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A mathematical model of mass and charge transport and reaction in the central membrane of the IDEAL cell

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1. Introduction

Innovative Dual Membrane Fuel Cell (IDEAL cell) is the new concept for fuel cell proposed by Association de Recherche des écoles des MINES in Paris[1]. In the IDEAL Cell, the anode and the electrolyte of a protonic SOFC (pSOFC) and the cathode and the electrolyte of an anionic SOFC (aSOFC) are connected (see figure 1) through a central membrane(CM) made by composite proton-conducting and anion-conducting layer. The IDEAL cell then comprises five contacted layers of composite (anode, cathode and CM) and dense (electrolytes) materials. Protons are formed by electrochemical oxidation of molecular hydrogen at the anode and they migrate through the protonic electrolyte to the CM, where they react to produce water with oxygen anions migrated from the cathode through the anionic electrolyte. The IDEAL Cell presents some advantages compared to more conventional concepts (particularly aSOFC), most notably referred to the fact that water cannot come into contact with the electrodes because of the presence of the two dense electrolyte layers along the CM. As a consequence, the produced water does not dilute the fuel and does not interfere with the electrochemical activity at the anode.
The IDEAL cell presents some common feature with conventional SOFCs. In particular the presence of porous composite layers used to increase the active area in the electrodes. Modeling tools developed for such materials can then readily adapted to model reaction and mass transfer phenomena in the IDEAL. However, the ideal cell also presents some peculiar features, namely the mechanism of water formation in the central membrane, which require dedicated efforts. Since the reaction mechanism of charged species on solid state phase and the influence of water pressure on the reaction and cell operability are unknown, the main objective of this paper is to build a

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mathematic model for description of reaction and provide pressure distribution under various conditions. This information will serve as the guideline for designing a high efficient IDEAL cell.

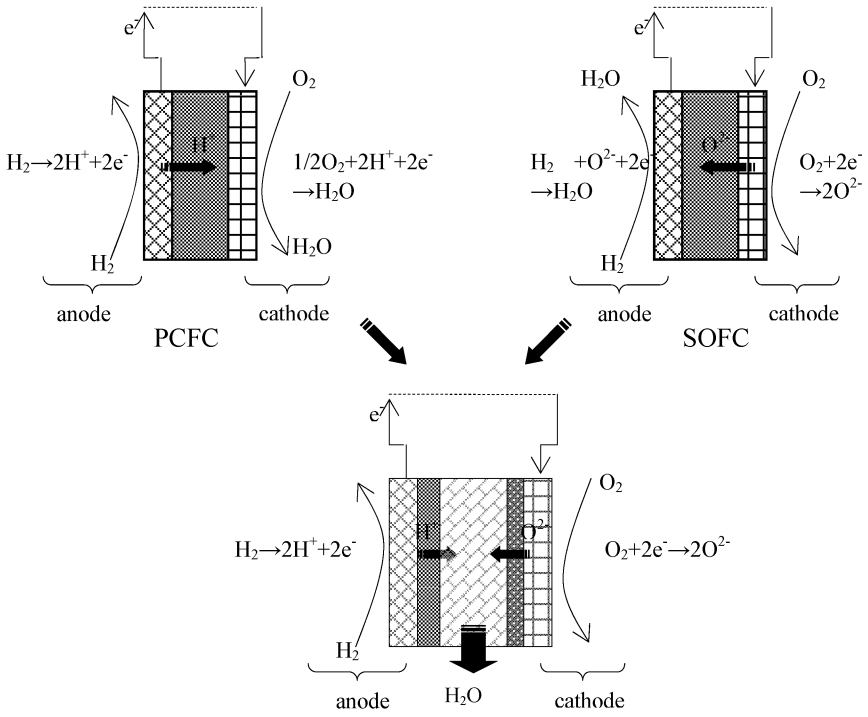

Figure 1. IDEAL cell concept built by combining PCFC and SOFC

1.1 Macro-kinetic model

Plenty of work have been done on simulation of electrodes, this marco-kinetic model only concerns about peculiar feature of IDEAL cell which are mainly about mass transfer and reaction in CM. The formation of water only occur in the proximity of a triple phase contact among the proton-conducting phase(PCP), the anion-conducting phase(ACP) and the gas phase in the pores(see Figure 2). The overall reaction mechanism can be simply represented as:

$$2H^{+}_{PCP} + O^{=}_{ACP} \Leftrightarrow H_2O_{ADS} \quad (1)$$

$$H_2O_{ADS} \Leftrightarrow H_2O_{GAS} \quad (2)$$

The first step is for the chemical recombination of two charged species, and the second step is physical desorption of water from either PCP or ACP. The kinetics of equation 1 is described using a lumped-parameter formula. The reacting system present some

analogies with ion exchange bipolar membranes[2]. On the basis of these analogies, the forward and backward reaction rates are assumed to depend on the potential difference between the two phases[3].

$$r_{\mathrm{M}} = \left(\frac{1}{r_M^0} + \frac{1}{r_{MT}^+} - \frac{1}{r_{MT}^-} \right)^{-1} \left[\exp\left(-(1-\alpha_{\mathrm{M}}) \frac{F}{R_g T} \eta_{\mathrm{M}} \right) - \exp\left(\alpha_{\mathrm{M}} \frac{F}{R_g T} \eta_M \right) \right] \tag{3}$$

$$\eta_{\mathrm{M}} = \Delta\phi_{\mathrm{eq}} - (\phi_{PCP} - \phi_{ACP}) \tag{4}$$

$$r_{MT}^+ = \frac{\theta_w H_M - P_w}{\sqrt{2\pi m k_B T} \cdot N_A} \tag{5}$$

$$r_{MT}^- = \frac{P_w}{\sqrt{2\pi m k_B T} \cdot N_A} \tag{6}$$

r_{M}^0 is the reaction rate constant with the unit of mol/(m^2·s) which takes into account surface concentration of reactive species. ϕ_{ACP} and ϕ_{PCP} are the local electric potential on two different particles. $\Delta\phi_{\mathrm{eq}}$ is the equilibrium potential of CM calculated on the basis of thermodynamic considerations. α_{M} is symmetric factor which is set at 0.5. r_{MT}^+, $r_{\mathrm{MT}}^-$are the water desorption rate and adsorption rate[4], separately. The fraction of surface coverage θ_{w} is defined as the ratio of adsorbed surface concentration to free adsorption site surface concentration, H_{M} is the desorption coefficient with the unit of Pa, P_{w} is the vapour pressure near TPB, N_{A} is Avogadro constant, k_{B} is the Boltzmann constant, T is the absolute temperature.

1.2 ACP-PCP interface

The contact surface between the PCP and the ACP is represented as an inter-phase layer where the chemical reaction of water formation occurs. Because of chemical reaction and flow of protons from the PCP and oxygen ions from the ACP, both interfaces of the transition layer with the ACP and the PCP are characterised by strong gradients of surface concentrations of reacting species (protons on the PCP side and oxygen ions on the ACP side). These interfaces may be theoretically demonstrated to behave as double

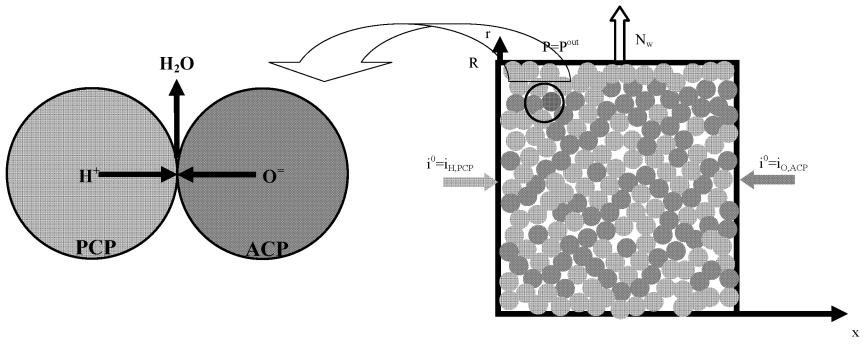

***Figure 2**. a) Overall mechanism of water recombination at the interface between the PCP and the ACP in the central membrane, b) Integration domain in the central membrane*

electrochemical layers at electrode-electrolyte interfaces, which can be described by using the same governing equations. As a consequence, a resistive-capacitive behaviour can be expected for the central membrane subjected to transient current loading (as in EIS), with a resistance associated to the reaction and a capacitance associated to the double layer charge and discharge under transient conditions.

1.3 Mass and charge transport

The molar fluxes of protons and oxygen ions are calculated as a function of current density by neglecting charging and discharging currents of the double layer. Current densities in the conducting phases are related to potentials through the Ohm law, and water flux is related to the pressure inside the membrane through the Blake-Kozeny equation[5]:

$$\nabla \cdot N_{H,PCP} = -2a_{TPB}r_M \tag{7}$$

$$\nabla \cdot N_{O,ACP} = -a_{TPB}r_M \tag{8}$$

$$\nabla \cdot N_w = -a_{TPB}r_M \tag{9}$$

$$N_{H,PCP} = i_{H,PCP}/F = -\sigma_{PCP}^{eff}\nabla\phi_{PCP}/F \tag{10}$$

$$N_{O,PCP} = i_{O,ACP}/2F = \sigma_{ACP}^{eff}\nabla\phi_{ACP}/2F \tag{11}$$

$$N_w = C_{w,GAS}v = -P_w d_p^2 \varepsilon^3 \nabla P_w / 150\mu R_g T(1-\varepsilon)^2 \tag{12}$$

Where $N_{H,PCP}$ is the proton flux in PCP, $N_{O,ACP}$ is the anion flux in ACP, N_w is the vapour flux in radius direction, a_{TPB} is the effective three phase boundary length with the unit of 1/m. $i_{H,PCP}$ is the proton current density with the unit of A/m^2, $i_{O,ACP}$ is the anion current density with the unit of A/m^2, σ_{PCP}^{eff}, σ_{ACP}^{eff} are the effective conductivity of PCP and ACP which are only dependent on material property and temperature, d_p is the average particle size of PCP and ACP, ε is the porosity of CM, μ is the viscosity of vapor under operating conditions with the unit of Pa·s.

1.4 Boundary Conditions

The continuity equations for the reacting species can be integrated over the membrane domain (see Figure 2) to give the concentration, flux and pressure profiles in the membrane. Continuity equations can be solved for assigned conditions of current loading at the membrane boundaries. Eq.(3)-(12) set the relationship between current and potential difference at the two sides of the membrane.

$$\begin{aligned}
&x = 0 : \phi_{ACP} = 0, i_{O,ACP} = 0, i_{H,PCP} = I_{tot} \\
&x = \delta_M : i_{H,PCP} = 0, i_{O,ACP} = -I_{tot} \\
&r = 0 : \partial P/\partial r = 0; \partial\phi_{PCP}/\partial r = 0; \partial\phi_{ACP}/\partial r = 0 \\
&r = R : P_w = P^{out}; \partial\phi_{PCP}/\partial r = 0; \partial\phi_{ACP}/\partial r = 0
\end{aligned} \tag{13}$$

2. Simulation Results

The model is implemented by COMSOL Multiphysics Software. Several geometric parameters are fixed in Table 1. Total current density is expected at 2000 A/m^2 when calculating pressure distribution and overpotential distribution. Varying the thickness of CM, the distribution plots of overpotential and pressure of vapor have be drawn in the Figure 3:

Table 1 constants used for calculation pressure and overpotential

T(K)	ε	d_p (μm)	$\Phi_{PCP/ACP}$	σ_{PCP}^{eff} (S/m)	σ_{ACP}^{eff} (S/m)	R(cm)	r_M^0 (mol/(m^2·s))
873	0.5	1	0.5	2.1	0.71	1.5	10^{-5}

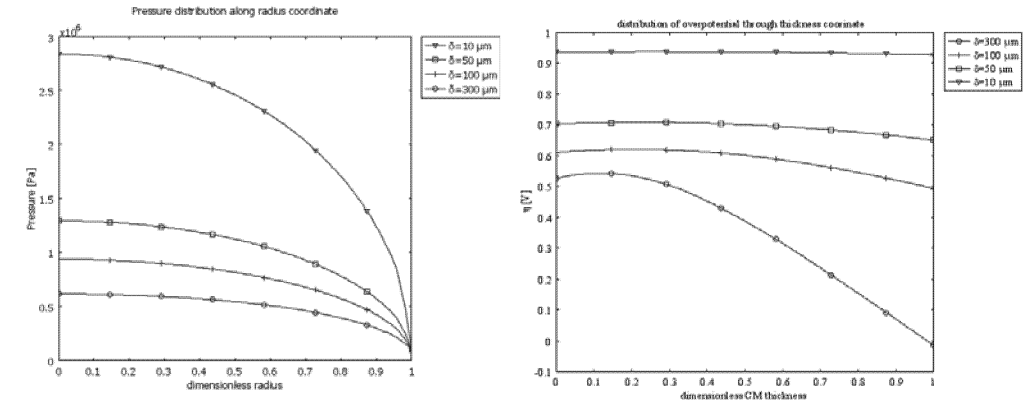

Figure 3 a) pressure of vapour in cylindric CM b) local polarization along CM thickness

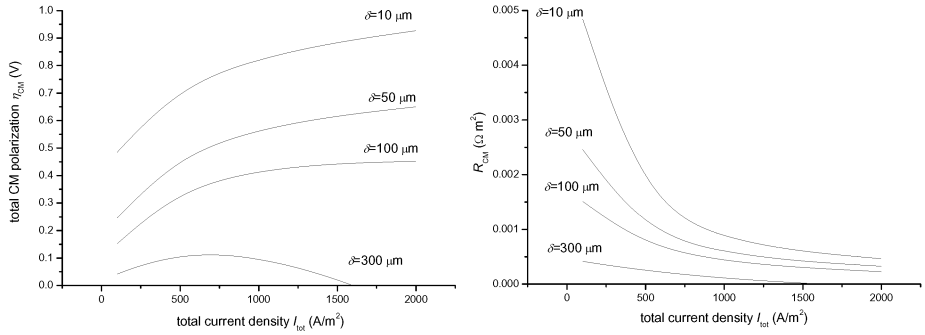

Figure 4 a)total potential loss calculated under different current density b) total CM resistance calculated under different current density

As depicted in Figure 2b, vapor flux only along radius coordinate due to gradient of pressure, the pressure outside of CM is considered as 1 atm. It can be noticed that overpotential along the CM thickness presenting a maximum value in the CM which

means that reaction mainly takes place there. In the case that CM thickness is very thin, the place of reaction occurring is uniformly distributed along CM thickness, which shows that overpotential is uniform. In the case that CM thickness is very large, ions can not migrate to the other extreme of CM due to large ohmic potential loss. The majority of ions are consumed in the middle, and the peaks of potential loss appears close to the left side due to less Ohmic potential loss by conducting protons. Figure 3b shows that higher local potential loss exist in case of thicker CM because that the desired current density is fixed, in order to supply such amount of current, more reaction is required which consequently results in higher activation overpotential.

$$R_M = \frac{\eta_{\mathrm{CM}}}{I_{tot}} = \frac{\Delta\phi_{\mathrm{CM,\ equil}} - \phi_{PCP}\Big|_{x=0} + \phi_{PCP}\Big|_{x=\delta_M}}{I_{tot}} \tag{14}$$

Total potential loss which is the sum of ohmic potential loss and activation potential loss is written in equation 14. When CM thickness is as large as 300 μm, under fixed reaction rate constant r_M^0, limit current density is reached at 1600 A/m^2. The possible explanation might be the effect of mass transfer becomes significant.

3. Conclusion

The mathematic model has been built for predicting CM performance of an innovative fuel cell. The pressure and overpotential formed in CM are mainly concerned under preliminarily assumed reaction rate constant. The model is for the description of steady state CM while the velocity of mass transfer is not under consideration. However, when the CM thickness is at large extent, mass transfer should also be taken into account.

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