Model of the isotropic anode in the molten carbonate fuel cell

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An isotropic one-dimensional model is proposed for the porous anode of a molten carbonate fuel cell, requiring the thickness of the electrolyte film in the pores as the only one adjustable parameter. The solution of the model equations is presented in a general form and calculations are made by approximation. The wetting of the whole electrode inner surface by the electrolyte is assumed. The model shows that, practically, the current is generated in a thin reaction zone in the electrode. The model may be fitted well to the experimental polarization curves [4], when 0.057 μm is the electrolyte film thickness.

Nomenclature

a_i, b_i, c_i	electrode reaction orders
c_k	molar concentration of the kth gas component at the electrode/electrolyte interface
c_k^0	equilibrium molar concentration of the kth gas component
d	parameter in Equation 21
D_k	diffusion coefficient of the kth component
F	Faraday's constant
H_k	Henry's constant of the kth component
i	Faradaic current density
i_0	exchange current density
i_k^{lim}	limiting current density of the kth reagent
j_E, j_M	ionic and electronic current density, respectively
j_T	total anodic current density
k	rate constant in Equation 19
l	electrode thickness
p_k	partial pressure of the kth component
PD	penetration depth
Q	parameter, defined by Equation 41
R	gas constant
S	specific internal surface of the electrode
T	temperature
V_E	relative electrolyte volume in the electrode
x	dimensionless coordinate, $x = z/l$
Z_F	$\eta(i)$ function slope at zero current
Z	total electrode impedance per unit area of electrode
β	symmetry coefficient
δ	electrolyte film thickness
η	overpotential
η_0, η_1	overpotentials at the gas/electrode ($x = 0$) and the electrode/electrolyte ($x = 1$) interfaces, respectively

η', η'' dummy variables of the integration
η_m measured overpotential
κ_E, κ_M specific electrolyte and electrode metal conductivity, respectively
$\kappa_E^{eff}, \kappa_M^{eff}$ effective electrolyte and electrode metal conductivity, respectively
ν stoichiometric number
ξ tortuosity factor
ϕ_E, ϕ_M electrolyte and electrode metal potentials, respectively
$\Delta\phi^{eq}$ equilibrium electrode metal-electrolyte potential difference

1. Introduction

An adequate model of a porous electrode which would enable us to describe precisely the relation between the electrode performance and the structure of pores, is one of the main problems in fuel cell electrochemistry. In the numerous studies on this topic we can distinguish two different approaches to this complicated problem. One approach consists in an approximation of the porous electrode structure by a set of parallel capillaries, usually of the same radius. The walls of these capillaries are covered with a thin film of the electrolyte. The resulting electrode performance depends on the kinetics of the processes and on the transport of reagents through the thin film of the electrolyte.

The second approach, neglecting the electrode reaction mechanism and kinetics, brings into relief the parameters of the porous electrode structure: pore size distribution, tortuosity, as well as the distribution of the electrolyte in the electrode as dependent on the capillary pressure in the pores.

Recently porous electrode modelling has been successfully applied in connection with the molten carbonate fuel cell (MCFC) project. The capillary approach has been used by Wasan *et al.* [1], Szymański and Kunz [2] and by Wilemski *et al.* [3]. Polarization curves of the MCFC porous nickel anodes calculated on the base of the model by Wilemski *et al.* [3] can be fitted to the respective experimental dependences [4] by means of two adjustable parameters. Recently Yuh and Selman [5] have proposed a model in which the problem of molten carbonate electrolyte distribution in the porous electrode is taken into account.

In this paper we present a new attempt at a process model in the MCFC porous anode.

2. Theory

The following assumptions have been made:

(a) There are two kinds of pores: (i) pores completely filled with electrolyte, electrochemically inactive, but playing an important role in the electric charge transfer process; (ii) pores wetted by the electrolyte film of a constant thickness.

(b) The fluxes of reagents across the electrolyte film are constant.
Fig. 1 presents the scheme of the proposed model.

2.1. Equations

A one-dimensional model is being considered (see Fig. 1). In accordance with Ohm's law we can write for the currents flowing through the model electrode (j_M) and the electrolyte (j_E):

$$\frac{d\phi_E}{dz} = -j_E(z)/\kappa_E^{eff} \tag{1}$$

$$\frac{d\phi_M}{dz} = -j_M(z)/\kappa_M^{eff} \tag{2}$$

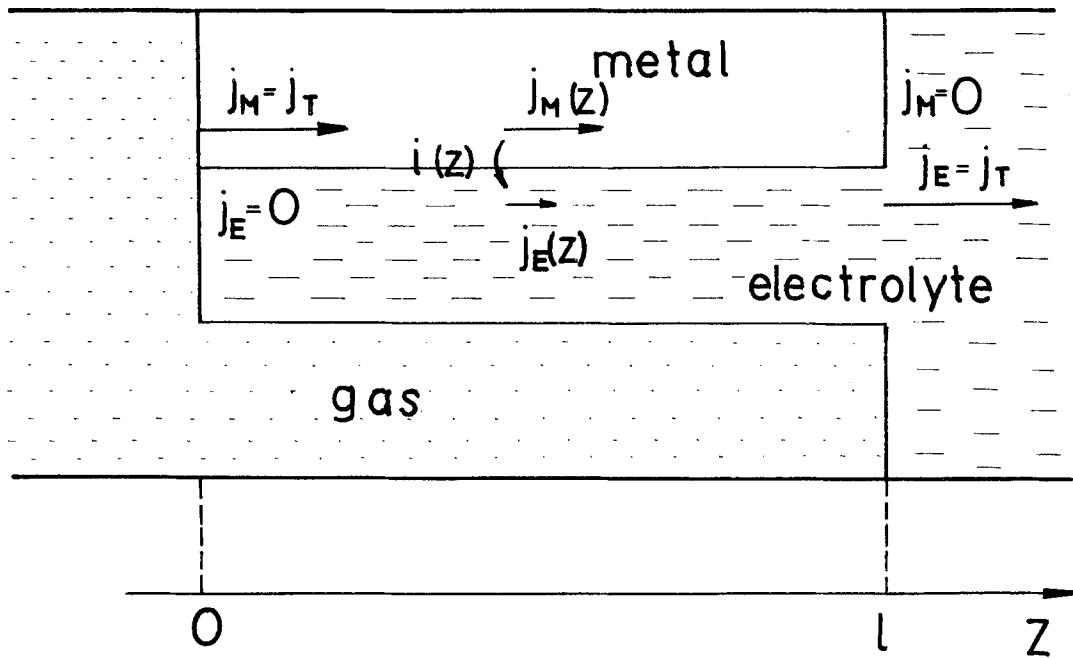respectively. The boundary conditions are:

Fig. 1. Schematic model representation.

$$j_E(z = 0) = 0 \tag{3}$$

$$j_M(z = 1) = 0 \tag{4}$$

The current densities j_M and j_E are related at any electrode point z to the total current density by a simple relation:

$$j_E(z) + j_M(z) = j_T = \text{const.} \tag{5}$$

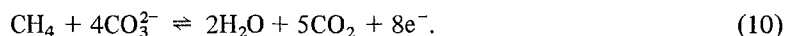For the overpotential at any point of the electrode one can write:

$$\frac{d\eta}{dz} = \frac{d\phi_M}{dz} - \frac{d\phi_E}{dz} = \frac{j_E(z)}{\kappa_E^{eff}} - \frac{j_M(z)}{\kappa_M^{eff}} = j_E(z)\left(\frac{1}{\kappa_E^{eff}} + \frac{1}{\kappa_M^{eff}}\right) - \frac{j_T}{\kappa_M^{eff}}. \tag{6}$$

The current generated in a differential geometric volume is:

$$\frac{dj_E}{dz} = Si(\eta). \tag{7}$$

The parameter S denotes the ratio of the area of the inner electrode surface covered with the electrolyte film and the geometric volume of the electrode. The function $i(\eta)$ denotes the Faradaic current density generated on the electrode surface covered with the electrolyte film.
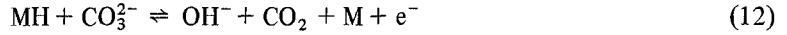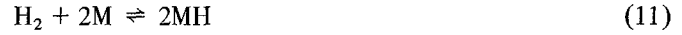
To calculate the $i(\eta)$ function we must make some assumptions concerning the electrode reaction mechanism and conditions of the transport of reagents through the electrolyte film. The overall stoichiometry of the anodic oxidation of the C–H–O fuel components in molten carbonates is:

$$H_2 + CO_3^{2-} \rightleftharpoons H_2O + CO_2 + 2e^- \tag{8}$$

$$CO + CO_3^{2-} \rightleftharpoons 2CO_2 + 2e^- \tag{9}$$

$$CH_4 + 4CO_3^{2-} \rightleftharpoons 2H_2O + 5CO_2 + 8e^-. \tag{10}$$
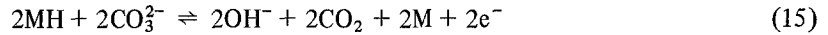
Methane oxidation is usually neglected because of its low concentration in the fuel [6–8]. With anodic

overpotentials below 200 mV the rate of the electrochemical Reaction 9 is also small [7] and, therefore, only H_2 electrochemical oxidation according to Reaction 8 is considered in this paper.

Two alternative hydrogen oxidation mechanisms should be taken into account: (i) the Ang and Sammells [6] mechanism:

$$H_2 + 2M \rightleftharpoons 2MH \tag{11}$$

$$MH + CO_3^{2-} \rightleftharpoons OH^- + CO_2 + M + e^- \tag{12}$$

$$MH + OH^- \rightleftharpoons H_2O + M + e^- \tag{13}$$

with Reaction 12 as the rate determining step, and (ii) derived by us from the Ang and Sammells experimental results [6]:

$$H_2 + 2M \rightleftharpoons 2MH \tag{14}$$

$$2MH + 2CO_3^{2-} \rightleftharpoons 2OH^- + 2CO_2 + 2M + 2e^- \tag{15}$$

$$2OH^- + CO_2 \rightleftharpoons H_2O + CO_3^{2-} \tag{16}$$

with step 15 as rate determining.

The dependences of the current density on the electrode overpotential derived by the assumption of either of the mechanisms (i) and (ii) take the form:

$$i = i_{0,(i)} \left\{ \left(\frac{C_{H_2}}{C_{H_2}^0} \right)^{1/2} \exp \left[(2 - \beta) \frac{F\eta}{RT} \right] - \left(\frac{C_{H_2}}{C_{H_2}^0} \right)^{-1/2} \left(\frac{C_{CO_2} C_{H_2O}}{C_{CO_2}^0 C_{H_2O}^0} \right) \exp \left(-\beta \frac{F\eta}{RT} \right) \right\} \tag{17}$$

and

$$i = i_{0,(ii)} \left\{ \left(\frac{C_{H_2}}{C_{H_2}^0} \right)^{1/2} \exp \left[(1 - \beta) \frac{F\eta}{RT} \right] - \left(\frac{C_{CO_2} C_{H_2O}}{C_{CO_2}^0 C_{H_2O}^0} \right)^{1/2} \exp \left(-\beta \frac{F\eta}{RT} \right) \right\} \tag{18}$$

respectively, when a Langmuir adsorption isotherm is assumed and when the anode surface is covered with the adsorbed hydrogen to a small extent. The exchange current density satisfies the relation:

$$i_0 = k_i (p_{H_2})^{a_i} (p_{CO_2})^{b_i} (p_{H_2O})^{c_i}. \tag{19}$$

The exchange current density i_0 depends on the electrode material, electrolyte, reaction mechanism and on temperature.

The relation between the concentration of reagents at the electrolyte/gas interface and their partial pressures in the gas phase obeys Henry's law:

$$C_i^0 = H_i p_i. \tag{20}$$

Assuming constant fluxes of reagents across the electrolyte film during the electrode process one can write the relation:

$$i = \pm nFD_k (C_k^0 - C_k)/d \tag{21}$$

where d is a parameter depending on the diffusion geometry, which interrelates the rate of mass transfer across the film with the density of the current generated at the three-phase boundary on the electrode metal surface. Relation 21 can be rewritten in the form:

$$\frac{i}{i_k^{lim}} = 1 - \frac{c_k}{c_k^0} \tag{22}$$

where i_k^{lim} is the limiting current density of the kth reagent defined by:

$$i_k^{lim} = \pm nFD_k c_k^0/d. \tag{23}$$

Equation 17 or 18 together with Equation 23 give the nonlinear algebraic equation of the form $F(i, \eta) = 0$. This equation, in general, must be solved numerically to obtain the $i(\eta)$ function.

The effective ionic conductivity κ_E^{eff} of the porous slab, partially filled with electrolyte depends on the specific electrolyte conductivity κ_E and the tortuosity factor ξ [9] by:

$$\kappa_E^{eff} = \kappa_E V_E / \xi^2 \tag{24}$$

where the parameter V_E denotes the relative volume of the electrolyte in the electrode. Depending on the pore structure assumed, one can obtain different ξ vs V_E relationships [10]. For an ideally anisotropic porous structure of parallel cylindrical pores: $\xi = 1$ and $\kappa_E^{eff} = \kappa_E V_E$, and for an ideally isotropic capillary structure according to the experimentally confirmed Archie's law:

$$\xi = V_E^{-1/2} \tag{25}$$

and

$$\kappa_E^{eff} = \kappa_E V_E^2 \tag{26}$$

2.2. General solution

A system of differential Equations 6 and 7 is equivalent to a single second order differential equation:

$$\frac{d^2\eta}{dx^2} = Sl^2 \left(\frac{1}{\kappa_E^{eff}} + \frac{1}{\kappa_M^{eff}} \right) i[\eta(x)] \tag{27}$$

with the boundary conditions:

$$\left. \frac{d\eta}{dx} \right|_{x=0} = -j_T l / \kappa_M^{eff} \tag{28}$$

and

$$\left. \frac{d\eta}{dx} \right|_{x=1} = j_T l / \kappa_E^{eff} \tag{29}$$

where $x = z/l$ is the dimensionless coordinate.

To solve this boundary value problem we can introduce a new variable $y = d\eta/dx$. Then Equation 27 takes the form:

$$y \, dy = Sl^2 \left(\frac{1}{\kappa_E^{eff}} + \frac{1}{\kappa_M^{eff}} \right) i(\eta) \, d\eta \tag{30}$$

which can be explicitly integrated in the interval $0 \leqslant x \leqslant 1$. After some rearrangement one can obtain the basic equation for the total current density as dependent on the integrated $i(\eta)$ function:

$$j_T = \left(\frac{2S\kappa_E^{eff}}{1 - \kappa_E^{eff}/\kappa_M^{eff}} \int_{\eta_0}^{\eta_1} i(\eta) \, d\eta \right)^{1/2} \tag{31}$$

where $\eta_0 = \eta(x = 0)$ and $\eta_1 = \eta(x = 1)$.

The measured overpotential:

$$\eta_m = \phi_M(x = 0) - \phi_E(x = 1) - \Delta\phi^{eq} \tag{32}$$

may be expressed using Equation 6 and integration:

$$\eta_m = (\kappa_E^{eff} + \kappa_M^{eff})^{-1} (j_T l + \kappa_M^{eff} \eta_1 + \kappa_E^{eff} \eta_0). \tag{33}$$

The overpotential distribution across the electrode is obtained in an implicit form by integrating twice Equation 30 in the $[0, x]$ interval and using Equations 28 and 31:

$$xl \left[2S \left(\frac{1}{\kappa_E^{eff}} + \frac{1}{\kappa_M^{eff}} \right) \right]^{1/2} = \int_{\eta_0}^{\eta} \left[\int_{\eta_0}^{\eta'} i(\eta'') \, d\eta'' - \frac{(\kappa_E^{eff})^2}{(\kappa_M^{eff})^2 - (\kappa_E^{eff})^2} \int_{\eta_0}^{\eta_1} i(\eta'') \, d\eta'' \right]^{-1/2} d\eta'. \tag{34}$$

Putting $x = 1$ and $\eta = \eta_1$ into Equation 34 one gets the relation between the overpotentials on both boundaries of the electrode η_0 and η_1, respectively.

2.3. Approximations

Information concerning κ_E^{eff}, κ_M^{eff} as well as the $i(\eta)$ function are necessary for calculating the density of the total current generated on the porous electrode, using Equation 31.

The effective ionic conductivity of the electrolyte in the pores may be well approximated by Archie's law [9]. For the isotropic model of the porous electrode structure, it is expressed by Relation 26.

The effective conductivity of the metallic electrode, the pores of which are wetted with the molten electrolyte, is practically determined by the electrolyte effective conductivity. Therefore, the general assumption that $\kappa_M^{eff} \to \infty$ seems to be reasonable. In this case Equations 31, 33 and 34 become:

$$j_T = \left[2S\kappa_E^{eff} \int_{\eta_0}^{\eta_1} i(\eta) \, d\eta \right]^{1/2} \tag{35}$$

$$\eta_m = \eta_1 \tag{36}$$

$$xl(2S/\kappa_E^{eff})^{1/2} = \int_{\eta_0}^{\eta} \left[\int_{\eta_0}^{\eta'} i(\eta'') \, d\eta'' \right]^{-1/2} d\eta'. \tag{37}$$

The form of these three equations may be simplified by the approximation of the $i(\eta)$ function by a linear relationship:

$$\frac{\eta}{i} \equiv Z_F = \frac{RT}{2F} \left(\frac{1}{i_{H_2}^{lim}} + \frac{1}{|i_{CO_2}^{lim}|} + \frac{1}{|i_{H_2O}^{lim}|} + \frac{\nu}{i_0} \right). \tag{38}$$

By this approximation we get the following relationships:

For the total impedance of the electrode:

$$Z = (Q\kappa_E^{eff} \tanh Ql)^{-1}. \tag{39}$$

For the distribution of the overpotential in the electrode:

$$\eta(x) = \frac{j_T \cosh Qlx}{Q\kappa_E^{eff} \sinh Ql} \tag{40}$$

where

$$Q^2 = \frac{S}{Z_F\kappa_E^{eff}}. \tag{41}$$

3. Results and discussion

To test this model the dependence of the total current density on measured overpotential has been calculated for the MCFC anode. The approximation concerning κ_E^{eff} and κ_M^{eff} mentioned above has been used, whereas, in respect to the shape of the $i(\eta)$ function no assumptions have been made. This function has been calculated numerically on the basis of the physical parameters characterizing the electrode process: the exchange current density and the transfer coefficients according to the electrode reaction mechanism (ii), as well as the reagents properties: the diffusion coefficients and Henry's constants according to the experimental data [11]. All the calculations were carried out for the $Li_2CO_3 + K_2CO_3$ eutectic mixture as the electrolyte and for nickel as the electrode metal, at the temperature 923 K.

By using the appropriate transport equations one can choose amongst the different diffusion geometry conditions: spherical, cylindrical and planar diffusion. The planar approximation has been used because the ratio of the thickness of the electrolyte film in the pores and the pore radii is small, and the convexity or concavity of the electrode surface contribute only to a very small extent to the numerical results. On the other hand, one should remember that the electrode is composed of both concave and convex surfaces, the effect of which is compensated [12].

To calculate explicitly the MCFC anode polarization curves by the model proposed in this paper only one parameter remains unknown: the electrolyte film thickness δ. Therefore, this model requires only
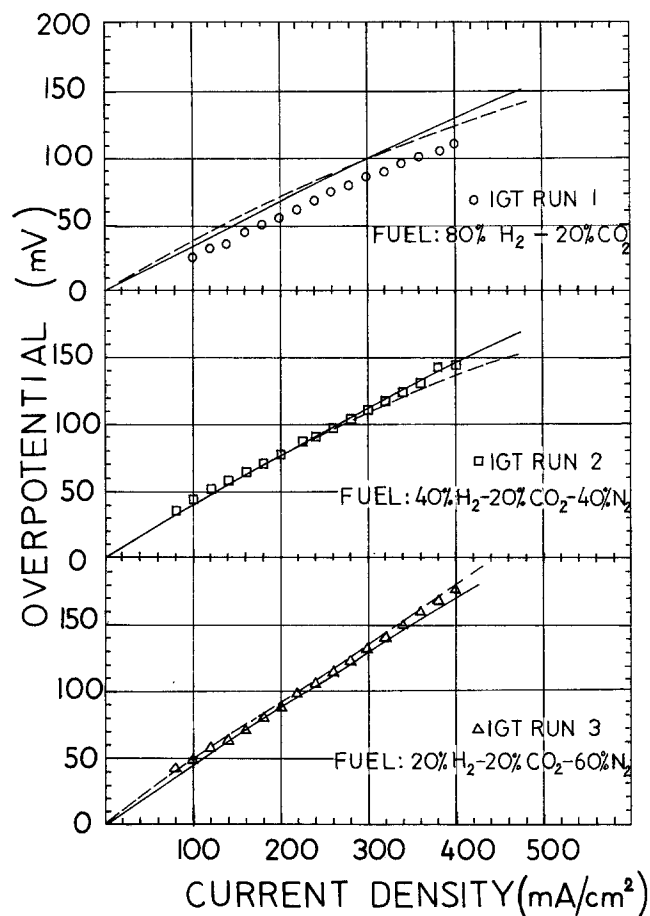
Fig. 2. Anodic polarization curves computed on the basis of the proposed model (continuous line) and Wilemski's *et al.* [3] model (broken line) compared with the IGT experimental data [4] for different fuel gas compositions. Oxidant composition: 30% CO_2, 15% O_2, 55% N_2.

one adjustable parameter unlike that of Wilemski's *et al.* anisotropic model which requires two such parameters [3]. The determination of the δ parameter is made by fitting the polarization curves calculated for different δ parameters to the experimental curve corresponding to the following C–H–O fuel composition: 40% H_2, 20% CO_2, 40% N_2. The δ value determined in this way was 0.057 μm and the polarization curve corresponding to this value is demonstrated in Fig. 2. The other two curves in this figure, corresponding to other C–H–O fuel compositions, have been calculated using this value. The agreement with the experimental data by the research team of the Institute of Gas Technology (IGT), Chicago [4] is better than that obtained by the two-adjustable parameters model of Wilemski *et al.* [3].

In Fig. 3 there are reported the distributions of the dimensionless Faradaic current density generated along the electrode. This diagram shows that practically all the current is generated in a thin layer of the electrode near to the electrode/electrolyte interface ($x = 1$ in Fig. 1). This conclusion seems to us to be practically important. The concept of the electrochemical reaction zone in the porous electrode, the so called 'penetration depth' is known in the literature concerning porous electrode for fuel cells [13]. This constituted the second adjustable parameter in the model by Wilemski *et al.* [3].

On the basis of the above calculations one can evaluate the validity of the approximated version of the model utilizing the assumption of the linearity of $i(\eta)$ function. In Fig. 4 this function has been calculated for three gas compositions and one can evaluate the range of overpotentials where this approximation can be used. By same approximation one can estimate the 'penetration depth' (*PD*) for a given electrode according to the definition:
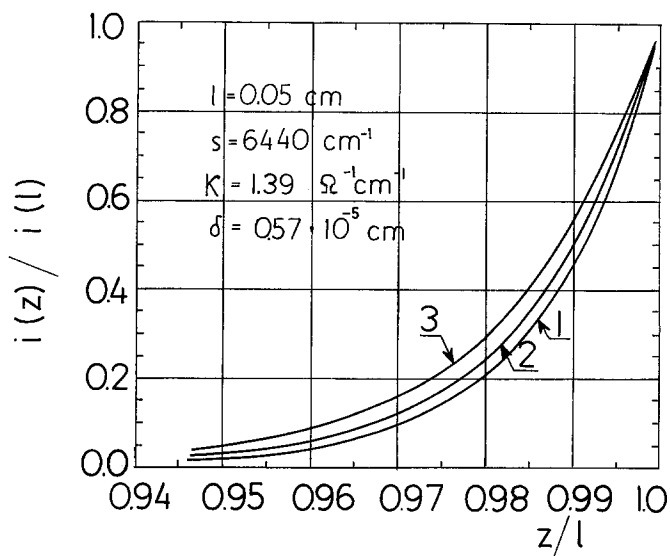
$$i(l-PD) = i(l)/e. \tag{42}$$

Fig. 3. Faradaic current density distribution along the porous anode, calculated for different gas compositions (see Fig. 4).

This parameter is:

$$PD = l - \frac{1}{Q} \text{arcosh} \left[\cosh (Ql)/e \right] \tag{43}$$

For $Ql \gg 1$: $PD \cong 1/Q$, $\eta_0 \cong 0$ and:

$$j_T \cong \left(2S\kappa_E^{\text{eff}} \int_0^{\eta_m} i(\eta) \, \mathrm{d}\eta \right)^{1/2} \tag{44}$$
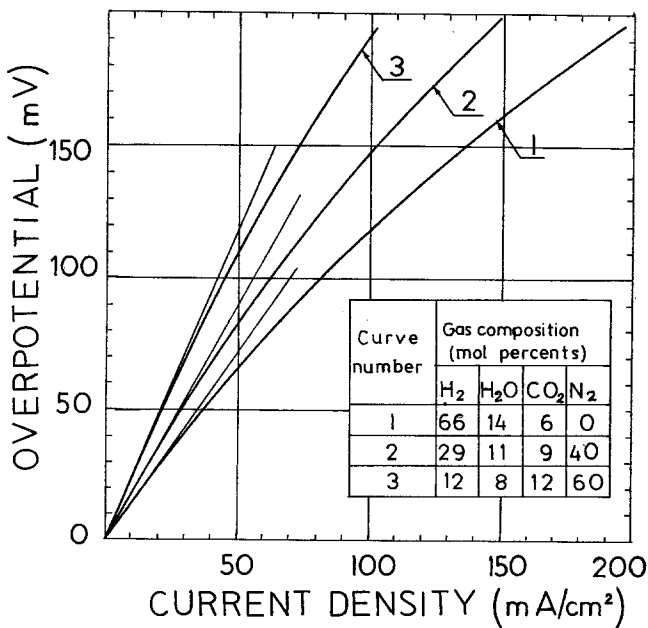
Acknowledgement

Fig. 4. Calculated $\eta(i)$ curves (thick lines) for different fuel compositions (equilibrated), thin lines – theoretical $\eta(i)$ slope at zero current.

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