Cathodic Current Density Distribution Modeling in Proton Exchange Membrane Fuel Cells

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***Abstract*— A numerical model of the cathode of a Proton Exchange Membrane Fuel Cell (PEMFC) is presented. The model, based on the Discrete Geometric Approach (DGA), couples the discrete formulation of steady-state current conduction problem in a non-isotropic media with non-linear boundary conditions representing the charge transfer rate at catalyst layers. Constant voltage or constant current operation modes are analyzed in order to assess the cell performance with different load conditions.**

I. Introduction

During the last decade the idea of a sustainable development based on eco-compatible technologies has taken more and more relevance, with particular attention to the energy production by clean, efficient and low impact processes, such as the chemical processes within the fuel cells [1], [2]. These devices produce electric power from oxidation of hydrogen or other fuels, which are continuously supplied. Fuel cells are an important technology for a wide variety of applications including auxiliary power, transportation power and stationary power for buildings and other distributed generation applications. Among different types of cells, proton exchange membrane fuel cells (PEMFCs) are considered to be most suitable for transportation and portable applications due to their low operating temperature, high energy density and efficiency. In this context mathematical models are useful for interpreting experimental data and designing optimized configurations. An higher average current density for a given cell voltage and more uniform density on the section area are the current issues.

Proton exchange membranes consist of a Membrane Electrode Assembly (MEA), sandwiched between anode (acc) and cathode (ccc) current collectors, Fig. 1. The MEA can be divided into five layers compounded together: catalyst layers (ccl, acl) are dispersed on both sides of the polymeric membrane (pem), which is interleaved between gas diffusion layers (adl, cdl). Chemical reactions take place at catalyst layers, where three-different phases coexist (TPB, triple phase boundary). The reactants flows through GDLs from flow channels to the catalyst layers. Oxygen is typically taken from the atmospheric air and hydrogen is stored in high-pressure vessels or in metal hydride cartridges. Electric charges follow different paths: electrons are drawn from the TPB by the anode diffusion layer and flow to the external circuit through current collectors, while protons flow through the PEM. Electrons and protons are consumed in the oxygen reduction reaction producing water.

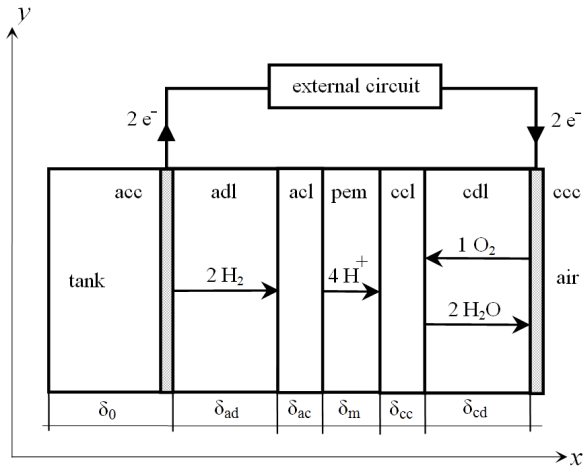

Fig. 1: Sandwiched structure of a PEMFC.

The aim of this paper is to develop a numerical simulation model of the electronic conduction inside the cathodic cdl attached to a segmented graphite current collector. The electric scalar potential distribution is simulated by solving a non-linear, anisotropic conduction problem, where field equations are expressed directly in algebraic form by means of the Discrete Geometric Approach (DGA) [6] [8] [7]. The current density distribution can be easily computed from potential distribution in order to estimate its degree of uniformity through the entire active area of the electrodes [4]. As a result, it is possible to increase the current density for a given working cell potential.

II. Discrete Geometric Model

We propose a 2D discrete geometric model of the cathodic region, where the electronic conduction occurs. Due to the periodic symmetry of the model only a part of the electrode structure is considered. We denote with $D = D_{GDL} \cup D_a \cup D_b$ the domain of interest, consisting of a GDL region D_{GDL} and one half of two adjacent graphite current collectors plates D_a, D_b separated by an insulating region D_i (Fig. 2). The upper part of the boundary of D_{GDL} region is in tight contact with the catalyst layer, where electric charges are consumed due to the oxygen reduction reaction. The catalyst layer is assumed to be a zero-thickness region since its dimension is typically negligible if compared to that of the other layers of the MEA.

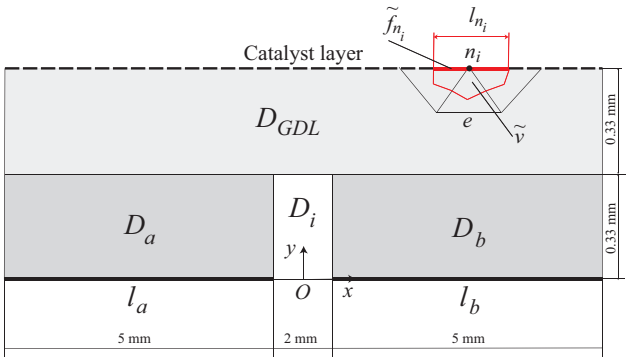

Fig. 2: Two-dimensional model of a segmented electrode at the cathode (the picture is not scaled proportionally).

According to the DGA the computational domain D is discretized into a pair of interlocked cell complexes, one dual of the other. In the case of a 2D field problem, i.e. current density and electric field are assumed to be parallel to xy-plane; the primal cell complex consists of nodes n, edges e, and faces f[1]. The dual cell complex, consisting of dual faces $\tilde{f}$[2], dual edges $\tilde{e}$ and dual nodes $\tilde{n}$, is obtained according to barycentric subdivision from the primal cell complex [7], [8].

The behavior of the cathode catalyst layer is simulated by introducing appropriate non-linear Neumann boundary conditions, which account for the electric charge transfer rate. The electron current $I^s_{n_i}$ flowing across the dual face $\tilde{f}_{n_i}$ in Fig. 2 (in one-to-one correspondence with a primal node n_i in the catalyst layer) is modeled according to the Butler-Volmer equation [3], [4]

$$I^s_{n_i}(V_{n_i}) = -|\tilde{f}_{n_i}| J_0 (10^{[(V_{n_i}-E^0)/\eta_c]} - 10^{[-(V_{n_i}-E^0)/\eta_c]}), \quad (1)$$

where E^0 is the standard electrode potential, η_c is the Tafel slope, J_0 is the apparent exchange current density and $|\tilde{f}_{n_i}|$ is the area of the dual face $\tilde{f}_{n_i}$. Such a steady state current conduction problem is formulated according to the DGA [9] by forming a charge balance on dual cells, as

$$\mathbf{G}^{\mathrm{T}} \boldsymbol{\sigma} \mathbf{G}\, \mathbf{V} + \mathbf{I}_s(\mathbf{V}) = \mathbf{0}, \quad (2)$$

where $\mathbf{V}$ is the array of electric scalar potentials, $\mathbf{G}$ is the primal edges-nodes incidence matrix, and $\boldsymbol{\sigma}$ is a constitutive matrix (with dimension N equal to the number of primal nodes) discretizing Ohm's law $\mathrm{J} = \sigma \mathrm{E}$ [9]; conductivity tensor σ in the D_{GDL} region is diagonal but conductivities along orthogonal directions are different ($\sigma_{xGDL} = 0.785$ S/cm, $\sigma_{yGDL} = 3.14$ S/cm), while the conductivity of graphite collectors D_a, D_a is isotropic ($\sigma_{D_{a,b}} = 670$ S/cm). The source current vector $\mathbf{I}_s(\mathbf{V})$ is constructed by assembling entries computed with (1). Terms corresponding to nodes not belonging to the catalyst layer are set to zero. Equation (2) is solved by imposing the electric scalar potential along l_a and l_b lines (Dirichlet boundary conditions) and periodic symmetry boundary conditions along the lateral sides of D Fig. 2. Therefore, the potential has to be computed on the entire boundary of D except l_a, l_b.

[1]Each surface is of unit thickness and its trace is a line in xy-plane.
[2]Each dual surface is of unit thickness and its trace is a line in xy-plane.

III. Numerical results

We analyzed the current density distribution within the cathode of a PEMFC by considering only a part of the entire domain due to periodic symmetry conditions Fig. 2). The non-linear system (2) is solved resorting to Newton-Raphson method. As a boundary condition, we implemented the so-called constant voltage operation of the fuel cell, where the potential of the primal nodes on l_a, l_b is imposed to $V_{l_a} = V_{l_b} = 0.695$ V. In the full paper, we will also show the so-called constant current operation, where the total current crossing dual faces along l_a and l_b is imposed, and consequently potentials V_{l_a} and V_{l_b} have to be determined. Fig. 3 shows the current density distribution within the cathodic GDL and the segmented current collector. These results are in a good agreement with those presented in [4], obtained by means of a finite difference method.

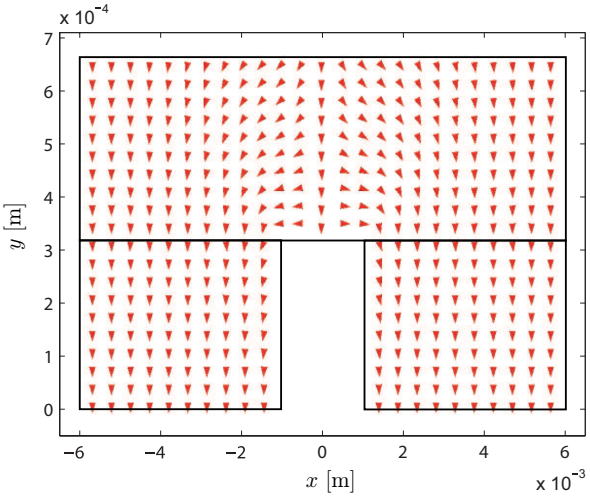

Fig. 3: Current density distribution in the cathode.

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