Two-dimensional Analytical Modelling of a Direct Methanol Fuel Cell

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1. Introduction

Direct Methanol Fuel Cells (DMFCs) are considered now a promising energy source for portable electronics. The development of DMFCs typically follows two research paths: the first one centred on the synthesis of new materials for PEMs and electro-catalysts; the second one related to the production of multi-physics analytical and numerical models, able to simulate the overall cell behaviour in order to simulate experimental set-ups and to provide tools for the development of industrial optimized designs of minimum size [2][3].

In this work a two-dimensional model suitable for design optimizations of active-feed DMFCs is proposed. It is based on the one-dimensional coupled approach and the two-dimensional isothermal approach presented in [4][5]. The proposed model accounts for these phenomena:

- electrochemical reactions occurring at catalyst layers;
- protonic conduction and methanol crossover across the PEM;
- diffusion of reactants in porous media layers;
- fluid motion inside flow channels;
- coupled heat and mass transfer.

2. Direct Methanol Fuel Cell Model

A direct methanol fuel cell consists basically of an anode flow channel (AFC), an anode diffusion layer (ADL), an anode catalyst layer (ACL), a proton exchange membrane (PEM), a cathode catalyst layer (CCL), a cathode diffusion layer (CDL) and a cathode flow channel (CFC).

The following approximations on the fuel cell system are considered basically:

- Water at cathode is at the vapour state and the air at the cathode flow channel is saturated;
- Transport of reactants along the y-axis in catalyst and diffusion layers is neglected as their thickness are two orders of magnitude less than their widths;
- The concentration change of reactants across catalyst layers is neglected as the thickness of diffusion layers is one order of magnitude larger than that of catalyst layers;
- The crossover methanol completely reacts at the cathode catalyst layer, so the methanol concentration is negligible there;

The methanol concentration C_{ah} along the anode flow channel depends on the methanol flow N_{ad} from the channel to the diffusion layer, as follows:

$$\delta_{ah} v_{ah} \frac{dC_{ah}}{dy} = -N_{ad} \qquad (1)$$

On the other hand, the methanol flow across the diffusion layer can be determined as well by using the Fick's law and by the mass conservation law:

$$N_{ad} = \frac{J_a}{6F} + N_m \qquad (2)$$

where J_a is the current density at the anode and N_m is the methanol crossover flow:

$$N_m = -D_m \frac{C_{ac}}{\delta_m} + n_d \frac{J_a}{F} \qquad (3)$$

where C_{ac} is the methanol concentration at the CCL.

The current density at the anode in (2) is related to the activation voltage overpotential at the anode η_a by the Butler-Volmer equation [6], as

$$J_a = J_{a,ref} \left(\frac{C_{ac}}{C_{ac,ref}}\right)^{\gamma} \exp\left(\frac{\alpha_a F}{RT}\eta_a\right) \qquad (4)$$

where $J_{a,ref}$, $C_{ac,ref}$ are the reference current density and concentration at the anode. The current density J_a can be considered to be equal to the average current density J obtained as a ratio between the current flowing in the external circuit and the fuel cell cross-section. As shown in [4], this can be derived from (4) as:

$$J = \frac{\frac{\xi_3(\exp\xi_4-1)}{\xi_4(1+\xi_3)}\frac{D_m}{D_{ad}}\frac{\delta_{ad}}{\delta_m}C_{ah,in}}{\frac{1}{6F}-\frac{n_d}{F}\left[\frac{\exp\xi_4-1}{\xi_4\xi_5(1+\xi_3)}-\frac{1}{\xi_5}\right]} \qquad (5)$$

where parameters ξ_3, ξ_4, ξ_5 depend all on the activation overpotential η_a, and $C_{ah,in}$ is the anode inlet methanol concentration (5) is strongly non-linear, so that it should be inverted numerically in order to obtain $\eta_a = \eta_a(J)$.

Similar relationships can be written for the cathode side, so that J can be expressed this time as a function of the inlet oxygen concentration at cathode $C_{ch,in}$, as:

$$J = \frac{\frac{D_{cd}}{\delta_{cd}} C_{ch,in} - \frac{3}{2}\frac{D_m}{\delta_m}\frac{\exp \xi_4 - 1}{\xi_4 \xi_5 (1 + \xi_3)} C_{ah,in}}{\frac{1}{4F}\frac{1 + \xi_1}{\xi_1} + \frac{3}{2F}\frac{n_d}{\xi_5}} \qquad (6)$$

where ξ_1 is again a dimensionless parameter. The cathode activation overpotential can be obtained by inverting (6) as $\eta_c = \eta_c(J)$ and it can be computed by using current and overvoltage values obtained from (5).

In the proposed model heat generation is taken into account as shown in [5]. The specific heat generations at the anode and at the cathode are expressed as

$$q_{ac} = \eta_a i - \frac{H_a - G_a}{6F} i \qquad (7)$$

$$q_{cc} = \eta_c i - \frac{H_c - G_c}{6F} i - h_v N_{H_2O} \qquad (8)$$

where H, G are the enthalpy and the Gibbs' free energy at catalyst layers, h_v is the latent evaporation heat for water, and N_{H_2O} is the water vapour flow. The total heat generation can be computed as $q_{tot} = q_{ac} + q_{cc}$. The temperature at catalyst layers can be obtained by using Newton's coolig law as shown in [5].

Finally, the fuel cell voltage, depending on catalyst layer temperatures, can be computed from the previous anode and cathode overpotentials, as:

$$V(J) = E_o + \frac{\partial E}{\partial T}\Delta T - \eta_a(J) - \eta_c(J) - \frac{\delta_m}{\sigma_m} J - R_s J \qquad (9)$$

where E_o is the (constant) standard cell potential, σ_m is the electric conductivity of the membrane, and R_s is the overall contact resistance per unit cross-section.

The proposed model is validated on experimental data provided in [8] for an active DMFC, maintained at a constant temperature of 90°C. Fig. 3 shows the polarization curves, obtained for various anode inlet methanol concentrations varying from 0.125 M to 0.625 M. It can be observed that numerically computed data are in good agreement with the experimental ones. Other applications of the model are provided in the full paper.

4. Conclusion

A two-dimensional model for analyse active-feed direct methanol fuel cells has been proposed. Electrochemical reactions at the anode and cathode electrodes, methanol crossover, fluid flow in channels, reactant mass transport in diffusion layers and heat transfer effects are taken into account. As a result, the model can be used for predicting the optimal design parameters of DMFC fuel cells under development at Padova University.

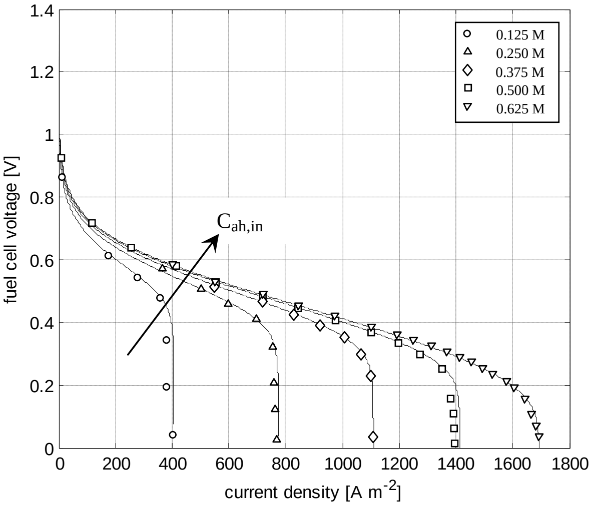

Fig. 1. Polarisation curves *v-i* for different methanol concentrations at the anode inlet (experimental values provided in [8] are compared with the computed ones).

References

[1] J. Larminie, A. Dicks, Fuel Cell Systems Explained, Wiley, Chichester (UK) (2003).

[2] V. Di Noto, M. Piga, L. Pigam, S. Polizzi and E. Negro, "New inorganic-organic proton conducting membranes based on Nafion® and $[(ZrO_2)(SiO_2)_{0.67}]$ nanoparticles: Synthesis, vibrational studies and conductivity," to be published in *Journal of Power Sources.*

[3] V. Di Noto, E. Negro, M. Piga, L. Piga, S. Lavina, G. Pace, "New Platinum-free Carbon Nitride Eletrocatalysts for PEMFCs prepared using as precursors $PAN/M(CNCH_3)_x$ complexes (M=Pd, Co, Au, Ni)," ECS Trans., vol. 11, p. 249, 2007.

[4] H. Guo and C.-F. Ma, "2D analytical model of a direct methanol fuel cell," Electrochemistry Communications, Vol. 6, pp. 306-312, 2004.

[5] R. Chen and T. S. Zhao, "Mathematical modelling of a passive-feed DMFC with heat transfer effect," Journal of Power Sources, Vol. 152, pp. 122-130, 2005.

[6] A. J. Bard, L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York (2001).

[7] P. Argyropoulos, K. Scott, W. M. Taama, "One-dimensional thermal model for direct methanol fuel cell stacks. Part 1: model development", Journal of Power Sources, Vol. 79, pp.169-183, 1999.

[8] K. Scott, W. M. Taama, S. Kramer, P. Argyropoulos, K. Sundmacher, "Limiting current behaviour of the direct methanol fuel cell", Electrochemical Acta, Vol. 45, pp. 945-957, 1999.