planar [15] geometry and, as a consequence, no further development has been observed in research on this topic. The known alternative is the numerical integration of the agglomerate impedance response, as done by D. Gerteisen et al. [13], which increases significantly the simulation time.

The idea behind this work is to develop a new, fast and simple method that leads to an accurate analytical expression for the impedance response of FAM, regardless of the agglomerate geometry. During EIS, a small sinusoidal oscillation of potential is imposed over steady state and causes a small oscillation of the reaction rate. In turn, the local oxygen consumption and oxygen concentration in the flooded agglomerate oscillate. As hypothesis of FAM [12] the agglomerates are considered as totally flooded by the electrolyte and thus oxygen is dissolved in it. In the general case, the volume of dissolved oxygen within the agglomerate compensates for dynamical consumption, damps the oscillation and introduces a phase-shift between the sinusoidal oscillation of potential and the sinusoidal oscillation of agglomerate current. The presented approach is based on the observation that the volume of the agglomerate is quite small, in agreement with recent works [6], and dynamics of oxygen concentration are very fast and occur at high frequency. It is thus concluded that phase-shift or damping due to oxygen accumulated in the agglomerate is negligible at typical cathode charge transfer frequency. For this reason it has no visible effect on EIS because it occurs in a frequency range in which the double layer acts as a short circuit. The reported assumption, which validity is recognized to be wide and discussed in Section 3.1, significantly reduces the mathematical and numerical complexity of the impedance response. In the following sections, the theory of generalized FAM is discussed by creating an analogy between the steady state solution and the solution with superimposition of a small sinusoidal signal.

2. Theory

2.1. Generalized flooded agglomerate steady state or DC model equations

The representation of the cathode of a PEMFC according to flooded agglomerate model is reported in Fig. 1. The catalyst layer is simplified as composed of two subdomains: the secondary macro pores that are responsible for oxygen transfer across the CL; the porous agglomerates where electrochemical reaction takes place.

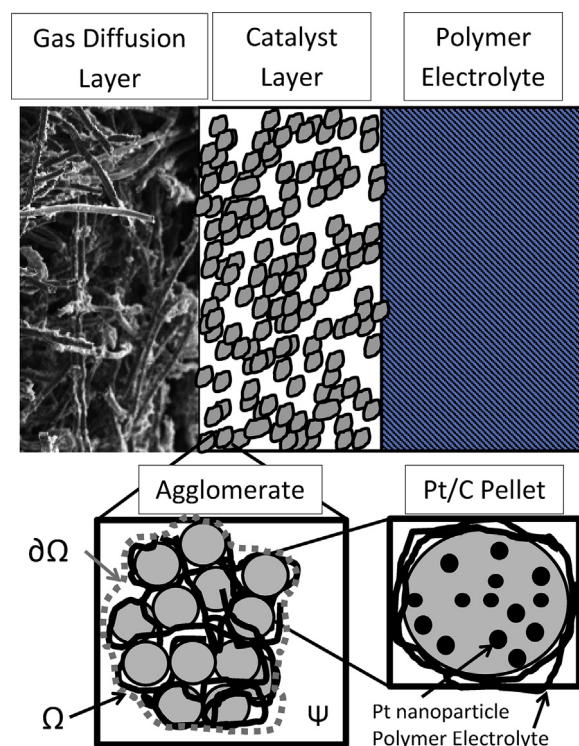


Fig. 1. Schematic illustration of the cathode of a PEMFC. Gas Diffusion Layer, Catalyst Layer and Polymer Electrolyte Membrane are highlighted. The agglomerate sub-domain composed of Platinum/Carbon pellets and polymer binder is shown in the bottom left zoom. Platinum/Carbon porous catalyst pellets are reported in the bottom right zoom. Ω is the agglomerate subdomain and $\partial\Omega$ the boundary between agglomerate and secondary pores/other agglomerates.

Accordingly with other works [12], primary porosity in the agglomerates is supposed to be totally flooded by the polymer electrolyte. W. K. Epting, and S. Litster [8] estimated that the void fraction in the agglomerate is low, approximately 0.10 and it is mostly composed of solid and polymer phases.

The generalized flooded agglomerate domain considered in this work is described below. The overall domain is indicated by Ψ and is a three dimensional portion of the CL which is divided in two regions or subdomains. The agglomerate subdomain is indicated by Ω and is the volume containing the Pt/C catalyst pellets totally flooded by the electrolyte, *i.e.* Nafion, phosphoric acid or the proton conducting medium. The porous subdomain is the region of the CL where gas and/or liquid water are present. By definition, the porous region is indicated by $[\Psi - \Omega]$. The boundary between the agglomerate and porous subdomains or other agglomerates that are in proximity (indicated by $\partial\Omega$) is the frontier through which proton and oxygen are transferred to the active catalyst sites. According to the previous notation, the definition of CL porosity is:

$$\varphi_{CL} = \frac{\iiint_{\Psi-\Omega} dV}{\iiint_{\Psi} dV} \quad (5)$$

In the agglomerate subdomain four variables are defined: the scalar overpotential for ORR (η), the scalar concentration of dissolved oxygen in the electrolyte (C), the proton flux vector (J_H) and the oxygen diffusive flux vector (J_O). If the agglomerate length scale is significantly higher than the diffusion and catalyst nanoparticle length scales, continuum approximation is valid, thus proton conservation (Eq. (6)) and oxygen conservation (Eq. (7)) are:

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