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# Concentration polarisation in heterogeneous electrochemical reactions: a consistent kinetic evaluation and its application to molten carbonate fuel cells

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**Abstract**

Aim of this work is to focus attention on how the concentration polarization, in all electrochemistry applications, is often formulated on the basis of only thermodynamic statements and how it should be written in a kinetic more consistent expression. Moreover, the application of this study to the analysis of molten carbonate fuel cell (MCFC) behaviour has been discussed with reference to diffusion limited operating conditions.
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*Keywords:* Concentration polarisation; Limit current; Molten carbonate fuel cell

## 1. Introduction

The study of polarisation losses in electrode kinetics is one of the main subjects of electrochemistry and of major interest today considering the ever-increasing worldwide interest in many practical applications of electrochemistry, such as fuel cells.

The irreversibilities occurring in an electrode reaction are usually summarised in three polarisation losses to be deducted from the ideal Nernst potential: activation polarization, ohmic polarization, and concentration polarization [1].

Activation and ohmic polarisation can be expressed by theoretical, semi-empirical or empirical equations which depend on materials, temperature, pressure and gas composition [2].

Concentration polarisation is very important when the electrode is working at high current densities and it is related to transport phenomena of each gaseous reactant in the complex structure of the electrodes (diffusion, solution, adsorption, etc.). The literature usually explains this voltage decay by means of thermodynamic considerations [1,3,4].

However, it is worth recalling that only ideal or maximum efficiency depends on electrochemical thermodynamics, whereas the effective efficiency depends on electrode kinetics.

By correctly taking thermodynamic constraints into account in a kinetic analysis in this work, we wish to put in evidence the connection between a consistent concentration polarisation expression and the usual thermodynamic formulation.

## 2. Concentration polarisation on the basis of thermodynamic statements

In the following we introduce, with a formulation of wide validity, the thermodynamic concentration polarisation ($\Delta E_{TC}$) usually used without details in literature [1,3,4].

We will refer to a generic heterogeneous electrochemical reaction

$$\sum \nu_i M_i^{z_i} + \nu_e e^- = 0 \tag{1}$$

where the species $M_i$ migrates to or from the electrodes.

On the bases of the difference of Nernst voltage when the electrochemical reaction occurs (that is at electrode surface concentration $c_{is}$) and when no current is supplied (that is at bulk concentration $c_{ib}$), the thermodynamic voltage decay due to reactant transport phenomena can be written as follows:

$$\Delta E_{TC} = E_s - E_b = \frac{RT}{\nu_e F} \sum \nu_i \ln\left(\frac{c_{is}}{c_{ib}}\right) \tag{2}$$

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**Nomenclature**

| | |
|---|---|
| $c_i$ | reactant concentration of the component $i$ (mol m$^{-3}$) |
| $e^-$ | electron |
| $E$ | voltage (V) |
| $\Delta E$ | polarisation (V) |
| $F$ | Faraday's constant (A s mol$^{-1}$) |
| $J$ | current density (A m$^{-2}$) |
| $k'$ and $k''$ | kinetic constants (A m mol$^{-1}$) |
| $K_C$ | mass transport coefficient (m s$^{-1}$) |
| $K_e$ | thermodynamic equilibrium constant |
| $M_i$ | chemical component |
| $R$ | gas constant (J mol$^{-1}$ K$^{-1}$) |
| $s$ | real positive number in Eq. (14) |
| $T$ | temperature (K) |
| $z_i$ | charge of the component $i$ |

*Greek letters*

| | |
|---|---|
| $\alpha_e$ and $\beta_e$ | reaction rate orders related to $e^-$ transfer coefficients |
| $\alpha_i$ and $\beta_i$ | reaction rate orders related to the component $i$ |
| $\gamma$ | thermodynamic consistency parameter in Eq. (14) |
| $\eta$ | dimensionless polarisation |
| $\nu_e$ | stoichiometric coefficient of $e^-$ |
| $\nu_i$ | stoichiometric coefficient of component $i$ |

*Subscripts*

| | |
|---|---|
| an | anodic |
| act | related to reaction activation |
| $b$ | bulk |
| cat | cathodic |
| $C$ | related to concentration polarisation |
| s | electrode surface |
| 0 | reference |
| $L$ | limiting value |
| $T$ | thermodynamic |
| ohm | related to ohmic resistance |
| TOT | total |

Moreover, the fraction $c_{is}/c_{ib}$ can be expressed by means of a variable with more direct physical meaning and easier experimental evaluation: the local limit current density $J_L$, that is the maximum current reachable when the limiting reactant concentration on the electrode surface approaches zero.

In fact, on the basis of Faraday and Fick's laws, the following equation can be derived for current density [5]:

$$J = FK_{Ci}\frac{\nu_e}{\nu_i}(c_{ib} - c_{is}) \tag{3}$$

where $K_{Ci}$ is the mass transport coefficient.

The limiting current density $J_L$ imposed by reactant $i$ corresponds to $c_{is} = 0$ and so it is

$$J_{Li} = FK_{Ci}\frac{\nu_e}{\nu_i}c_{ib} \tag{4}$$

Inserting Eq. (4) in Eq. (3), it is possible to determine $c_{is}/c_{ib}$ as a function of $J_{Li}$

$$\frac{c_{is}}{c_{ib}} = 1 - \frac{J}{J_{Li}} \tag{5}$$

and so the concentration polarisation can be written as

$$\Delta E_{TC} = \frac{RT}{\nu_e F}\sum \nu_i \ln\left(1 - \frac{J}{J_{Li}}\right) \tag{6}$$

Moreover, the limiting effects of only one reactant ($i = L$) will be significant in comparison to the other ones, so, in dimensionless form, we can write

$$\eta_{TC} = \frac{\Delta E_{TC}F}{RT} \cong \frac{\nu_L}{\nu_e}\ln\left(1 - \frac{J}{J_L}\right) \tag{7}$$

with $J_L$ equal to the minimum among the $J_{Li}$.

However, this approach is not a completely coherent combination of thermodynamic and kinetic statements. In fact, $\Delta E_{TC}$ is a purely thermodynamic parameter here, just like $E_b$, whereas we should be interested in a non-equilibrium configuration at $J \neq 0$.

## 3. Concentration polarisation on the basis of kinetic statements

The Butler–Volmer expression for current density, usually used in studying electrochemical reactions [6–8], is here used as starting point in order to deduce the concentration polarisation directly from kinetic statements and not only thermodynamic ones. So, we assume [9]

$$J = J_{0b}\left[\prod\left(\frac{c_{is}}{c_{ib}}\right)^{\alpha_i} e^{\alpha_e \eta} - \prod\left(\frac{c_{is}}{c_{ib}}\right)^{\beta_i} e^{\beta_e \eta}\right] \tag{8}$$

where the exchange current $J_{0b}$ is

$$J_{0b} = k'\prod_i c_{ib}^{\alpha_i} e^{\alpha_e E_b F/RT} = k''\prod_i c_{ib}^{\beta_i} e^{-\beta_e E_b F/RT} \tag{9}$$

and assuming $\eta = (E_s - E_b)F/RT$.

At $J = 0$ the following thermodynamic consistency constraints can be obtained

$$\frac{\beta_i - \alpha_i}{\nu_i} = \frac{\beta_e + \alpha_e}{\nu_e} = s \tag{10}$$

$$\frac{k'}{k''} = K_e^s = \prod c_{ib}^{\nu_i s} e^{-\nu_e s E_b F/RT} \tag{11}$$

where $s$ is a real positive number. Eqs. (10) and (11) are a straightforward generalisation of electrochemical reactions of similar statements of common use in chemical kinetics, where the difference in the sign for $\alpha_e$ in Eq. (10) is due to the opposite direction of the chemical specie $e^-$ and conventional electrical current.

Moreover, $J_{0b}$ is dependent on the bulk concentration $c_{ib}$ according to Eqs. (9) and (11)

$$J_{0b} = k^* \prod c_{ib}^{\gamma_i} \tag{12}$$

with

$$k^* = k' k_e^{-\alpha_e/\nu_e} \tag{13}$$

and

$$\gamma_i = \alpha_i + \frac{\nu_i \alpha_e}{\nu_e} \tag{14}$$

The consistency Eqs. (10)–(14) highlight the number of degrees of freedom of the kinetic parameters; when the dependence of the current on concentrations is known (namely $k^*$ and $\gamma_i$), together with stoichiometry, the knowledge of other two parameters is sufficient for the determination of the number $s$ and of all the orders of reaction left.

In particular, it is worth noting that the usual position $s = 1$ is consistent with only one possible stoichiometric choice.

Now, taking into account Eqs. (6), (10) and (12) the electrochemical kinetic can be expressed as

$$J = J_{0b} \prod \left(1 - \frac{J}{J_{Li}}\right)^{\alpha_i} e^{\alpha_e \eta} \left[1 - \prod \left(1 - \frac{J}{J_{Li}}\right)^{\nu_i s} e^{-\nu_e s \eta}\right] \tag{15}$$

A comparison between kinetic dimensionless polarisation ($\eta$) from Eq. (15) and the thermodynamic concentration polarisation ($\eta_{TC}$) as defined by Eq. (7) can be obtained by considering only the actual contribution of limiting reactant $L$ and then eliminating the current density $J$.

In particular, after some manipulation we obtain

$$J_L(1 - e^{\nu_e \eta_{TC}/\nu_L})\, e^{-\nu_e \eta_{TC} \gamma_L/\nu_L} = J_{0b}\, e^{\alpha_e(\eta - \eta_{TC})} \left[1 - e^{-\nu_e s(\eta - \eta_{TC})}\right] \tag{16}$$

with $J_L$ equal to the minimum among the $J_{Li}$.

Studying this equation, we can observe that $\eta$, involving all the irreversibilities, is higher than $\eta_{TC}$, which is related to the only reactant diffusion.

In particular, the linear contribution when $\eta \to 0$ is

$$\eta \cong \left(1 - \frac{J_L}{J_{0b} s \nu_L}\right) \eta_{TC} > \eta_{TC}, \quad \nu_L < 0 \tag{17}$$

More interesting is the value of polarisation when diffusion phenomena are rate determining, that is when the electrode is working near limiting conditions with $\eta \to \infty$. In this case the value of $\eta$ identifies the concentration polarisation $\eta_C$ consistent with kinetic statements and is

$$\eta \cong \eta_C \cong \frac{1}{\alpha_e} \ln\left(\frac{J_L}{J_{0b}}\right) + \eta_{TC}\left(1 - \frac{\nu_e \gamma_L}{\alpha_e \nu_L}\right) \cong -\eta_{TC} \frac{\nu_e \alpha_L}{\alpha_e \nu_L} \tag{18}$$

so a difference between $\eta_C$ and $\eta_{TC}$ remains when $\gamma_L \neq 0$, that is $\alpha_L/\alpha_e \neq -\nu_L/\nu_e$.

In the light of these considerations, the concentration polarisation has to be written

$$\Delta E_C \cong -\frac{\alpha_L}{\alpha_e} \frac{RT}{F} \ln\left(1 - \frac{J}{J_L}\right) \tag{19}$$

and is a function not only of $J/J_L$, but also of the coefficients $\alpha_e$ and $\alpha_L$, which are not known a priori like the stoichiometric coefficients $\nu_e$ and $\nu_L$.

Fortunately, on the condition that the limiting current is well determined, the difference between thermodynamic and kinetic formulations

$$\frac{\eta_C - \eta_{TC}}{\eta_{TC}} = \frac{\Delta E_C - \Delta E_{TC}}{\Delta E_{TC}} = -\frac{\alpha_L \nu_e}{\alpha_e \nu_L} - 1 = -\frac{\gamma_L \nu_e}{\alpha_e \nu_L} \tag{20}$$

is not very important. Also when $\gamma_L$ is significantly different from zero, the consistent kinetic polarisation and thermodynamic one show differences in the $V/J$ performance curve only concerning the shape of the "knee" in the transition from linear behaviour to limit current.

## 4. Application to molten carbonate fuel cells

The definition of fuel cell performance is a key point in the development of these electrochemical devices and, even if fuel cells are usually said to be working at current density much lower than the limiting one, the operative purpose of maximising the fuel utilisation factor approaches the diffusion region, so that the cells work under apparently safe conditions, but with possible local running in diffusion limit conditions [10,11].

This has been shown for example in the case of molten carbonate fuel cells (MCFCs), demonstrating the importance of a correct evaluation of concentration polarisation, that we will discuss below.

In MCFCs the electrochemical reactions are the following:

$$H_2 + CO_3^{2-} \to H_2O + CO_2 + 2e^- \quad \text{anode} \tag{21}$$

$$CO_2 + \tfrac{1}{2}O_2 + 2e^- \to CO_3^{2-} \quad \text{cathode} \tag{22}$$

Gaseous reactants are then anodic $H_2$ and cathodic $CO_2$ and $O_2$. Each of these has to pass through the entire complex electrode structure to reach the reaction site and this contributes to concentration polarisation.

In Fig. 1 a simplified scheme is presented for a reference planar MCFC. In this picture main gas flow and local transport phenomena directions are shown: concentration polarisation effects will have to be calculated for each particular position along the cell channels.

In particular, if the cell voltage $V$ is locally written as

$$V = E_{s_{cat}} - E_{s_{an}} = (E_{b_{cat}} + \Delta E_{act_{cat}} + \Delta E_{ohm_{cat}} + \Delta E_{C_{cat}}) - (E_{b_{an}} + \Delta E_{act_{an}} + \Delta E_{ohm_{an}} + \Delta E_{C_{an}}) \tag{23}$$

we obtain $\Delta E_{C_{TOT}} = \Delta E_{C_{cat}} - \Delta E_{C_{an}}$ with $\Delta E_{C_{cat}} < 0$ and $\Delta E_{C_{an}} > 0$.

The concentration polarisation can be written simply as an algebraic sum of terms

$$\Delta E_{C_{TOT}} = -\frac{RT}{F}\left[\frac{\alpha_{CO_2}}{\alpha_{e_{cat}}} \ln\left(1 - \frac{J}{J_{LCO_2}}\right) + \frac{\alpha_{O_2}}{\alpha_{e_{cat}}} \ln\left(1 - \frac{J}{J_{LO_2}}\right) - \frac{\alpha_{H_2}}{\alpha_{e_{an}}} \ln\left(1 - \frac{J}{J_{LH_2}}\right)\right] \tag{24}$$

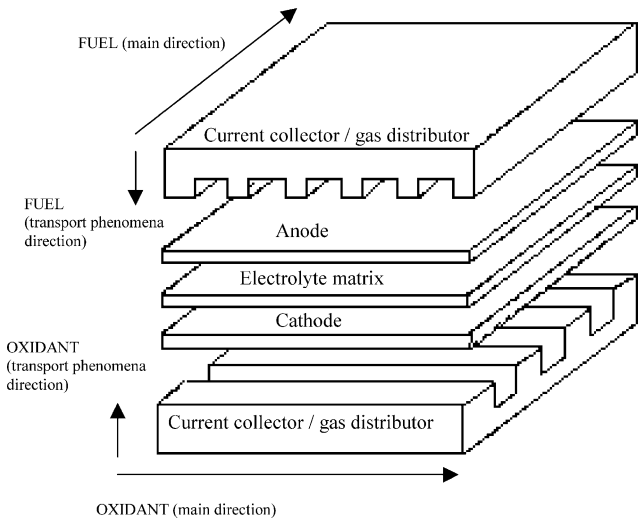


Fig. 1. Simplified scheme of a reference planar MCFC.

where $J_{LH_2}$ is related to anodic reaction, while both $J_{LCO_2}$ and $J_{LO_2}$ to the cathodic one, so that the higher among these last will result negligible as a function of the operating conditions.

Now, evaluation of $\Delta E_{C_{TOT}}$ required the knowledge of the reaction orders as well as the $\alpha_{ean}$ and $\alpha_{ecat}$ coefficients, while all these data are neglected in the purely thermodynamic analysis.

However, experimental data collected from the authors on single and stacked cells operating in the pressure range 1–3.5 atm show that anodic $H_2$ and cathodic $CO_2$ concentrations strongly affect thermodynamic voltage in accordance with Nernst prediction, but do not affect performance curve slope [2,10]. So, if we assume empirical kinetics independent of the concentrations of $H_2$ and $CO_2$, we can write $\gamma_{H_2} = \gamma_{CO_2} = 0$. This statement means that the order of reactions can be assumed equal to the opposite of stoichiometric coefficients.

On the contrary, the earlier mentioned tests [2,10] showed empirical kinetics depending on the concentration of $O_2$ according to an exponent $\gamma_{O_2} = 0.67$.Then, remembering that $v_{ean} = 2$, $v_{ecat} = -2$, $v_{O_2} = -0.5$ and $v_{H_2} = v_{CO_2} = -1$, we can write

$$\Delta E_{C_{TOT}} = \frac{RT}{F}\left[\frac{1}{2}\ln\left(1-\frac{J}{J_{LCO_2}}\right) + \left(\frac{1}{4}+\frac{\gamma_{O_2}}{\alpha_{e_{cat}}}\right) \times \ln\left(1-\frac{J}{J_{LO_2}}\right) + \frac{1}{2}\ln\left(1-\frac{J}{J_{LH_2}}\right)\right] \quad (25)$$

So, the evaluation of concentration polarisation should also need the knowledge of the $\alpha_{ecat}$ coefficient. This is usually considered to be equal to 1, on the basis of the current assumptions $s = 1$ and $\alpha_e = \beta_e$ (some authors maintaining $s = 1$ distinguish $\alpha_e$ from $\beta_e$ [6]). Nevertheless, an expression of concentration polarisation different from the thermodynamic one is always obtained.

However, generally $O_2$ diffusion effects are negligible: MCFCs always work with air fed in large excess to the cathode, that is under conditions in which the density current $J$ is much lower than the limiting current due to oxygen transport phenomena. So, the second term of Eq. (25) can be neglected and the concentration polarisation deduced from the thermodynamic demonstration is acceptable, but only on the basis of certain conditions.

On the basis of these considerations, the following concentration polarisation equation:

$$\Delta E_{C_{TOT}} = \frac{RT}{2F}\left[\ln\left(1-\frac{J}{J_{LH_2}}\right) + \ln\left(1-\frac{J}{J_{LCO_2}}\right)\right] \quad (26)$$

seems to be useful for MCFC study.

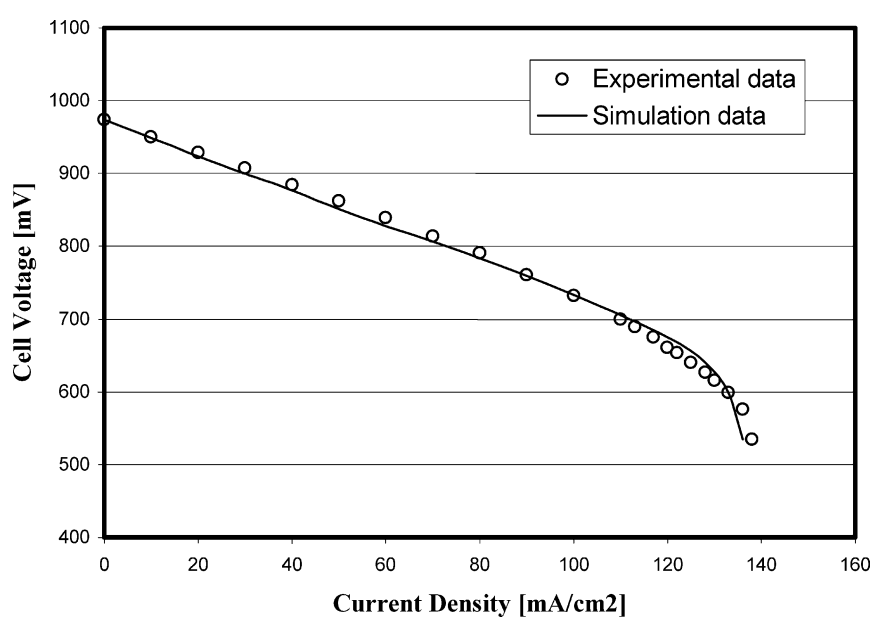


Fig. 2. Comparison between MCFC experimental and simulation data.

So, in order to verify this assumption, the Eq. (26) has been integrated into a detailed MCFC model [2] which allows the evaluation of global MCFC performance thanks to local balances of mass, energy and momentum.

Fig. 2 shows an example of the very satisfactory agreement obtained between simulation results and experimental data collected on a laboratory single cell of Ansaldo fuel cells (anode: $CO_2$ $1.4 \times 10^{-5}$ mol/s, $H_2$ $5.7 \times 10^{-5}$ mol/s, $H_2O$ $2.3 \times 10^{-5}$ mol/s, $N_2$ $16.6 \times 10^{-5}$ mol/s; cathode: $CO_2$ $14.3 \times 10^{-5}$ mol/s, $N_2$ $125 \times 10^{-5}$ mol/s, $O_2$ $15.1 \times 10^{-5}$ mol/s). Other examples at different operating conditions are available in [11].

## 5. Conclusions

Literature usually presents a concentration polarisation expression derived only from thermodynamic considerations.

In this paper, we have proposed a more general expression taking account of the thermodynamic constraints in a kinetic analysis. The difference between the two approaches can be particularly evident when limiting operating conditions are considered and reaction orders are not equal to stoichiometric coefficients.

On the other hand, we noted that thermodynamic results can be acceptable in MCFC application thanks to a particular combination of conditions.

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