Modeling of Gas Diffusion Electrode: dc and ac models

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1. Introduction:

In polymer electrolyte fuel cell (PEFC), slow diffusion in the gas backing can be responsible for oxygen depletion in the case of air cathode. Most theoretical works have focused on the dc and ac responses of the active layer[2-6] less on the gas diffusion backing from which an approximated solution has been proposed[1]. The aim of this work is to develop dc and ac models of a Gas Diffusion Electrode (GDE) including mass transport limitations in both the gas backing and the active layer. This approach allows to investigate the influence of the mass transport within the gas backing.

2. The Model and basic equations:

Figure 1 schematically shows the gas diffusion backing and the active layer region of the GDE. The classical Stefan-Maxwell equations[1] allow us to describe diffusion in the gas backing while the agglomerate model is used to explain the functioning of the active layer[2]. Based on the steady state solution[4] and neglecting the ohmic drop, the ac solution is obtained from the mass balance equations respectively within the gas backing and the active layer:

$$\varepsilon c_{tot}\frac{\partial x_i}{\partial t} = -\frac{\partial N_i}{\partial y} \text{ with : } c_{tot}\frac{dx_i}{dy} = \sum_{j\neq i}\frac{x_i N_j - x_j N_i}{D_{i-j}^{eff}} \qquad \text{Eq.1}$$

$$\varepsilon'\frac{\partial c_i}{\partial t} = D_i^{eff}\frac{\partial^2 c_i}{\partial z^2} - a_v\frac{j_0}{n_i F}\exp\left(\frac{2.3|\eta|}{b}\right)\frac{c_i}{c_{r,i}} \qquad \text{Eq.2}$$

where ε is the porosity, x the mole fraction, c the concentration, N the flux, D the diffusion coefficient, a_v the specific area, $|\eta|$ the over-potential and j_0, b the kinetic parameters of the Tafel law.

The dc solution enables us to calculate the concentration distributions versus y abscissa (Fig.2). When a small sinusoidal modulation Δj is added to the applied (dc) current density j, the species concentrations are also modulated in a sinusoidal way around their steady state values. In this way, the ratio $\Delta X_{i,0}/\Delta j$ at the gas backing/active layer interface can be determined by solving the Laplace transform of the mass balance equations (Eq.1) through a numerical method. The Faradaic impedance of the GDE is then expressed from the ac solution expressed in the same way as for the flooded homogeneous model (Eq.2)[5].

3. Results and discussion:

The Figures 2, 3 and 4 present respectively the distribution of mole fraction of O_2, water and N_2 in the gas backing, the polarization curve and the corresponding impedance diagrams for three over-potentials. The contributions of the charge transfer resistance and the diffusion in the agglomerates[6] are confounded as a capacitate arc in the Nyquist plane (Fig.4). Moreover, mass-transport within the gas backing could lead to a true limiting current and to a restricted diffusion impedance in the low frequency domain (Fig.4). A clear separation of charge transfer and diffusion arcs is ensured only for a very small double layer capacitance, which is not the case for PEFC cathodes.

References:

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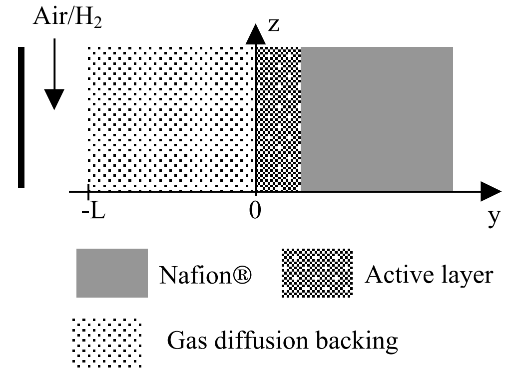

Fig1. Schematic illustration of a half PEMFC

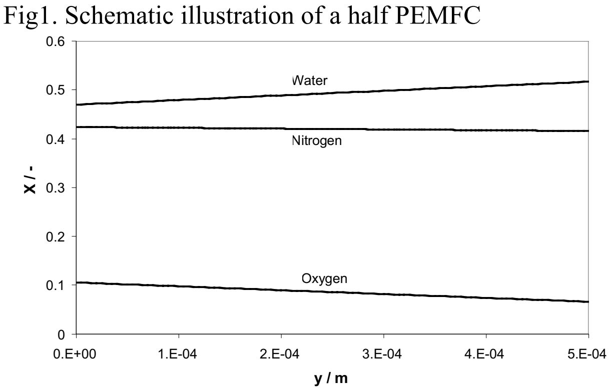

Fig.2 Gas concentration distribution within the gas backing

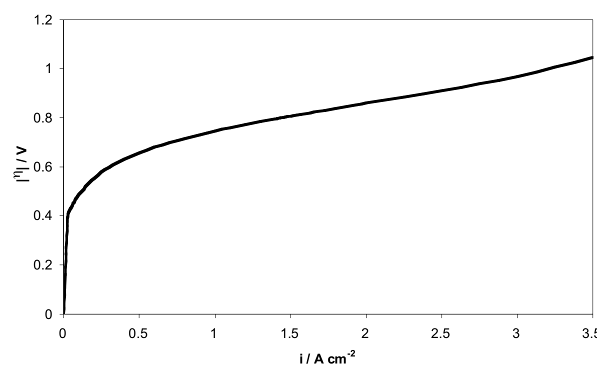

Fig.3 Simulated cathode polarization curve

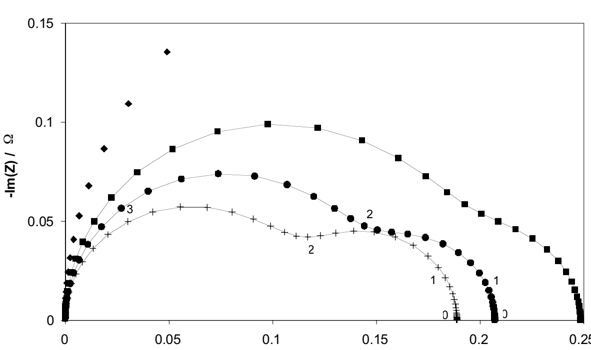

Fig.4 Simulated impedance diagrams (◆: 0.5 A cm^{-2}; ■: 1 A cm^{-2}; •: 1.5 A cm^{-2}; +: 2 A cm^{-2})