

Mathematical Modelling of Transport and Reaction in an Innovative Solid Oxide Fuel Cell

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A mathematical model for the description of transport phenomena and reactions in an innovative solid oxide fuel cell (IDEAL-Cell) is presented. Modelling focuses on the central membrane (CM), a porous composite layer of proton-conducting and anion-conducting phases between cathodic and anodic compartments where water is produced. The model is based on charge and mass balances using effective parameters (continuum approach) related through percolation theory to morphology and material properties. The model is validated with experimental data, providing an estimation of the kinetic parameter of water recombination reaction. Simulations show that the main contribution to cell polarization resistance is the ohmic resistance of CM, so cell performance can be improved by decreasing CM thickness and porosity respectively to 150 μ m and 40%.

1. Introduction

Fuel cells are electrochemical devices that convert the chemical energy of a combustible and a combusive agent (e.g. respectively hydrogen and air) directly into electric energy, without passing through a Carnot thermodynamic cycle. Among them, conventional Solid Oxide Fuel Cells (SOFCs) and Proton Conducting Solid Oxide Fuel Cells (PCFC) have attracted research interest due to high expected performance and efficiency.

IDEAL-Cell (Innovative Dual mEmbrANE fueL-Cell) is a new concept based on the junction between the anodic part of a PCFC (i.e. anode and dense protonic electrolyte) and the cathodic part of a SOFC (i.e. cathode and dense anionic electrolyte) through a porous composite ceramic central membrane (CM) of proton-conducting and anion-conducting phase that operates in the range 600-700°C (Figure 1a). Water recombination occurs in the CM, thus avoiding several drawbacks connected to the presence of water at electrodes in both SOFC and PCFC concepts (Thorel et al., 2009).

CM represents the real innovation of the IDEAL-Cell. In order to interpret experimental results and to optimize cell performance, a mathematical model for the description of transport phenomena and reactions in the CM is presented. The model is based on charge and mass balances in a continuum approach, which models the porous composite structure as a continuum phase characterized by effective transport and kinetic parameters (conductivities, reaction constants, gas diffusivities, etc.). This approach has been employed in several modelling studies of composite electrodes yielding valuable results (Costamagna et al., 1998).

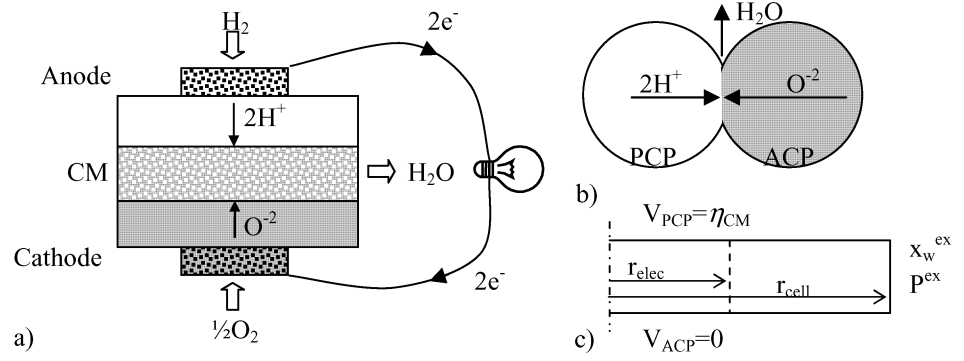


Figure 1: a) IDEAL-Cell configuration; b) water recombination reaction at TPB in CM; c) slice of CM in continuum approach with main boundary conditions.

In this paper, the model is validated with existing experimental data providing an estimation of the kinetic parameter of water recombination reaction, *a priori* unknown. After a sensitivity analysis on uncertain parameters, a design analysis regarding CM porosity and thickness is performed to evaluate how to optimize cell performance.

2. Mathematical modelling

CM is a composite layer made of proton-conducting and anion-conducting particles (PCP and ACP) randomly distributed and sintered to give enough porosity for water evacuation into gas phase. Electrochemical reaction between protons, coming from the anodic compartment, and oxygen ions, coming from the cathodic compartment, occurs at the three phase boundary (TPB) among PCP, ACP and gas phase (Figure 1b):



Since reaction (1) involves electrochemical species, reaction kinetics is assumed to follow a Butler-Volmer expression:

$$i_e = i_0 \left\{ \exp\left(\alpha \frac{F}{R_g T} \eta\right) - \exp\left(- (1-\alpha) \frac{F}{R_g T} \eta\right) \right\} \quad (2)$$

where i_e represents the current exchanged per unit of length of TPB, i_0 is the kinetic parameter, α the transfer coefficient (set equal to 0.5) and η the overpotential, i.e. the driving force of the reaction, defined as:

$$\eta = -\frac{R_g T}{2F} \ln\left(\frac{p_w}{p_w^{ex}}\right) - (V_{ACP} - V_{PCP}) \quad (3)$$

where V_{ACP} and V_{PCP} represent electric potential of ACP and PCP while p_w is the local partial pressure of water. In the CM structure, reaction can occur at any TPB, provided that the three phases (PCP, ACP and gas phase) are connected either with external sources of reactants (i.e. protonic and anionic electrolyte for protons and oxygen ions respectively) or with sink of product (external atmosphere for water).

Protons and oxygen ions are assumed to reach the TPB by conduction through their respective conducting phases following the Ohm law. Mixed conduction of both ionic species is neglected in both solid phases. Mass transport in the pores of gas phase is described by using the Dusty-Gas Model (Arnošt and Schneider, 1995), considering convection and diffusion (both ordinary and Knudsen diffusion) of water, produced by reaction (1), and nitrogen as the inert gas that surrounds CM.

Water produced by reaction (1) goes into the gas phase and exits in the outer atmosphere in the radial direction by gas transport. Water is partially adsorbed in PCP (Kreuer, 2003) and moves through this phase by bulk diffusion (Coors, 2007), affecting positively the conductivity of PCP, that can be expressed as (Bard and Faulkner, 2001):

$$\sigma_{PCP} = \sigma_{PCP}^{sat} \frac{C_{w,PCP}}{C_{w,PCP}^{sat}} \quad (4)$$

where the superscript "sat" refers to saturation limit.

The model of CM is represented by molar balance equations in steady-state conditions for the 5 species involved (i.e. protons in PCP, oxygen ions in ACP, water adsorbed in PCP, water and nitrogen in gas phase) as reported in Table 1. CM is modelled as a continuum, assuming homogeneous effective morphological properties such as the length of TPB (λ_{TPB}^v) and external PCP surface (a_{PCP}^v) per unit volume or effective ionic conductivities, calculated by percolation theory (Chen et al., 2009); temperature is assumed to be uniform throughout the CM.

Due to the axial symmetry of the system, equations are applied to the CM domain in 2D. Boundary conditions are represented in Figure 1c, i.e. on electrodes projection V_{ACP} is taken as 0 (reference) at the cathodic electrolyte interface while the overpotential applied to the whole CM (η_{CM}) is assigned at V_{PCP} at the anodic electrolyte interface; external conditions of pressure (P^{ex}) and molar fraction of water (x_w^{ex}) are assigned at the boundary with outer atmosphere.

Table 1: Model equations

Species	Balance	Molar flux
Protons	$\nabla \cdot N_{H^+} = -i_e \lambda_{TPB}^v / F$	$N_{H^+} = -\sigma_{PCP}^{eff} \nabla V_{PCP} / F$
Oxygen ions	$\nabla \cdot N_{O^{2-}} = -i_e \lambda_{TPB}^v / (2F)$	$N_{O^{2-}} = \sigma_{ACP}^{eff} \nabla V_{ACP} / (2F)$
Water adsorbed	$\nabla \cdot N_{w,PCP} = v_{ads} a_{PCP}^v$	$N_{w,PCP} = -D_{w,PCP}^{eff} \nabla C_{w,PCP}$
Water (gas phase)	$\nabla \cdot N_{w,g} = i_e \lambda_{TPB}^v / (2F) - v_{ads} a_{PCP}^v$	$N_{w,g} = \alpha_w \nabla x_w - \beta_w \nabla P$
Nitrogen	$\nabla \cdot N_{N,g} = 0$	$N_{N,g} = \alpha_N \nabla x_w - \beta_N \nabla P$

The model is implemented and solved by using COMSOL Multiphysics 3.5. The main model outcome is i_{tot} , i.e. the total density of current passed through the axial direction of the CM referred to electrodes area. Polarization resistance ($R_{p_{CM}}$) is defined by the ratio of CM overpotential (η_{CM}) and the total density of current.

3. Results and discussion

3.1 Validation

Model is validated by using experimental data measured for the whole cell at 600°C (Ou et al., 2009) in which BCY15 was used as PCP and YDC15 as ACP; external pressure was 1atm while external molar fraction of water was 0.03. Sample conditions are reported in Table 2.

Physical properties for gas and water transport in PCP are taken respectively from Todd and Young (2002) and from Coors (2007). Conductivities of pure materials are taken from Katahira et al. (2000) for PCP and from Van herle et al. (1996) for ACP. Polarization resistances of anode and cathode (both in platinum) were singularly measured to be respectively $3 \cdot 10^{-4} \Omega m^2$ and $4.2 \cdot 10^{-4} \Omega m^2$.

Figure 2 shows the comparison between simulated and experimental polarization curves. In simulations, the kinetic parameter i_0 is set to $6 \cdot 10^{-9} A/m$ as the best fit of experimental data. Main resistances are due to CM since the ratio $R_{p_{CM}}/R_{p_{cell}}$, calculated in simulation, is over 95%. The linear behaviour between current and cell overpotential suggests that losses are due mainly to ohmic resistances in CM.

Table 2: Sample conditions for validation

Thickness electrolytes and CM	500 μ m	CM particles diameter	0.2 μ m
Electrodes radius	2mm	CM porosity	50%
Cell radius	5mm	CM composition (PCP-ACP)	50-50%

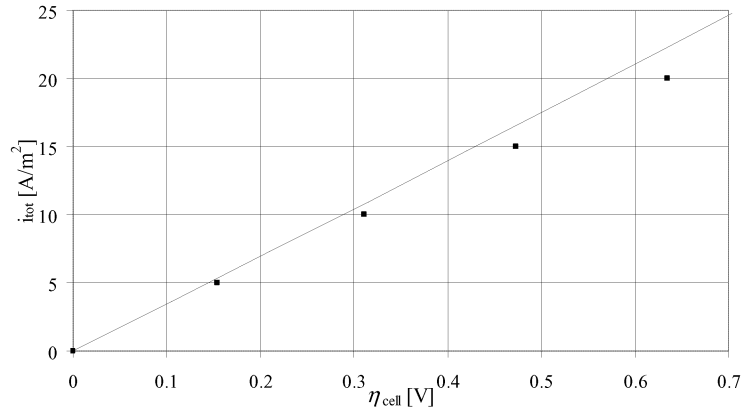


Figure 2: Validation: comparison between experimental (dots) and simulated (line) polarization curves.

3.2 Sensitivity and design analyses

The kinetic parameter of recombination reaction i_0 and effective conductivities of solid phases in CM are uncertain parameters because they are respectively fitted on experimental data and calculated using a correction factor on conductivities of pure materials. In Figure 3 the sensitivity analysis shows that polarization resistance is strongly affected by the effective resistivity correction factor while uncertainties on the kinetic parameter have a smaller influence. It means that a very accurate estimation of effective properties is required to obtain good simulation results. The linear behaviour between R_{pCM} and ρ^{eff}/ρ confirms that main resistances are ohmic.

Figure 4 shows the design analysis on CM thickness and porosity. Simulation shows that polarization resistance can be reduced by reducing CM thickness and porosity. It is reasonable because both operations lead to a reduction of effective ohmic resistances. An optimum of R_{pCM} is reached at about $150\mu\text{m}$; for lower thicknesses the total number of reaction sites decreases giving an increase of R_{pCM} due to kinetic activation losses.

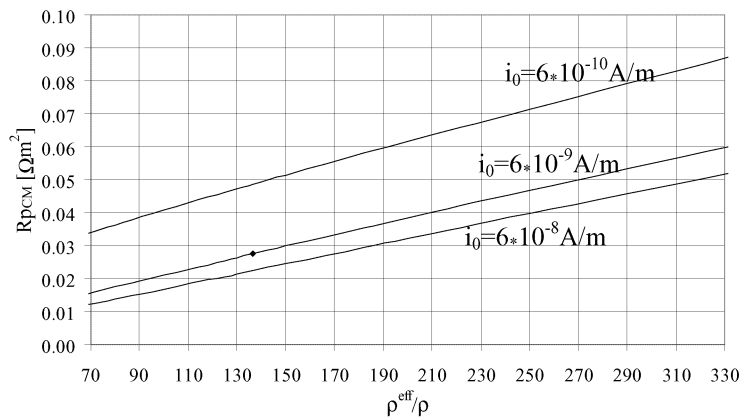


Figure 3: Sensitivity analysis on ohmic and kinetic parameters. Dot represents default conditions used in validation.

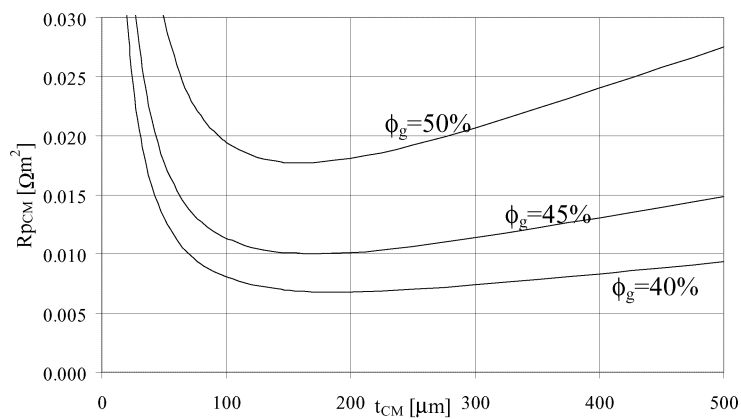


Figure 4: Design analysis on thickness and porosity of CM.

4. Conclusions

A mathematical model of electrochemical reaction, charge and mass transports inside CM of IDEAL-Cell was developed, based on conservation equations in a continuum approach. The model was validated using experimental data and a kinetic parameter for water recombination reaction has been estimated by best fitting.

Simulations show that CM is in ohmic regime. Consequently, i) a good estimation of effective conductivities is required to obtain valuable results from the model ii) reduction of CM polarization resistance can be achieved by reducing CM thickness and porosity, i.e. by increasing effective conductivities.

Model can be used as a valuable tool to interpret experimental data, to optimize cell design and to predict future performances and developments.

Acknowledgements

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