JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 359–368

Macroscopic analysis of polarization characteristics of gas-diffusion electrodes in contact with liquid electrolytes
Part I: First order reactions*

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Received 29 April 1997; revised 25 June 1997

In this paper principles of gas–liquid chemical reaction engineering are applied to analyse the current–potential characteristics of gas-diffusion electrodes (GDE) in contact with liquid electrolytes. A macroscopic electrode model is formulated which accounts for mass transfer in the external diffusion films, in the gas layer and in the flooded layer. The set of model equations accounts for material balances, mass transport kinetics and Butler–Volmer polarization kinetics. Several dimensionless parameter groups are introduced which allow a compact reformulation of the proposed model. For first order reactions its solution can be derived analytically. The introduced parameter groups allow a classification of the different operating modes of a GDE, that is, slow reaction, fast reaction and instantaneous reaction.

Keywords: *gas diffusion electrodes*, *current–potential behaviour*, *liquid electrolyte*, *macroscopic model*, *first order reactions*

List of symbols

a	specific surface area ($\mathrm{m^{-1}}$)
$\mathrm{A_1}$	gaseous reactant
$\mathrm{A_2^{z2}}$	ionic reactant with charge number z_2
Bi_m^G	gas side Biot number
Bi_m^L	liquid side Biot number
c_1^L	molar liquid phase concentration of $\mathrm{A_1}$ ($\mathrm{mol\,m^{-3}}$)
c_1^Le	solubility of $\mathrm{A_1}$ in liquid electrolyte ($\mathrm{mol\,m^{-3}}$)
c_1^*	dimensionless concentration of $\mathrm{A_1}$
d	thickness of electrode (m)
$d^\mathrm{GL/FL}$	thickness of gas layer and flooded layer respectively (m)
d^*	dimensionless flooded layer thickness
D^*	ratio of mass transport resistances (gas layer/flooded layer)
$D_{\mathrm{eff},1}^{\mathrm{GL/FL}}$	effective diffusion coefficient of $\mathrm{A_1}$ in gas layer or flooded layer ($\mathrm{m^2\,s^{-1}}$)
$Đ_{\mathrm{eff},1}^{\mathrm{G/K}}$	effective gas phase diffusion coefficient of $\mathrm{A_1}$ for molecular (G) or Knudsen (K) transport
$Đ_1^{\mathrm{G/L}}$	gas or liquid phase molecular diffusion coefficient of $\mathrm{A_1}$
E	enhancement factor
F	Faraday's constant ($\mathrm{C\,mol^{-1}}$)
H_1	Henry's coefficient ($\mathrm{Pa\,m^3\,mol^{-1}}$)
Ha	Hatta number
$\widetilde{Ha}$	modified Hatta number (dependent on overpotential)
i_n	transfer current per unit of inner pore surface area ($\mathrm{A\,m^{-2}}$)
i_0	exchange current density ($\mathrm{A\,m^{-2}}$)
i_n^*	dimensionless transfer current density
i_lim	superficial limiting current density ($\mathrm{A\,m^{-2}}$)
$k_1^\mathrm{G/L}$	gas side or liquid side mass transfer coefficient of $\mathrm{A_1}$ ($\mathrm{m\,s^{-1}}$)
n	number of electrons transferred in electrode reaction
N_1	mass flux density of $\mathrm{A_1}$ ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
P	total operating pressure (Pa)
p_1^GB	partial pressure of $\mathrm{A_1}$ in gas bulk (Pa)
R	universal gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
R^layer	dimensionless mass transport resistance (layer = GF, GL, FL, LF)
T	temperature (K)
U	electrode potential (V)
U_0	equilibrium potential related to bulk phase conditions (V)
z	spacial coordinate (m)
z^*	dimensionless spacial coordinate

Greek letters

$\alpha_\mathrm{a}, \alpha_\mathrm{c}$	anodic, cathodic transfer coefficient
η^*	dimensionless total overpotential

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[*] Presented in part at the Fourth European Symposium on Electrochemical Engineering, Prague, 28–30 August 1996.

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0021-891X

ν_1	stoichiometric coefficient of A_1

Superscripts and subscripts

GB	gas bulk
GS	gas side external surface of GDE
GF	external gas film
GL	porous gas layer of GDE
I	gas–liquid interface
LB	liquid bulk
LS	liquid side external surface of GDE
LF	external liquid film
FL	flooded layer of GDE

1. Introduction

Gas-diffusion electrodes (GDE) are key devices in fuel cells and batteries. Recently they have also been increasingly applied to synthesis, sensors and separation processes. In Table 1 some gas consuming reactions of technical relevance are given in which GDEs were used successfully. It can be seen that GDEs have been applied for the production of electrical energy, as energy saving counter electrodes, for the production of substances and for gas purification. Depending on the application, GDEs are in contact with liquid or solid electrolytes. The present contribution is dedicated to GDEs operating in gas/liquid processes. This is motivated by the facts that GDEs are in contact with liquid electrolytes either in a number of technically relevant production processes, for example, oxygen reduction for hydrogen peroxide generation, or as a first step in a development towards a later solid electrolyte application, for example, hydrogen oxidation for PEM fuel cells.

Figure 1 shows a schematic sketch of a single pore of a GDE. There are three phases: the gas phase, where the reactant A_1 is present, the electrically conductive solid phase, which is often loaded or coated with catalytically active particles, and the liquid phase electrolyte solution.

The most important physicochemical processes taking place are as follows:

(i) The reactant A_1 is transported from the gas bulk (GB) to the external surface of the GDE via film diffusion.
(ii) The reactant diffuses through the porous gas layer (GL) to the gas–liquid interphase.
(iii) The reactant A_1 is dissolved at the gas–liquid interphase. In some cases solvent evaporation can occur.
(iv) The reactant A_1 is transported through the flooded layer (FL) via liquid phase diffusion.
(v) The ionic reactant A_2^{z2} is transferred from the liquid bulk (LB) to the external GDE surface by diffusion and migration. Due to electroneutrality condition the counterions A_3^{z3} are dragged along with the ions A_2^{z2}.
(vi) The ions A_2^{z2} and A_3^{z3} are transported by diffusion and migration through the flooded part of the pore.
(vii) At the wetted pore walls there takes place the electrochemical reaction A_1 and A_2^{z2} accompanied by electron charge transfer. In addition sorption processes and chemical reactions can be involved. The rate of these chemical reactions can be accelerated by catalysts.
(viii) The electrons are transported in the solid matrix by electrical conduction to or from the current collector.

The present analysis is restricted to one single reaction of (pseudo)first order with respect to A_1. The

Table 1. Some examples of gas consuming reactions that can be carried out at gas-diffusion electrodes

Arrows indicate desired directions of reactions

Anodic reactants$\longleftrightarrow$Cathodic reactants	*Electrolytes*	*Processes*	*References*
$H_2(g) \longrightarrow 2\ H^+(aq) + 2\ e^-$	solid polymers acid solutions	fuel cell, H_2-consuming counter anode, gas purification	[1–3]
$CH_3OH(g) + H_2O(g) \longrightarrow CO_2(1) + 6\ H^+(aq) + 6\ e^-$	solid polymers, acid solutions	vapour phase DMFC	[4, 5]
$H_2O(1) \longleftarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$	solid polymers, acid, alkaline solutions;	fuel cell, O_2-consuming counter cathode, gas purification	[6–8]
$H_2O_2(1) + OH^-(aq) \longleftarrow O_2(g) + 2\ H_2O(1) + 2\ e^-$	alkaline solutions	production of hydrogen peroxide	[9]
$HCOH(1) + H_2O(1) \longleftarrow CO_2(g) + 4\ H^+(aq) + 4e^-$	acid solutions	production of partial oxidized hydrocarbons	[10]
$2\ Cl^-(aq) \longleftarrow Cl_2(g) + 2\ e^-$	acid solutions	fuel cells, gas purification	[11, 12]

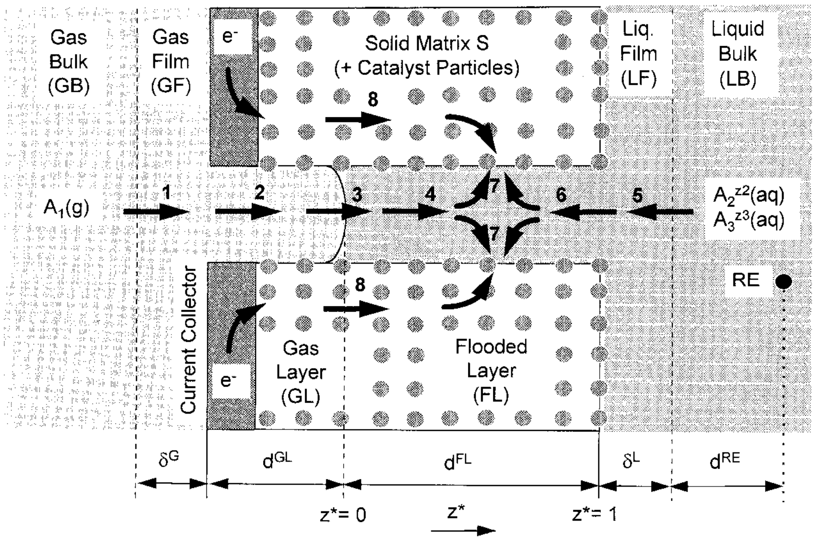

Fig. 1. One-dimensional, single pore model for the electrochemical reaction of a gaseous reactant A_1 with a liquid reactant A_2^{z2} in a GDE.

influence of the ionic reactant A_2^{z2} is considered in Part II of this contribution [12]. The components in the liquid electrolyte phase are assumed not to be evaporated. In addition we assume that the ohmic drops in the electrode matrix and the electrolyte solution are negligible.

2. Macroscopic model for gas–liquid reactions in GDE

Many models of different complexity have been proposed to describe the operating behaviour of GDEs. Some authors favoured a quasihomogeneous (macroscopic) approach [13–15], others a heterogeneous model [16–20]. The latter often require many adjustable parameters. Due to the limited accuracy of experimental data, some of the model parameters have little statistical significance. Therefore it is reasonable to follow Newman [21] and apply a macroscopic model in terms of volume-averaged quantities.

2.1. *Material balances*

In the four layers considered (i.e., gas film, gas layer, flooded layer and liquid film) the following mass balances of component A_1 are valid:
Gas film:

$$\frac{dN_1^{GF}}{dz} = 0 \quad \Rightarrow N_1^{GF} = \text{const.} \tag{1}$$

Gas layer:

$$\frac{dN_1^{GL}}{dz} = 0 \quad \Rightarrow N_1^{GL} = \text{const.} \tag{2}$$

Flooded layer:

$$\frac{dN_1^{FL}}{dz} = -\nu_1 \frac{ai_n}{nF} \quad \text{with} \quad \begin{matrix} N_1^{FL}(z=0) = N_1^{GL} \\ N_1^{FL}(z=d^{FL}) = N_1^{LF} \end{matrix} \tag{3a,b,c}$$

Liquid film:

$$\frac{dN_1^{LF}}{dz} = 0 \quad \Rightarrow N_1^{LF} = \text{const.} \tag{4}$$

The mass flux densities in the nonreactive layers are constant. In the flooded layer the mass flux varies according to the transfer current density per electrode ai_n. Depending on the reaction direction, the stoichiometric coefficient ν_1 is positive (anodic reactant) or negative (cathodic reactant).

2.2. *Mass transport*

The mass flux densities of the gaseous reactant, N_1, in the four layers are expressed by means of following linear transport laws:
Gas film:

$$N_1^{GF} = k_1^G \frac{(p_1^{GB} - p_1^{GS})}{RT} \quad \text{with} \quad k_1^G = \frac{\text{Đ}_1^G}{\delta^G} \tag{5}$$

Gas layer:

$$N_1^{GL} = \frac{D_{\text{eff},1}^{GL}}{d - d^{FL}} \frac{(p_1^{GS} - p_1^{I})}{RT} \tag{6a}$$

with

$$\frac{1}{D_{\text{eff},1}^{GL}} = \frac{1 - p_1^{GB}/p}{\text{Đ}_{\text{eff},1}^{G}} + \frac{1}{\text{Đ}_{\text{eff},1}^{K}} \tag{6b}$$

Flooded layer:

$$N_1^{FL} = -D_{\text{eff},1}^{FL} \frac{dc_1^L}{dz} \tag{7}$$

Liquid film:

$$N_1^{LF} = k_1^L \left(c_1^{LS} - c_1^{LB}\right) \quad \text{with} \quad k_1^L = \frac{\text{Đ}_1^L}{\delta^L} \tag{8}$$

In the stagnant gas film, the flooded layer and the stagnant liquid film the component A_1 is assumed to be transported via molecular diffusion. In the nonflooded gas layer of the porous electrode, besides molecular diffusion there can be a contribution of Knudsen diffusion. Both transport mechanisms can be lumped together by addition of the corresponding mass transport resistances, that is, the reciprocal diffusion coefficients $\text{Đ}_{\text{eff},1}^{G}$ and $\text{Đ}_{\text{eff},1}^{K}$. The gas and liquid film thicknesses δ^G and δ^L have to be determined from secured mass transfer correlations for the used electrochemical cell. For this purpose a cell with a well-defined flow field at both external surfaces of the GDE should be used. This can be achieved best in a horizontal cyclone flow cell [22].

2.3. *Reaction kinetics*

The local transfer current density related to the inner pore surface i_n is expressed by a Butler–Volmer type polarization equation which is of first order with respect to A_1:

$$i_n = i_0 \left(\exp\left\{ \frac{(n-\alpha_c)F}{RT}(U-U_0) \right\} - \exp\left\{ -\frac{\alpha_c F}{RT}(U-U_0) \right\} \frac{c_1^{L}}{c_1^{Le}(p_1^{GB})} \right) \tag{9}$$

Equation 9 is valid for electrochemical reduction of A_1, the corresponding oxidation can be formulated in analogous manner. The exchange current density, i_0, and the open circuit potential, U_0, are related to the liquid phase molar equilibrium concentration of A_1 under conditions of the gas bulk phase (i.e., $c_1^{Le}(p_1^{GB})$). This quantity is related to the partial pressure in the gas bulk by Henry's law:

$$p_1^{GB} = H_1 c_1^{Le}(p_1^{GB}) \tag{10}$$

2.4. *Introduction of dimensionless parameter groups*

The introduction of the dimensionless coordinate z^* and the dimensionless concentration c_1^*, that is,

$$z^* \equiv \frac{z}{d^{FL}} \tag{11}$$

$$c_1^* \equiv \frac{c_1^{L}}{c_1^{Le}(p_1^{GB})} \tag{12}$$

into the model equations yields a set of dimensionless numbers given in Table 2.

The most important of these numbers are the Hatta number, *Ha*, and the flooded layer thickness, d^*, which appear in the dimensionless mass balance for the flooded layer:

$$\frac{d^2 c_1^*}{dz^{*2}} = \nu_1 d^{*2} Ha^2 i_n^* \tag{13}$$

The local current density, i_n^*, can be expressed in terms of the total overpotential, η^*, as follows:

$$i_n^* = \exp\{\alpha_a \eta^*\} - \exp\{-\alpha_c \eta^*\} c_1^* \tag{14}$$

2.5. *Boundary conditions*

For the formulation of the two boundary conditions needed for the differential Equation 13, the continuity of mass fluxes between the layer interfaces, as expressed in Equation 3(b) and (c), must be accounted for. After rearrangement the following boundary conditions are obtained:

$$-\left.\frac{dc_1^*}{dz^*}\right|_{z^*=0} = \frac{1 - c_1^*(z^*=0)}{\frac{D^*}{Bi_m^G d^*} + \frac{D^*(1-d^*)}{d^*}} \tag{15a}$$

$$-\left.\frac{dc_1^*}{dz^*}\right|_{z^*=1} = Bi_m^L d^* \left(c_1^*(z^*=1) - c_1^{*LB} \right) \tag{15b}$$

The parameter group D^* in Equation 15(a) describes the ratio of pore diffusion velocities in the gas layer and in the flooded layer (see Table 2). The resistances in the gas and the liquid films at the outer electrode surface are considered by the Biot mass numbers Bi_m^G and Bi_m^L, respectively.

Table 2. Definition and interpretation of used dimensionless numbers

Number	*Definition*	*Interpretation*
Dimensionless total overpotential	$\eta^* \equiv \frac{U - U_0(p_1^{GB}, c_2^{LB})}{RT/F}$	$= \frac{\text{overpotential related to bulk conditions}}{25.7\,\text{mV}}$
Hatta number	$Ha \equiv d\sqrt{\frac{a i_0/(nF)}{D_{eff,1}^{FL} c_1^{Le}(p_1^{GB})}}$	$= \frac{\text{reaction rate under LB conditions}}{\text{pore diffusion of } A_1 \text{ in FL}}$
Dimensionless flooded layer thickness	$d^* \equiv \frac{d^{FL}}{d}$	$= \frac{\text{thickness of flooded layer}}{\text{thickness of electrode}}$
Ratio of mass transport resistances (GL/FL)	$D^* \equiv \frac{D_{eff,1}^{FL} c_1^{Le}(p_1^{GB})}{D_{eff,1}^{GL} p_1^{GB}/(RT)}$	$= \frac{\text{pore diffusion of } A_1 \text{ in FL}}{\text{pore diffusion of } A_1 \text{ in GL}}$
Biot number for gas side	$Bi_m^G \equiv \frac{k_1^{GF} d}{D_{eff,1}^{GL}}$	$= \frac{\text{mass transfer of } A_1 \text{ in GF}}{\text{pore diffusion of } A_1 \text{ in GL}}$
Biot number for liquid side	$Bi_m^L \equiv \frac{k_1^{LF} d}{D_{eff,1}^{FL}}$	$= \frac{\text{mass transfer of } A_1 \text{ in LF}}{\text{pore diffusion of } A_1 \text{ in FL}}$
Dimensionless liquid bulk concentration of A_1	$c_1^{*LB} \equiv \frac{c_1^{LB}}{c_1^{Le}(p_1^{GB})}$	$= \frac{\text{LB concentration of } A_1}{\text{equilibrium concentration of } A_1 \text{ at } p_1^{GB}}$
Dimensionless local current density	$i_n^* \equiv \frac{i_n}{i_0(p_1^{GB}, c_2^{LB})}$	$= \frac{\text{local current density on pore surface}}{\text{exchange current density}}$
Dimensionless total current density	$i^* \equiv \frac{\nu_1 i d^{GL}}{(nF) D_{eff,1}^{G} p_1^{GB}/(RT)}$	$= \frac{\text{total current density}}{\text{maximum limiting current density}}$

3. Polarization characteristics

The maximum limiting current $i_{\text{lim,max}}$ is achieved if only the gas layer resistance dominates the electrochemical conversion. This is calculated from

$$i_{\text{lim,max}} = (nF)\frac{D^{\text{GL}}_{\text{eff},1}}{d^{\text{GL}}}\frac{p_1^{\text{GB}}}{RT} \tag{16}$$

It is reasonable to use this quantity for the definition of a dimensionless current density, i^*, that has values in the range $0 < i^* < 1$:

$$i^* \equiv \frac{i}{i_{\text{lim,max}}} = i^*\left(\eta^*, Ha, n, \alpha_c, d^*, D^*, Bi_m^{\text{G}}, Bi_m^{\text{L}}, c_1^{*\text{LB}}\right) \tag{17}$$

From Equation 17 it can be seen that the shape of the current– potential characteristics is determined by the set of dimensionless numbers presented in Table 2 and, in addition, by the transfer coefficient, α_c, and the number of electrons transferred, n.

In Table 3 typical ranges for the values of these influence parameters are given. From the values of the Hatta number, Ha, it can be seen that slow, as well as fast, reactions are carried out with GDEs. The degree of flooding of a GDE can take values from nearly $d^* = 0$ to $d^* = 1$ depending on the electrode wettability. As expected, the values for D^*, that is, the ratio of mass transfer resistances in the gas layer and in the flooded layer, are very low according to the effective diffusion coefficients in the two layers. Moreover the solubility of gases in electrolyte solutions are low and of magnitude $c^{\text{Le}} = 1\,\text{mol}\,\text{m}^{-3}$. The Biot numbers on the gas side, Bi_m^{G}, typically are one decade below the liquid side numbers, Bi_m^{L}, because the gas film is significantly thicker than the corresponding film on the liquid side.

The total current density at a GDE can be calculated from the difference of the absorption rate of A_1 from the gas bulk and the leakage rate of A_1 to the liquid bulk. Therefore, the dimensionless total current density, i^*, is related to the difference in dimensionless concentration gradients at $z^* = 0$ and at $z^* = 1$:

$$i^* = D^*\frac{1-d^*}{d^*}\left(-\left.\frac{dc_1^*}{dz^*}\right|_{z^*=0} + \left.\frac{dc_1^*}{dz^*}\right|_{z^*=1}\right) \tag{18}$$

Table 3. Typical estimated values for the influence parameters of the polarization characteristics of a GDE for first order reaction

Number	*Symbol*	*Typical range (min, max)*
Dimensionless total overpotential	η^*	-10^2, $+10^2$
Hatta number	Ha	10^0, 10^4
Anodic and cathodic transfer coefficient	α_a, α_c	0.1, 2.0
Dimensionless flooded layer thickness	d^*	10^{-4}, 10^0
Ratio of mass transport resistances (GL/FL)	D^*	10^{-7}, 10^{-3}
Biot number for gas side	Bi_m^{G}	10^0, 10^2
Biot number for liquid side	Bi_m^{L}	10^1, 10^3
Dimensionless liquid bulk concentration of A_1	$c_1^{*\text{LB}}$	0.0, 1.0

3.1. *General analytical solution*

The combination of the mass balance, Equation 13, with the polarization Equation 14 yields a linear differential equation for the concentration profile $c_1^*(z^*)$. Its solution [23] is:

$$y(z^*) = \frac{y(z^*=1)\sinh\left(\widetilde{Ha}\,z^*\right)}{\sinh\left(\widetilde{Ha}\right)} + \frac{y(z^*=0)\sinh\left(\widetilde{Ha}(1-z^*)\right)}{\sinh\left(\widetilde{Ha}\right)} \tag{19}$$

with the transformed concentration

$$y(z^*) = c_1^*(z^*=1) - \exp(n\eta^*) \tag{20}$$

The shape of the concentration profile is influenced by the modified Hatta number

$$\widetilde{Ha} \equiv d^* Ha \exp\left(-\frac{\alpha_c}{2}\eta^*\right) \tag{21}$$

This important parameter group is a combination of the flooded layer thickness, d^*, the Hatta number, Ha, and the applied total overpotential, η^*.

From Equation 19 the absorption rate of A_1 (i.e., the concentration gradient at $z^* = 0$) and the leakage rate, (i.e., the concentration gradient at $z^* = 1$) are:

$$-\left.\frac{dc_1^*}{dz^*}\right|_{z^*=0} = E\left(\left(c_1^*(z^*=0) - \exp(n\eta^*)\right) - \frac{c_1^*(z^*=1) - \exp(n\eta^*)}{\cosh\widetilde{Ha}}\right) \tag{22a}$$

$$-\left.\frac{dc_1^*}{dz^*}\right|_{z^*=1} = E\left(\frac{c_1^*(z^*=0) - \exp(n\eta^*)}{\cosh\widetilde{Ha}} - \left(c_1^*(z^*=1) - \exp(n\eta^*)\right)\right) \tag{22b}$$

In both equations the enhancement factor E appears. This describes the acceleration of gas absorption by electrochemical reaction. For a first order reaction this is given by

$$E = \frac{\widetilde{Ha}}{\tanh\widetilde{Ha}} \tag{23}$$

The enhancement factor, E, is influenced by the overpotential, η^*, which enters the modified Hatta number in Equation 21. Therefore, the operator can adjust the operating regime of a GDE by changing the overpotential. With Equations 22(a) and (b) the total current density, i^*, (Equation 18) can be determined:

$$i^* = D^*\frac{1-d^*}{d^*}E\left(1 - \frac{1}{\cosh\widetilde{Ha}}\right)\left[c_1^*(z^*=0) + c_1^*(z^*=1) - 2\exp(n\eta^*)\right] \tag{24}$$

The unknown concentrations $c_1^*(z^*=0)$ and $c_1^*(z^*=0)$ are derived from the boundary conditions, Equations 15(a) and (b). These are given by the following expressions:

$$\frac{c_1^*(z^*=0)-\exp(n\eta^*)}{1-\exp(n\eta^*)} = \frac{R^{\mathrm{FL}}\left(R^{\mathrm{L}}\left(\frac{1}{\cosh\widetilde{Ha}}+1\right)+R^{\mathrm{FL}}\right)}{(R^{\mathrm{L}}+R^{\mathrm{FL}})(R^{\mathrm{G}}+R^{\mathrm{GL}}+R^{\mathrm{FL}})-\frac{R^{\mathrm{L}}(R^{\mathrm{G}}+R^{\mathrm{GL}})}{\left(\cosh\widetilde{Ha}\right)^2}} \tag{25}$$

$$\frac{c_1^*(z^*=1)-\exp(n\eta^*)}{c_1^{\mathrm{LB}*}-\exp(n\eta^*)} = \frac{R^{\mathrm{FL}}\left(\left(R^{\mathrm{G}}+R^{\mathrm{GL}}\right)\left(\frac{1}{\cosh\widetilde{Ha}}+1\right)+R^{\mathrm{FL}}\right)}{(R^{\mathrm{L}}+R^{\mathrm{FL}})(R^{\mathrm{G}}+R^{\mathrm{GL}}+R^{\mathrm{FL}})-\frac{R^{\mathrm{L}}(R^{\mathrm{G}}+R^{\mathrm{GL}})}{\left(\cosh\widetilde{Ha}\right)^2}} \tag{26}$$

Four dimensionless resistances, which dominate the performance of a GDE, are contained in Equations 25 and 26:

Resistance of gas film: $$R^{\mathrm{GF}} \equiv \frac{D^*}{d^*}\frac{1}{Bi_{\mathrm{m}}^{\mathrm{G}}} \tag{27}$$

Resistance of gas layer: $$R^{\mathrm{GL}} \equiv \frac{D^*}{d^*}(1-d^*) \tag{28}$$

Resistance of flooded layer: $$R^{\mathrm{FL}} \equiv \frac{1}{E} \tag{29}$$

Resistance of liquid film: $$R^{\mathrm{LF}} \equiv \frac{1}{d^*}\frac{1}{Bi_{\mathrm{m}}^{\mathrm{L}}} \tag{30}$$

In the following we discuss three operating modes: slow reaction, fast reaction and instantaneous reaction. In each cases, we assume no reactant A_1 to be present in the liquid bulk (i.e., $c_1^{\mathrm{LB}*}=0$). This corresponds to the desired operation under technical conditions.

3.2. *Operating modes*

3.2.1 Slow reaction. For modified Hatta numbers $\widetilde{Ha} < 0.3$ we have a slow electrochemical reaction compared to the mass transport in the flooded layer. For this case Fig. 2 illustrates the concentration profile of A_1 in a GDE.

For slow reaction the enhancement factor, E, can be approximated as follows:

$$E = \frac{\widetilde{Ha}}{\tanh\widetilde{Ha}} \approx 1+\frac{\widetilde{Ha}^2}{2} \Longrightarrow R^{\mathrm{FL}} \approx \frac{1}{1+\widetilde{Ha}^2/2} \tag{31}$$

Obviously the enhancement factor, E, has values slightly above unity. From Equation 29 it can be seen that the resistance of the flooded layer, R^{FL}, also has values near unity. If the gas sided transport resistances R^{G} and R^{GL} with R^{FL} are compared, for slow reactions we can conclude:

$$R^{\mathrm{G}}+R^{\mathrm{GL}} \ll R^{\mathrm{FL}} = \mathrm{O}(1)$$
$$\Longrightarrow \frac{D^*}{d^*}\left(\frac{1}{Bi_{\mathrm{m}}^{\mathrm{G}}}+(1-d^*)\right) \ll 1 \tag{32}$$

For most GDEs this condition is met, because D^* has quite low values (see Table 3). With the help of Equation 32 the general solution, Equations 24, 25 and 26, can be simplified to formulate an approximated solution for slow reactions:

$$i^* = D^*\frac{1-d^*}{d^*}\frac{\widetilde{Ha}^2}{2} \times \frac{\left(R^{\mathrm{L}}(4+\widetilde{Ha}^2)+2\right)1(1-\exp(n\eta^*))-2\exp(n\eta^*)}{R^{\mathrm{L}}(2+\widetilde{Ha}^2)+2} \tag{33}$$

$$\text{for } \widetilde{Ha} \equiv d^*Ha\exp\left(-\frac{\alpha_{\mathrm{c}}}{2}\eta^*\right) < 0.3$$

To analyse the dependence of current, i^*, on overpotential, η^*, we consider two limiting cases concerning R^{L}:

As $R^{\mathrm{L}} \to 0$:

$$i^* \approx D^*\frac{1-d^*}{d^*}\frac{\widetilde{Ha}^2}{2}(1-2\exp(n\eta^*)) \tag{34a}$$

As $R^{\mathrm{L}} \to \infty$:

$$i^* \approx D^*\frac{1-d^*}{d^*}\frac{\widetilde{Ha}^2}{2}\frac{4+\widetilde{Ha}^2}{2+\widetilde{Ha}^2}(1-\exp(n\eta^*)) \approx D^*\frac{1-d^*}{d^*}\widetilde{Ha}^2(1-\exp(n\eta^*)) \tag{34b}$$

In both cases the current density is proportional to the square of the modified Hatta number. The terms in brackets in Equations and 34(a) and (b) account

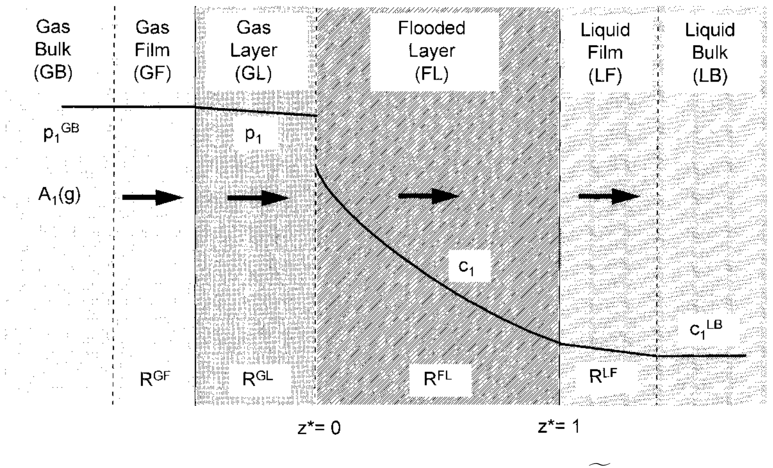

Fig. 2. Concentration profile of reactant A_1 in GDE for a slow electrochemical reaction ($\widetilde{Ha} < 0.3$).

for the backward reaction. These terms are of importance close to the electrochemical equilibrium (i.e., for $\eta^* \to 0$). Neglecting this, in the limiting case $R^{\mathrm{L}} \to 0$, the current density takes half the value observed in the limiting case $R^{\mathrm{L}} \to \infty$. This is due to the leakage effect of the reactant to the liquid bulk.

From Equations 34 we can express the current density, i (in dimensions), in terms of the electrode potential, U:

$$i \sim d^{\mathrm{FL}}(ai_{\mathrm{o}}) \exp\left(-\alpha_{\mathrm{c}} \frac{F}{RT}(U - U_0)\right) \tag{35}$$

It is evident that, for slow reactions, the current depends on the electrochemically active surface area, that is the product $d^{\mathrm{FL}}a$ and the exchange current density i_0. The dependence on electrode potential corresponds to the polarization kinetics, Equation 9.

3.2.2. Fast reaction. By increasing the overpotential $|\eta^*|$ we achieve a transition from a slow to a fast reaction. The concentration profile in Fig. 3 illustrates the fast reaction. The liquid film resistance R^{L} has no relevance, because the reactant A_1 is completely consumed inside the flooded layer and no leakage occurs. A fast reaction is characterized by Hatta numbers $\widetilde{Ha} > 3$ and in this case the enhancement factor can be approximated as follows:

$$E = \frac{\widetilde{Ha}}{\tanh \widetilde{Ha}} \approx \widetilde{Ha} \Longrightarrow R^{\mathrm{FL}} \approx \frac{1}{\widetilde{Ha}} \tag{36}$$

Now, the E values are significantly above unity, because the gas absorption is significantly enhanced by the electrochemical reaction. Therefore, the resistance of the flooded R^{FL} is dramatically reduced by the reaction. Starting from the general solution, Equations 24, 25 and 26, the total current density of fast reactions is approximated by

$$\begin{aligned} i &= D^* \frac{1 - d^*}{d^*} \frac{1}{R^{\mathrm{G}} + R^{\mathrm{GL}} + 1/\widetilde{Ha}} \\ &= \frac{1 - d^*}{\frac{1}{Bi_{\mathrm{m}}^{\mathrm{G}}} + (1 - d^*) + \frac{1}{D^* Ha \exp\left(-\frac{\alpha_{\mathrm{c}}}{2}\eta^*\right)}} \end{aligned} \tag{37}$$

for

$$\widetilde{Ha} \equiv d^* Ha \exp\left(-\frac{\alpha_{\mathrm{c}}}{2}\eta^*\right) > 3 \quad \text{and} \quad \exp(n\eta^*) \to 0$$

For moderately fast reactions, the resistances on the gas side R^{G} and R^{GL} are negligible in comparison to the flooded layer resistance R^{FL}. For these reactions the dimensionless current density is given by

$$i^* = D^* \frac{1 - d^*}{d^*} \widetilde{Ha} = D^*(1 - d^*) Ha \exp\left(-\frac{\alpha_{\mathrm{c}}}{2}\eta^*\right) \tag{38}$$

for

$$R^{\mathrm{G}} + R^{\mathrm{GL}} \ll R^{\mathrm{FL}} \Rightarrow \frac{D^*}{d^*}\left(\frac{1}{Bi_{\mathrm{m}}^{\mathrm{G}}} + (1 - d^*)\right) \ll \frac{1}{\widetilde{Ha}}$$

Based on Equation 38, the following dependence of the current density on the system parameters ensues:

$$i \sim \sqrt{D_{\mathrm{eff},1}^{\mathrm{FL}}(ai_0)} \exp\left(-\frac{\alpha_{\mathrm{c}}}{2} \frac{F}{RT}(U - U_0)\right) \tag{39}$$

According to Equation 39 for moderately fast reactions the current is influenced by the geometric average of two rate constants: that is, the exchange current density, i_0, and the effective diffusion coefficient in the flooded layer, $D_{\mathrm{eff},1}^{\mathrm{FL}}$. The dependence on the electrode potential is less distinct than for slow reactions. This is due to the halving of the transfer coefficient α_{c} in Equation 39. The flooded layer thickness, a^{FL}, has no influence according to the fact that even for moderately fast reactions, the component A_1 is completely depleted inside the flooded layer.

3.2.3. Instantaneous reaction. For very high modified Hatta numbers $\widetilde{Ha}$ there is a transition from a fast reaction to an instantaneous reaction. In this situation the reactant is totally consumed at the gas–liquid interface and its concentration there drops to zero. This is illustrated in Fig. 4.

The flooded layer resistance R^{FL} has no importance, because the gas component A_1 no longer enters the flooded layer. The resulting total current density,

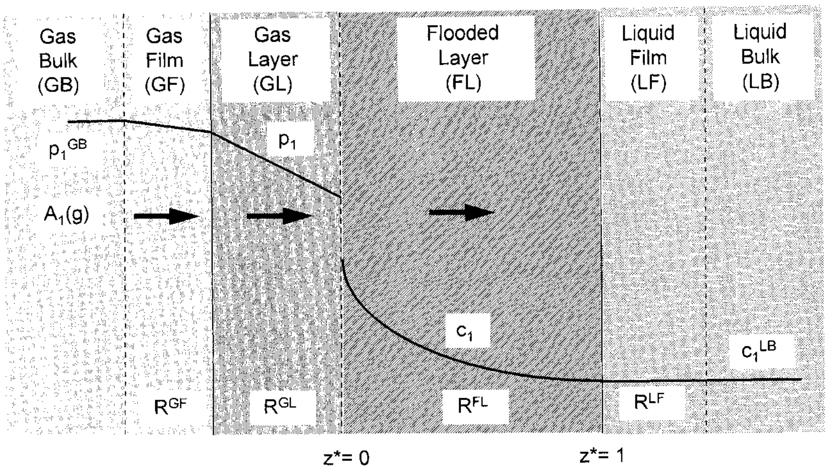

Fig. 3. Concentration profile of reactant A_1 in GDE for a fast electrochemical reaction ($\widetilde{Ha} > 3$).

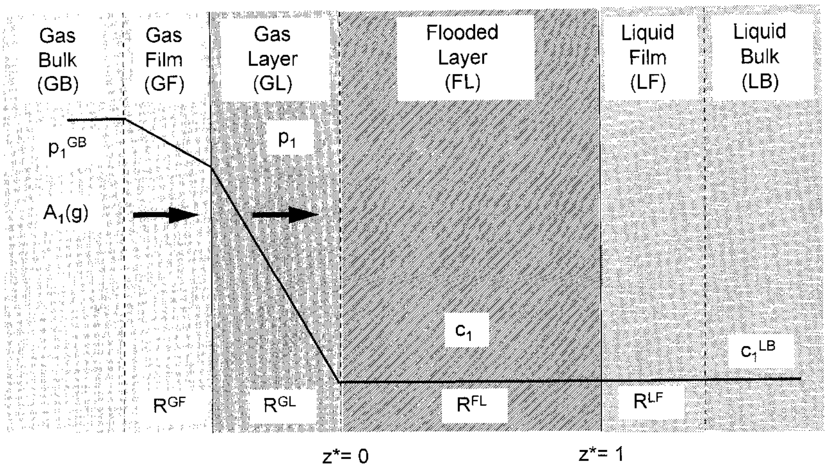

Fig. 4. Concentration profile of reactant A_1 in GDE for an electrochemical instantaneous reaction ($\widetilde{Ha} \to \infty$).

i^* achieves its maximum value, the limiting current density, $i^*_{\lim}$

$$i^* = i^*_{\lim} = D^* \frac{1-d^*}{d^*} \frac{1}{R^G + R^{GL}} = \frac{1-d^*}{\frac{1}{Bi^G_m} + (1-d^*)} \quad (40)$$

for

$$R^G + R^{GL} \gg R^{FL} \Rightarrow \frac{D^*}{d^*}\left(\frac{1}{Bi^G_m} + (1-d^*)\right) \gg \frac{1}{\widetilde{Ha}}$$

The maximum limiting current density is characterized by negligible gas film resistance, R^G, in comparison to the resistance that is exerted by the gas layer, R^{GL}:

$$i^* = i^*_{\lim,\max} = D^* \frac{1-d^*}{d^*} \frac{1}{R^{GL}} = 1 \quad (41)$$

for

$$R^G \ll R^{GL}, \quad R^{GL} \gg R^{FL} \Rightarrow Bi^G_m \gg \frac{1}{1-d^*};$$

$$\frac{D^*}{d^*}(1-d^*) \gg \frac{1}{\widetilde{Ha}}$$

4. Discussion and conclusions

Figure 5 shows a simulated dimensionless polarization curve of a GDE for a typical set of parameters. Increasing the overpotential, the reaction rate is more and more accelerated and we have a transition from a slow reaction to fast reaction and finally to an instantaneous reaction.

The kinetic parameters of the electrochemical reaction can be determined from a plot of the logarithm of the ratio $i^*/(1-d^*)$ against the applied overpotential. This term does not depend on the unknown flooded layer thickness, d^{FL}, and therefore can be determined directly from experimental data. From Fig. 6 a linear dependence in the region of moderately fast reaction is evident. This is in agreement with Equation 38 which can be expressed in logarithmic form:

$$\ln \frac{i^*}{1-d^*} = \ln(D^* Ha) - \frac{\alpha_c}{2}\eta^* \quad (42)$$

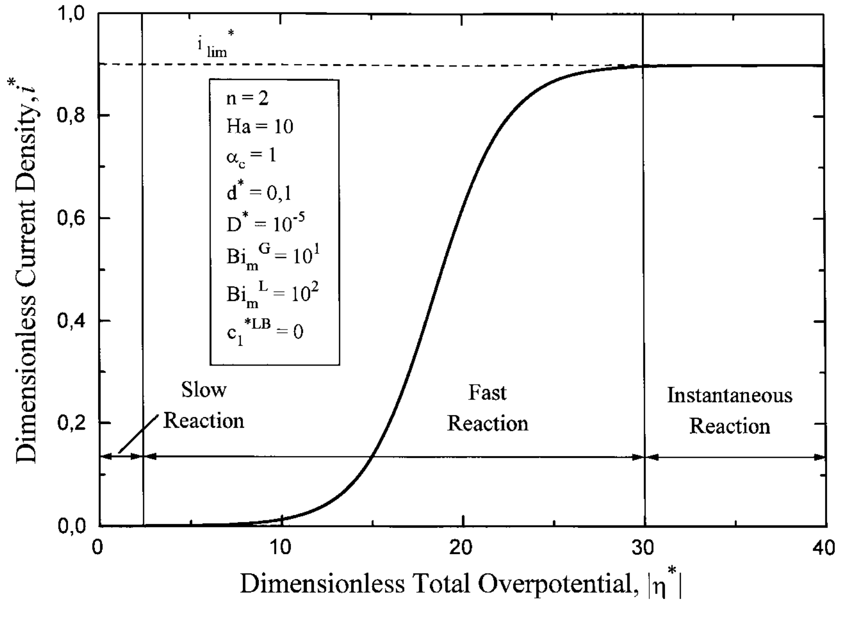

Fig. 5. Simulated polarization curve of a GDE for an electrochemical reduction of first order: $v_1 A_1(g) + ne^- + \ldots \to$ products.

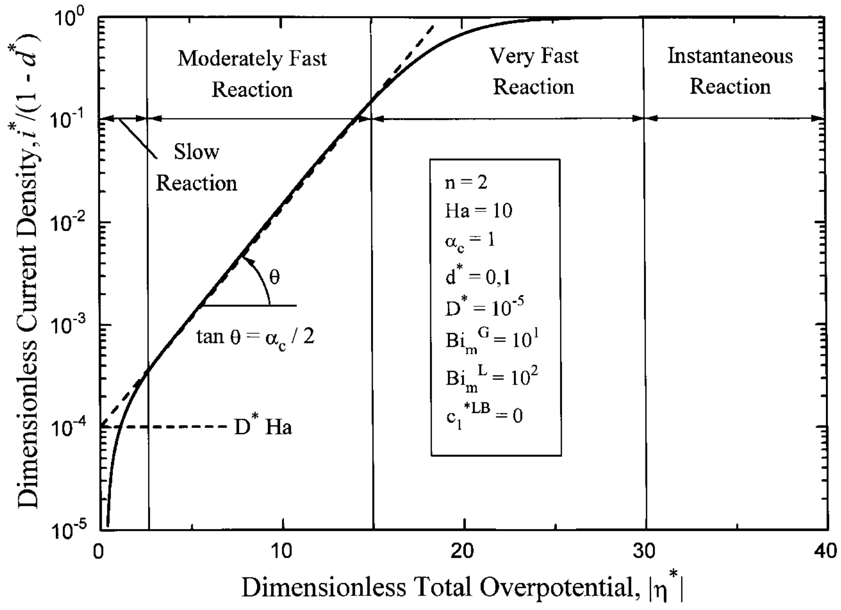

Fig. 6. Determination of cathodic transferr coefficient, α_c and Hatta number, *Ha*, from the current–potential characteristics of a GDE for a first order reaction: $\nu_1 A_1(g) + ne^- + \ldots \rightarrow$ products.

Thus, the transfer coefficient, α_c, can be determined from the slope of the curve and the intersection of the dashed approximation line with the ordinate yields the group D^*Ha. The parameter D^* can be estimated from component properties and therefore we obtain the Hatta number *Ha*. From the Hatta number the volume based exchange current density (ai_o) can be extracted.

To determine the essential mass transport parameter, the gas side pore diffusion coefficient, $D^{GL}_{\mathrm{eff},1}$, measurements in the mode of instantaneous reaction must be carried out. At high overpotentials we obtain the limiting current i^*_{lim}. According to Equation 40 this depends on the gas Biot mass number, Bi^{G}_{m}, and on the flooded layer thickness, d^*. If d^* is known, it is possible to calculate the Biot number and from this the pore diffusion coefficient, $D^{GL}_{\mathrm{eff},1}$, of the reactant A_1. This requires an experimental cell where a well defined gas film mass transfer coefficient, k^{GF}_1 can be adjusted. The unknown parameter d^* can be found from measurements in the region of slow reaction, that is, at low overpotentials. At higher overpotentials the modified current density, $i^*/(1-d^*)$, is independent on d^*, and in the region of instantaneous reaction this parameter group shows only a weak dependence on d^*. In the case that the degree of flooding cannot be determined exactly, it is advised to start with $d^* \rightarrow 0$. This is reasonable because GDEs are very often weakly wetted by the electrolyte solution. In many cases this is a precondition to run successfully GDE-based electrochemical reactors in

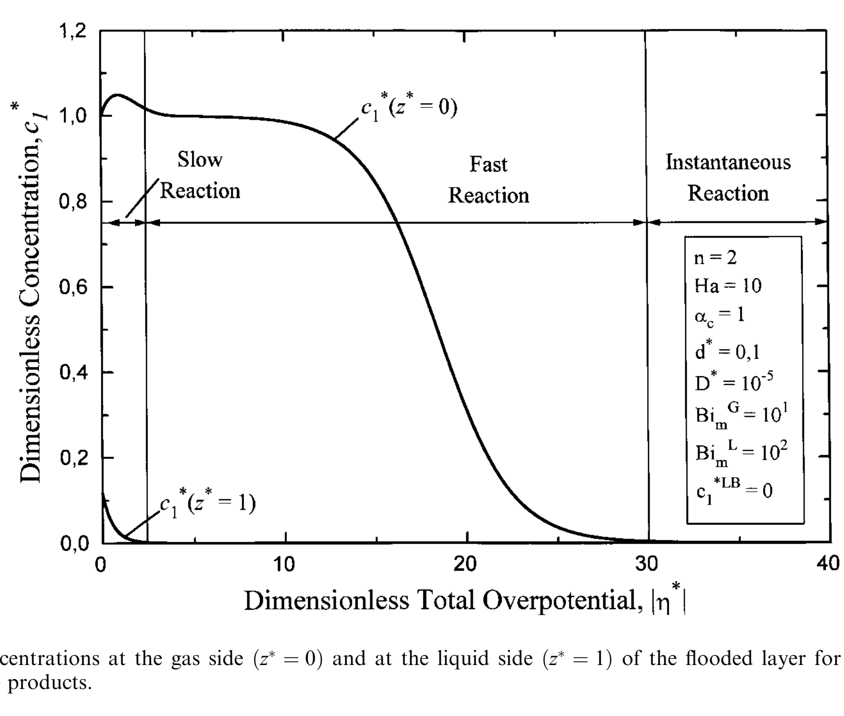

Fig. 7. Simulated concentrations at the gas side $(z^* = 0)$ and at the liquid side $(z^* = 1)$ of the flooded layer for a first order reaction: $\nu_1 A_1(g) + ne^- + \ldots \rightarrow$ products.

order to avoid flooding of the gas compartment. The liquid side Biot number, $Bi_{\mathrm{m}}^{\mathrm{L}}$, is only of importance for slow reactions. However, in practical applications mostly fast or instantaneous reactions are used, so that there is nearly no significant influence of $Bi_{\mathrm{m}}^{\mathrm{L}}$.

Surprisingly at low overpotentials there can be $c_1^*(z^* = 0) > 1$ (see Fig. 7). For the interpretation of this phenomenon one has to keep in mind that the cathodic reaction depends on the overpotential, η^*, and the concentration, c_1^*, whereas the anodic reaction only depends on the overpotential. Due to the fact that no A_1 is assumed to be present in the liquid bulk, the anodic backward reaction becomes dominant at low overpotentials and forms A_1. This material leaves the GDE preferably at the gas side.

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