Diffusive resistance analysis in fuel cells
Part 1. Some theoretical considerations

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Abstract

This work proposes the use of a rigorous approach to the analysis of the fuel-cell diffusive resistances not only at the commercial scale, but also at the laboratory one. The attention used experimentally for checking diffusion resistances in electrodes, cells and stacks should imply the same attention in the corresponding data analysis techniques.

For this reason, some corrections to the most common interpretation and correlation procedures have been introduced on the basis of the study of complex electrodes and comparing these ones with simple ones.

In Part 1 of this work a theoretical discussion of some simple reference cases will be reported. In Part 2 some examples of applications to the interpretation of the experimental data will be given.
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Keywords: Fuel cells; Transport phenomena; Diffusion resistance; Electrode kinetics

1. Introduction

The experimental analysis of heterogeneous kinetics is based, on the one hand, on very sophisticated measurement methods while, on the other, it often uses simplified methods for the interpretation of the results. In particular, for electrochemical kinetics, this involves the analysis of the complex electrodes working on non-uniform concentration fields: the current–voltage experimental results are often just interpreted in the same manner as those of the simple electrodes, that is in terms of two parameters only, the exchange current and the limit current, and without any particular attention to the effects of the geometry, the flow pattern and the consequent distribution of concentration on the active surface.

The complexity of cells and stacks at the commercial scale is well known: ever more detailed and analytical answers to the problem can be found in detailed simulation tools [1–7]. But the detailed models often use data from laboratory-scale measurements [8,9], whose interpretation can be affected by the

scarce consideration of the complex phenomenology that also exists at relatively small scales. For this reason, a brief review of the recent history of applied research on fuel cells could be useful: in research laboratories, and specifically industrial ones, attention is being shifted more and more frequently from centimetre cell sizes ("postage stamp" scale) to decimetre cell sizes ("postcard" scale). The traditional methods for analysing the electrochemical kinetics, which have been elaborated for the smaller scale and applied to it with considerable success, are often too simplified for the larger scale, where the uniformity hypothesis (simple electrodes) is very often inadequate. In brief, the transition from the postage stamp to the postcard scale requires some changes in the handling of the laboratory data.

Similar situations, where the points of view can be articulated at a local level, or scale, an aggregate level and a macroscopic level, have been encountered in many different applicative fields, but perhaps the relationships between the levels have been better studied and understood for the heterogeneous chemical reactions of traditional chemical engineering (catalytic or non-catalytic fluid–solid reactions, fluid–fluid reactions, slurries, trickle beds, etc. [10]). From this wide scenario of cases, which are, for the major part, well established in the field of chemical engineering,

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Nomenclature

A	corrective coefficient, from the averaging operation (–)
c_o	see Eq. (B.5) (–)
c_L	see Eq. (B.7) (–)
C_i	volumetric concentration of the component i $(kmol/m^3)$
$d_\#$	see Eq. (B.9) (–)
D_A	diffusivity (m^2/s)
f_c	see Eq. (B.4) (–)
F	Faraday's constant (A s/mol)
j	current density (A/m^2)
J	mean electrode current density (A/m^2)
k, k'	kinetic constants (depending on the reaction orders)
k_a	apparent kinetic constant (m/s)
k_c	mass transfer coefficient (m/s)
k_f	flow dynamic coefficient (m/s)
k_o	intrinsic kinetic constant (m/s)
K	global kinetic constant, local value (m/s)
L	length (m)
n	stoichiometric coefficient for electrons, absolute value (–)
q	volumetric flow rate (m^3/s)
r	reaction rate, per unit surface $(kmol/m^2\,s)$
r_L	limit reaction rate $(kmol/m^2\,s)$
r_m	mean reaction rate $(kmol/m^2\,s)$
R	gas constant (j/mol K)
s	thickness (m)
S	electrode surface (m^2)
T	absolute temperature (K)
u	utilisation factor (–)
v	velocity (m/s)
v	(in Appendix A) adimensional voltage (–)
V	voltage (W/A)
x	reaction rate $(kmol/m^3)$
X	see Eq. (B.1) (–)
y	spatial coordinate, orthogonal to the electrode (m)
Y	see Eq. (B.2) (–)
z	spatial coordinate, parallel to the electrode (m)

Greek symbols

α_i	reaction orders, direct reaction (–)
β_i	reaction orders, inverse reaction (–)
β	symmetry factor (–)
η	a-dimensional voltage loss (–)
φ	effectiveness factor (–)
Φ	Thiele modulus (–)
ν_i	stoichiometric coefficient (–)
ζ	adimensional axial coordinate (–)

Apexes and indexes

A	key reagent (hydrogen at the anode, oxygen at the cathode)
c	concentration
eff	effective
eq	equilibrium
ex	external
i	generic component
L	limit
m	mean value
o	inlet
r	reference
s	electrode surface
*	exchange
#	refers to the shifting from the diagonal of Eq. (B.4)
'	refers to the other electrode

some useful approaches can be drawn for an analogous study of many cases of electrochemical interest.

In analysing complex electrodes, overcoming any immediate and substantially semi-empirical and superficial approach requires an advanced study of the transport phenomena of momentum, mass, heat and charge and the real electrode geometry and structure, so that non-trivial physical–mathematical simulation approaches and their related numerical tools are necessary at the laboratory scale [11]. In other words, a wider point of view is needed, through which, on the one hand, the level of complexity necessary and sufficient for a good analysis of a set of experimental data can be determined and, on the other hand, the correct formal analytical tools, at the proper level of simplification, can be found.

Of particular interest, and particular difficulty too, is an analysis that highlights the behaviour of a single electrode of a couple of complex electrodes. In such cases it is necessary to maintain the behaviour of the second electrode constant and uniform, approximating the behaviour of a simple electrode, so that it can be considered non-influential, while attention is concentrated on the protagonist electrode.

When this de-coupling operation succeeds one electrode can be usefully studied using the standard methods of the chemical reactor theory and the local electrode kinetics can be more easily determined. On the other hand, the results of these kinds of approaches should often only be considered as orienting, while an effective and quantitative kinetic characterisation requires the contemporaneous consideration of both the coupled electrodes and their complexity in terms of velocity and composition fields, that is the use of complex physical–mathematical models at the laboratory scale. The use of detailed models is always necessary, in particular, when the thermal regulation is not completely effective, so that the temperature field cannot be considered uniform.

Simpler cases are encountered when the experimental investigations use perturbation methods, that is transient conditions following variations, often very little variations, in some operative condition such as temperature, composition, velocity and so on. Some authors [12,13] have successfully used flow rate and composition perturbations on the electrodes of a molten carbonate fuel cell to characterise the diffusive limits of the anode and

cathode. This technique is now under discussion as a systematic diagnostic instrument for Ansaldo Fuel Cells' experimental cells. In the second part of this paper some preliminary data of this kind will be reported and analysed and the difficulties encountered in the interpretation will be underlined: in fact, when the variations are large enough to produce clearly measurable effects, they are often out of the linear range. Moreover, similar methods could be useful in the development of polymeric membrane fuel cells, for instance the ENEA PEMFCs, as discussed in the following chapters.

Passing from a theoretical discussion of some simple reference cases (Part 1) to some examples of their application to the interpretation of experimental data (Part 2), this work intends to recommend a rationalisation and generalisation of the approach to the analysis of the diffusive resistances at the laboratory scale. In this way, an improvement in the diagnostic experimental methods can be attained for different applicative sectors and, in particular, more precise and reliable results in the characterisation of different kinds of fuel cell electrodes.

Finally, it is to be underlined that the point of view considered in this work is typical of an engineering approach: as chemical engineers start from a known intrinsic chemical kinetics and work on it considering, in particular, mass, heat and momentum transport phenomena on both the aggregate level (e.g. solid particles, drops, bubbles) and the reactor level, similarly a known intrinsic electrochemical kinetics is here assumed (e.g. the Tafel equation) and then the effects of transport phenomena on the electrochemical kinetics are discussed. As said, on the commercial scale, mass and heat transport is fully relevant and have to be taken into account by means of detailed physical–mathematical models; on the laboratory scale the attention must be focused mainly on mass transport phenomena, as isothermal conditions are granted. At both scales momentum transport phenomena are generally less important in fuel cell electrodes, as laminar regimes at high Peclet numbers are involved. Intrinsic electrochemical kinetics is not discussed at all. This term, summarizing a number of complex molecular phenomena on a very small scale (transport through the ionomeric layer, activation steps, molecular electrochemical mechanisms, and so on), is here schematized by means of a relatively simple relationship. On the contrary, emphasis is given to the question of the reference conditions for the electrochemical kinetics: this is a relevant point in practical applications because the choice of an external reference allows to write a more explicit and univocal kinetic expression being dependent on the reaction advancement.

The usefulness in this research field of an engineering approach well established in chemical engineering procedures can be further underlined. Researchers starting from more specific electrochemical studies could found in this similitude some technical suggestions, while chemical engineers could start from here to fully recognize electrochemical processes as integrant part of their field of study. The following sections would give some attention to this ambitious aim; also for this reason the discussion is maintained, especially for the Part 1, at a general level, without a specific reference to a particular kind of fuel cell or electrode and following an analytical approach to focus attention on these basic concepts.

2. Local diffusive resistances

Fuel cell electrodes are open systems in which a neutral reagent A, e.g. the hydrogen at the anode, must migrate from the gaseous phase to the reaction place. The use of Tafel's equation for the electrode current is standard practice, but it is well known that attention has to be given to the concentration effects of neutral reagents and to the choice of the reference conditions. For a "simple" electrode, defined in terms of uniform temperature, voltage and concentrations, the choice of the reference is obvious; on the other hand, for a complex electrode, that is a "non-simple" one, at least in terms of a non-uniform composition field, the exchange current and the equilibrium voltage are locally related to the composition C_i, as well as to any other different reference composition C_{ir}, for instance the composition C_{io} of the inlet gas, with particular attention to the concentration C_{Ao} of the key reagent A. It is necessary, moreover, to assume some kind of dependence, for instance a simple proportionality, between the exchange current and the concentration C_{As} close to the electrode.

The choice of a reference condition is a delicate question that is very often underestimated and neglected. Further details are reported in Appendix A. Here it should be noted that the choice of a unique reference composition for all the points of an electrode, under uniform temperature and voltage conditions, makes it possible to express the local current density, that is the local reaction rate for unit surface, merely as a function of the composition (or the concentration of a key reagent, or the utilisation factor in relation to the key). The choice of a unique reference condition can be extended, when needed, to the electrode where the temperature and/or the voltage are not uniform.

It is worth noting, in particular, that the uniform voltage hypothesis implies a good de-coupling operation with respect to the other electrode: the corresponding total voltage losses are considered uniform or, at least, their distribution is assumed to be close to the mean value. On the contrary, in many instances, only the total voltage difference between the two electrodes can be assumed to be uniform, while the voltages of the electrodes are both non-uniform. Therefore, the de-coupling hypothesis has to be a priori deeply discussed and carefully a posteriori verified before judging the significance and the reliability of a single electrode analysis.

The choice of a unique and "external" reference, if coherent, can be of particular aid: for instance, when the inlet gas composition is chosen as the reference for both the reaction kinetics and the reaction rate and a linear and irreversible kinetic function, to simplify the discussion, is assumed, then the local electrode kinetics can be written as follows (see Appendix A)

$$j = j_{*o} \left(\frac{C_{As}}{C_{Ao}} \right) \exp \left(\beta \eta_o \right), \qquad \eta_o = (V - V_{eqo}) \frac{nF}{RT} \qquad (1)$$

where η_o expresses the electrical voltage difference between the electrode working under steady state conditions and a reference electrode under equilibrium conditions at the reference concentration C_{Ao}. The extension to linear reversible kinetics

is straightforward, the extension to non-linear kinetics is only a little more complex.

In Eq. (1) allowance must be made for the mass transfer resistances between the bulk fluid at concentration C_A, and the fluid at concentration C_{As} close to the electrode, by expressing the ratio C_{As}/C_A in terms of the limit current, that is the maximum diffusive flux of the limiting reagent

$$j_L = k_c C_A n F, \quad j_{Lo} = k_c C_{Ao} n F, \quad j = k_c (C_A - C_{As}) n F \quad (2)$$

In such a way the local electrode kinetics can be written

$$
\begin{aligned}
j &= j_{*o} \left(\frac{C_A}{C_{Ao}} \right) \left(1 - \frac{j}{j_L} \right) \exp(\beta \eta_o) \\
&= j_{*o} \left(\frac{C_A}{C_{Ao}} - \frac{j}{j_{Lo}} \right) \exp(\beta \eta_o)
\end{aligned} \quad (3)
$$

The second equation in (3), in particular, demonstrates that the local current density only depends on the local composition. In the equations in (3) it is explicitly considered that the electrode can be locally in contact with a bulk fluid at a concentration $C_A < C_{Ao}$; in turn, the concentration $C_{As} < C_A$ close to the electrode can be even lower due to diffusive resistances associated with the current. The voltage losses become negligible at very low currents and the reference concentration, but when the low current condition is stressed the equations in (3) tend to fail because they neglect the reversibility of the reaction. On the other hand, they are sufficiently general and reliable for many practical purposes and they are useful in a discussion of the role of transport and flow phenomena in the performance of the electrode. As said above, the extension to more complicated kinetics is only a matter of form.

For complex electrodes working with a continuous reagent flow, C_A and C_{As} are local values depending on their position. In such instances, the use of the local reference C_A

$$j = j_* \left(1 - \frac{j}{j_L} \right) \exp(\beta \eta), \qquad \eta = (V - V_{eq}) \frac{nF}{RT} \quad (4)$$

leads to a kinetic expression that is only apparently simpler than the second equation in (3). In fact, in Eq. (4) the parameters j_*, j_L and η are all local variables, depending on their position, while in the second equation in (3) the local current density depends only on the local concentration C_A. Of course, in both cases the current density J referring to the whole electrode corresponds to an averaging operation on the electrode surface.

However, when the operating current is much lower than the limit current (for instance $3j_{*o} < j < j_L/3$), the concentration polarisation, according to an acceptable approximation of the first equation in (3), can be assumed to be proportional to j/j_L,

$$\eta_o \approx \left(\frac{1}{\beta} \right) \left[\ln \left(\frac{j}{j_{*o}} \right) - \ln \left(\frac{C_A}{C_{Ao}} \right) + \frac{j}{j_L} \right] \quad (5)$$

$$\eta_{oc} \approx \frac{j}{\beta j_L} = \frac{\text{cost.} \, j}{C_A k_c} \quad (6)$$

This circumstance allows a simple and direct interpretation of voltage–current measurements, in order to evaluate the effects of mass transfer resistances. In particular, when perturbation

methods are used under constant current constraints [12], any k_c variation can be directly detected in terms of the electrode voltage. However, Eqs. (5) and (6) only have local validity and are valid for the whole electrode only in the case of a simple one, while the extension to non-uniform composition electrodes requires an averaging procedure.

Moreover, (5) demonstrates that the local voltage loss is partly imputable to diffusive effects ($C_{As} < C_A$) and partly to a non-uniform composition field ($C_A < C_{Ao}$): the measurement of η_o and its variations cannot be directly connected to the diffusive resistances unless there is information available to allow appropriate corrections to be made to the results in terms of non-uniform concentration fields.

3. The analogy with heterogeneous chemical kinetics

If, for simplicity, the discussion is limited to irreversible linear kinetics and the following definitions

$$k_o = \left(\frac{j_{*o}}{nFC_{Ao}} \right) \exp(\beta \eta_o), \quad r = \frac{j}{nF} \quad (7)$$

are used, so that an "intrinsic" kinetic constant k_o of the electrochemical reaction is defined as a function of the electrode over-potential, the classical formulation of a first order heterogeneous reaction on the boundary is obtained instead of Eqs. (1) and (3):

$$
\begin{aligned}
r = k_o C_{As} &= k_c (C_A - C_{As}) \\
&= K C_A, \qquad K = \left(\frac{1}{k_o} + \frac{1}{k_c} \right)^{-1}
\end{aligned} \quad (8)
$$

In local terms, or in terms of a simple electrode, the apparent kinetic constant and the limit kinetic constant coincide with the overall constant and the transport coefficient, respectively

$$k_a = \frac{r}{C_A} = K, \qquad k_L = \frac{r_L}{C_A} = k_c \quad (9)$$

and the relationship between the apparent (k_a), the limit (k_L) and the intrinsic (k_o) constants, equivalent to Eq. (4), is the well known

$$\frac{k_a}{k_L} = \left(\frac{k_o/k_L}{(1 + k_o/k_L)} \right) \quad (10)$$

or, in the form more common in electrochemistry,

$$k_a = k_o \left(1 - \frac{k_a}{k_L} \right),$$

$$\frac{j}{C_A} = \left(\frac{j_{*o}}{C_{Ao}} \right) \exp(\beta \eta_o) \left(1 - \frac{j}{j_L} \right) \quad (11)$$

For the simple electrode, according to Eq. (11), the dependence of the intrinsic constant k_o on the over-potential can be obtained from low current measurements ($3J_{*o} < J < J_L/3$), where $C_{As} = C_A$ and $k_o \ll k_L$ (negligible diffusive resistances); in turn, the limit constant can be obtained from high current measurements, where $k_o \gg k_L$ (negligible reaction resistances).

Eqs. (11) and (10) are different obviously only for the form, but they correspond to two different points of view, which must be reconciled in order to appreciate some other fundamental analogies. In heterogeneous chemical kinetics the constant k_o is considered as a real constant at constant temperature, it is often considered as not being directly measurable but deducible from global kinetic measurements (k_a) and transport coefficient evaluations (k_c). A variable and directly measurable intrinsic kinetic constant should be automatically felt as strange, even if, in principle, it could correspond to controlled temperature changes at the reaction site. On the contrary, in the electrode analysis, the control of the intrinsic kinetic constant can easily be obtained through voltage measurements: while k_a is still directly connected to global kinetics, that is the electrode current, k_o is a variable directly connected to the electrode over-potential by a kinetic equation like the first one in (7) and the measurement of both allows an evaluation and an analysis of the mass transfer phenomena occurring at the electrode in terms of the constant k_L, that is the limit current.

After clarifying the different points of view, the analogies existing between some electrochemical kinetic problems and some classical heterogeneous chemical kinetic formulations can be reviewed, so providing wide and well-established literature references. In particular, the recourse to such analogies in the averaging operations of complex electrodes often provides the opportunity for utilising in this case solutions already known in other contexts. A well known classical example is the analogy between porous electrodes and porous chemical catalysts [14]; here another analogy will be specifically used, the one between the kinetic behaviour of a planar electrode of finite dimensions in contact with a moving fluid and the well-known problem of diffusion with a chemical reaction at the boundary.

The relevance in terms of applications is confirmed taking in account that, even if fuel cells usually work at not too high current density, also under apparently safe conditions a large part of the cell can locally work in conditions where diffusion phenomena significantly affect performance [11].

Other analogous approaches that refer to the chemical reactor theory can be used when the optimisation of the electrode shape and the flow pattern in an electrochemical reactor are considered. As examples, the studies of the comparison between interdigitated and serpentine configurations in PEMFC electrodes can be cited [15,16], a topic which seems to be worth further discussion elsewhere. Here the comparison between a well-mixed and a longitudinal flow electrode will be discussed in some detail (see Part 2, Appendix D) and the results of the longitudinal-flow electrode study will be used in the analysis of MCFC anodes (see Part 2).

4. From local to global kinetics

Eq. (11) is valid in local terms, but it is usually extended to much wider contexts. It is worth exemplifying the conditions under which it can be correctly extrapolated.

For the whole electrode, the definition of the apparent and limit constants has to be made in terms of the mean values of the reaction rate (or current density), obviously with reference to the inlet concentration:

$$k_a = \frac{r_m}{C_{Ao}} = \frac{J}{nFC_{Ao}} = \frac{KC_{Am}}{C_{Ao}},$$
$$k_L = \frac{r_{mL}}{C_{Ao}} = \frac{J_L}{nFC_{Ao}} = \frac{k_c C_{AmL}}{C_{Ao}} \tag{12}$$

As a consequence, the local Eq. (11) can be quite inadequate and require a correction. By defining

$$\frac{1}{A} = \frac{C_{Am}}{C_{Ao}} = \frac{(\int_S C_A \, dS)}{(C_{Ao} S)}, \quad A > 1 \tag{13}$$

the preceding Eq. (12) can be summarised, for linear kinetics as

$$k_a = \frac{K}{A}, \qquad k_L = \frac{k_c}{A_L} \tag{14}$$

It is useful to compare a complex electrode, working at a non-uniform composition, with a corresponding simple electrode, working at uniform concentration C_{Ao}; for the simple electrode the local Eq. (11) can be written as

$$\frac{1}{K} = \frac{1}{k_o} + \frac{1}{k_c}, \qquad \frac{1}{j} = \left(\frac{1}{j_{*o}}\right) \exp(-\beta \eta_o) + \frac{1}{j_L} \tag{15}$$

For a complex electrode, instead of the local constant K, containing the reaction constant k_o and the transport constant k_c, reference can be made to an averaging operation on the electrode surface

$$\frac{1}{Ak_a} = \frac{1}{k_o} + \frac{1}{k_c} = \frac{1}{k_o} + \frac{1}{A_L k_L} \tag{16}$$

$$\frac{1}{AJ} = \left(\frac{1}{j_{*o}}\right) \exp(-\beta \eta_o) + \frac{1}{A_L J_L} \tag{17}$$

so that the apparent constant k_a and the limit constant k_L can be connected to local constants through the introduction of the coefficients A and A_L, which take account of all the effects of a non-uniform concentration field.

The validity range of Eq. (16) is wider than that of Eq. (15), but it has its limits. In the first place, as said above, k_o must be uniform, that is the electrode must be isothermal and efficaciously de-coupled. In the second place k_c must also be uniform: particular shapes or flow fields can be associated with local differences in the transport coefficient; this, moreover, can be affected by local non-linear phenomena such as those connected with the bulk flow towards the electrode (see Part 2, Appendix E).

However, in many instances, Eq. (16) can be taken as a guide for a better understanding of some typical operations in the analysis of chemical and electrochemical reactions. In heterogeneous chemical reactions reference can be made to the following typical identification problems:

- On the local scale, that is when it is possible to work on simple and uniform systems, the characterisation of the intrinsic kinetics (kinetic constants and reaction orders) is relatively easy.
- On a larger scale, that is in terms of aggregates or reactors, the characterisation of the intrinsic kinetics passes through a more

articulated physical–mathematical description of the system: the global or mean kinetics (k_a) are measured, the transport coefficients (k_c) are estimated, the composition fields (A) are simulated and averaged and the intrinsic kinetics (k_o) are, finally, determined. Only in rare cases the intrinsic kinetics are already known from preceding measurements on simpler systems, so that the transport phenomena can be the specific objective of the identification problem.

When dealing with electrochemical kinetics, the terms of the discussion remain substantially the same only when the local scale is under consideration (laboratory systems which can be considered simple electrodes), but they become rather different at greater scales (complex electrodes), where the identification problem involves the measurement of the mean kinetics (J, k_a) and intrinsic kinetics (V, k_o) as well as the interpretation of the limit kinetics (J_L, k_L) in terms of transport coefficients (k_c) by taking into account the concentration distribution (A, A_L). The identification problem is often complicated by other unknowns (symmetry factor β, reaction orders) appearing in the relationship between V and k_o.

In both cases the preliminary measurements are restricted, for what is possible, by well-controlled laboratory conditions, where the identification problem can be simplified by reference to uniform concentration fields ($A = A_L = 1$) and non-controlling transport phenomena ($k_c \gg k_o$). In both cases the experimentation, at the laboratory or pilot scale, is then extended to systems of larger sizes and greater complexity and, finally, the identification problems give way to prevision problems, in particular design problems relating to developmental and commercial purposes, on systems where the approximations under discussion are nearly always unsuitable.

In other words, and to stress the point, Eq. (16), or, in more electrochemical language, Eq. (17) shows that the identification of the global transport coefficient of an electrode, k_c, requires a number of operations that are not always straightforward or certain and, in any case, a non-superficial level of theoretic analysis.

- In the first place, the identification is possible by means of the consideration of only one electrode on condition that the other electrode is working under an approximately uniform voltage field. When this is not the case, the consideration of only one electrode cannot be considered significant and the transport phenomena of the two electrodes cannot be de-coupled.
- In the second place, the experimental work can be done according to essentially known methods, by achieving couples of values for the current (J, that is k_a) and the voltage (η_o, that is, substantially, k_o).
- Finally, an estimation of the mean electrode concentration (C_{Am}, that is the parameter A) has to be made for the various experimental conditions used and, in particular, for the limit current conditions (J_L, A_L). The evaluation of these means can be done experimentally, from local concentration measurements taken at various points on the electrode, but an alternative to this experimental burden can be found in the calculation, starting with few known concentration values:

usually, the inlet value C_{Ao} and the outlet value $(1-u)C_{Ao}$ are at least known, but employing a simple arithmetical mean, such as $C_{Am} = C_{Ao}(1-u/2)$, may be inadequate.

In addition, particular attention has to be given to the dependence of the transport coefficient on the flow conditions of the reagent fluid in relationship to the electrode. The effects of the flow conditions are usually appreciable on all the measured or estimated parameters, especially the transport coefficients and the averaging coefficient A. In the simplest cases the flow conditions can be taken into account in terms of a further kinetic parameter alone, the "flow dynamic" constant

$$k_f = \frac{q}{S} \tag{18}$$

that is the fluid flow rate per unit electrode surface, to be put beside the previously considered reaction and transport constants (see Appendix C1).

5. Analysis and correlation methods

The approach discussed here highlights the advantages of a unique and external reference. This approach will be underlined in Appendix A.

Some considerations on dealing with the organisation and the correlation of the experimental results according to what has been reported in the previous section are presented in Appendix B. In Appendix C some examples of a theoretical nature are discussed, with the aim of illustrating the real relevance of the averaging operations.

In Part 2 of this work different analysis methods will be discussed in relationship with different experimentation techniques. In addition, concrete examples of their application to Ansaldo Fuel Cells data will be presented in detail. In Appendixes D and E of Part 2, moreover, the effects of the flow field on the electrode performance will be discussed on the basis of the chemical reaction theory and its classical limit models. Many more examples could be added, but the ones cited can be considered sufficient to provide a comprehensive overview and to draw some conclusions and rules for a more exhaustive and reliable analysis of the experimental current–voltage data in terms of diffusive resistances.

6. Conclusions

The analysis of the diffusive resistance is made difficult by the non-linearity and complexity of the phenomena even at the laboratory scale.

The problem can be tackled at the experimental level by using a number of different techniques: differential or finite perturbation methods, constant flow or constant current methods, and so on. However, the effects of each variation cannot be interpreted as a simple phenomenon, but the result of at least two factors:

- the local diffusive resistances set and
- the concentration distribution of the electrode.

The first can only be determined after estimating the second by means of an adequate physical–mathematical description. To achieve this it is particularly useful to make recourse to a close analogy between electrode kinetics and heterogeneous chemical kinetics with the reaction at the boundary and to use this analogy within the chemical reactor theory.

As Part 2 will show in detail, this kind of analysis can be successfully applied to fuel cell experimental data.

Appendix A. Kinetic expressions and reference conditions

Given the local electrochemical kinetics of the kind

$$j = k\Pi_i C_{is}^{\alpha i} \exp(\beta v_s) - k'\Pi_i C_{is}^{\beta i} \exp[(\beta - 1)v_s],$$
$$v = \frac{VnF}{RT} \tag{A.1}$$

which contains the concentrations and the voltage acting on an electrode point (C_{is}, v_s) and must satisfy the thermodynamic consistence conditions

$$\frac{k}{k'} = \Pi_i C_i^{vi} \exp(-v_{eq}) = \Pi_i C_{is}^{vi} \exp(-v_{es})$$
$$= \Pi_i C_{ir}^{vi} \exp(-v_{er}) \tag{A.2}$$

a reference can be chosen at the equilibrium condition corresponding to an arbitrary composition C_{ir}

$$j_{*r} = k\Pi_i C_{ir}^{\alpha i} \exp(\beta v_{er}) = k'\Pi_i C_{ir}^{\beta i} \exp[(\beta - 1)v_{er}] \tag{A.3}$$

so that

$$j = j_{*r}\{\Pi_i\left(\frac{C_{is}}{C_{ir}}\right)^{\alpha i} \exp(\beta\eta_r) - \Pi_i\left(\frac{C_{is}}{C_{ir}}\right)^{\alpha i + vi}$$
$$\exp[(\beta - 1)\eta_r]\}, \quad \eta_r = v_s - v_{er} \tag{A.4}$$

In such a way, the local kinetics is written in terms of the voltage loss in relationship to the equilibrium voltage of the chosen external reference condition. This advantage has a price: the local voltage loss in respect to the bulk fluid at composition C_i, with which the irreversible phenomena of energy dissipation are associated, is different from the one appearing in the kinetic expression (A.4)

$$\eta = v_s - v_{eq} = v_s - v_{er} + v_{er} - v_{eq}$$
$$= \eta_r + \sum_i v_i \ln\left(\frac{C_{ir}}{C_i}\right) \tag{A.5}$$

As the electrode concentration C_{is} and the local concentration of the bulk fluid C_i are connected in transport equations, for instance under the form

$$j = -k_{ci}(C_i - C_{is})\frac{nF}{v_i}, \quad C_{is} = C_i + \frac{v_i j}{nFk_{ci}} \tag{A.6}$$

in Eq. (A.4) the concentration difference due to mass transfer can be taken into account in terms of the transport coefficient k_{ci}

or in terms of limit currents, with reference to local conditions (j_{Li}) or to reference conditions (j_{Lri})

$$j_{Li} = -k_{ci}C_i\frac{nF}{v_i}, \quad j_{Lri} = -k_{ci}C_{ir}\frac{nF}{v_i} \tag{A.7}$$

yielding

$$\frac{C_{is}}{C_{ir}} = \frac{C_i}{C_{ir}}\left(1 + \frac{v_i j}{nFk_{ci}C_i}\right) = \frac{C_i}{C_{ir}} + \frac{v_i j}{nFk_{ci}C_{ir}} = \frac{C_i}{C_{ir}} - \frac{j}{j_{Lri}} \tag{A.8}$$

and

$$j = j_{*r}\Pi_i\left[\frac{C_i}{C_{ir}} + \frac{v_i j}{nFk_{ci}C_{ir}}\right]^{\alpha i}$$
$$\exp(\beta\eta_r)\left\{1 - \Pi_i\left[\frac{C_i}{C_{ir}} + \frac{v_i j}{nFk_{ci}C_{ir}}\right]^{v_i} \exp(-\eta_r)\right\} \tag{A.9}$$

Besides the reaction order (α_i) and the other coefficients of a stoichiometric nature (v_i, β), this final form of the kinetic expression (A.9) contains

- the reference composition C_{ir};
- the exchange current j_{*r} at the reference composition;
- the transport coefficient between the fluid and electrode k_{ci} or, alternatively, the limit current j_{Lri} at the reference composition;
- the voltage loss η_r in relationship to the reference equilibrium;
- the local composition C_i.

In particular, in many instances, the variable η_r can be considered uniform on the electrode while, on the contrary, the local variable η surely is not. Moreover, the non-uniform concentration variable C_i, in many cases of practical interest, can be expressed through the definition of a unique degree of advancement

$$C_i = C_{ir}(1 + v_i x) \tag{A10}$$

or the utilization factor of a key reagent A

$$C_A = C_{Ar}(1 - u), \quad C_i = C_{ir} - \left(\frac{v_i}{v_A}\right)C_{Ar}u \tag{A.11}$$

Therefore, Eq. (A.9) is equivalent to a kinetic function, at constant temperature and voltage, depending on an advancement variable alone (x or u).

An electrode can be defined "simple" if all the local variables (T, P, η_r, x) are independent of their position, that is each assumes a unique uniform value on the electrode. For many complex electrodes, especially at the laboratory scale, the temperature, the pressure and the voltage can be still assumed to be uniform, while the composition (degree of advancement) cannot.

It is worthwhile commenting further on the electrode voltage. At uniform temperature and pressure the two coupled electrodes have, at least at the laboratory scale and with a reasonable

approximation, equal current and a uniform voltage difference:

$$\int_S j(\eta_r, x)\, dS = \int_{S'} j'(\eta'_r, x')\, dS',$$

$$(JS = J'S'), \qquad \eta_r + \eta'_r = \text{cost} \qquad (A.12)$$

When one of the electrodes is considered to be simple (for instance the one marked with the apex), the uniformity of η'_r implies the uniformity of η_r on the other electrode, although it is not considered simple. In such cases, electrode kinetics of the type

$$j = f(x) \qquad (A.13)$$

allow the extension of many of the identification, design and optimisation procedures of the classical theory of isothermal chemical reactors to electrochemical reactors.

According to Eq. (A.9), a particularly simple and interesting case to analyse as a reference example is the one regarding a unique limiting reagent A, with reaction order and stoichiometric coefficient equal to unity ($\alpha_A = -v_A = 1$). Then the kinetic expression becomes

$$j = \left[\frac{j_{*r}\exp(\beta\eta_r)}{C_{Ar}}\right]\left[C_A - \frac{j}{nFk_c} - C_{Ar}\exp(-\eta_r)\right] \qquad (A.14)$$

and, if

$$C_{Ae} = C_{Ar}\exp(-\eta_r) \qquad (A.15)$$

is the concentration at which the reagent fluid is in equilibrium under a given over-potential η_r, the electrochemical kinetics can then be reduced to simple linear kinetics

$$j = \left[\frac{j_{*r}\exp(\beta\eta_r)}{C_{Ar}}\right]\left[C_A - C_{Ae} - \frac{j}{nFk_c}\right] \qquad (A.16)$$

By putting

$$r = \frac{j}{nF}, \qquad K = \frac{r}{(C_A - C_{Ae})}, \qquad k_o = \frac{j_{*r}\exp(\beta\eta_r)}{nFC_{Ar}} \qquad (A.17)$$

Eq. (A.15) becomes simply

$$r = K(C_A - C_{Ae}), \qquad K = \left(\frac{1}{k_o} + \frac{1}{k_c}\right)^{-1} \qquad (A.18)$$

A similar result can also be achieved when more complex kinetics are considered. For instance, if two or more reagents and non-linear dependences are involved, an expression just like the preceding is derived in the range of validity of a linearisation of Eq. (A.9) for low utilisation factors ($u \ll 1$) and low currents ($j \ll j_{Lri}$).

Appendix B. How to determine the complexity

When the intrinsic kinetic constant k_o increases, the apparent kinetic constant k_a is limited by the limit constant k_L ($0 < k_a < k_L$). Therefore, both variables

$$X = \frac{k_a}{k_L}, \qquad (0 < X < 1) \qquad (B.1)$$

$$Y = \frac{(k_o - k_a)}{k_o}, \qquad (0 < Y < 1) \qquad (B.2)$$

can vary in the range between zero ($k_o = k_a = 0$) and unity ($k_o \gg k_L$; $k_a = k_L$).

In local terms, or for a simple electrode with linear kinetics, the limit constant coincides with the transport coefficient ($k_L = k_c$) and the apparent constant depends only on the intrinsic constant and the transport coefficient ($1/k_a = 1/K = 1/k_o + 1/k_c$), so that between X and Y the simple relationship

$$Y = X \qquad (B.3)$$

exists, that is equivalent to Eq. (15) and in an XY plot this corresponds to the square diagonal.

On the contrary, for a complex electrode, with linear kinetics, the composition distribution on the electrode, with $C_A < C_{Ao}$, implies that the apparent constant as well as the limit constant is less than the respective reference values ($k_L < k_c$; $k_a < K$). Therefore, Eq. (B.3) must be correct, for instance in the form

$$\frac{Y}{X} = 1 - f_c(X), \qquad f_c = \frac{(k_c - k_L)}{k_c} + (1 - A)\frac{k_L}{k_o} > 0 \qquad (B.4)$$

that is equivalent to Eq. (16).

When the corrective function f_c is null for all the values of k_o, Eqs. (15) or (B.3) are recovered, while Eq. (B.4) with $f_c > 0$ corresponds to a curve which is under the diagonal as much the non-uniformity of the diffusive phenomena taking place at the electrode is important.

Of greater interest are the asymptotic solutions to which Eqs. (16) and (B.4) degenerate at the extremes of the range. At one extreme, in the field of low currents, a proportionality between X and Y can be assumed

$$k_o \ll k_L, \qquad Y = c_o X, \qquad c_o = \lim\left[\frac{Y}{X}\right]_{X\to 0} \qquad (B.5)$$

and the value of the constant c_o can be obtained as an asymptote of the experimental XY plot or in terms of the derivatives of k_a in relationship to k_o. If $X = Y = 0$, $k_o/k_a = 1$ and dk_a/dk_o also $= 1$. In the neighbourhood of this point the difference between k_a and k_o is only appreciable in terms of the second order derivative, that is $k_a = k_o + (d^2 k_a/dk_o^2)\,k_o^2/2$. Therefore the proportionality constant is

$$c_o = -\left(\frac{k_L}{2}\right)\left(\frac{d^2 k_a}{dk_o^2}\right)_{k_a = k_o}$$

$$= \frac{1}{A_L} + k_L\left(\frac{dA}{dk_o}\right)_{k_a = k_o}, \qquad f_{co} = (1 - c_o) \qquad (B.6)$$

At the other extreme, in the high current field, the proportionality can be assumed to be between $1 - X$ and $1 - Y$

$$k_o \gg k_c, \qquad 1 - Y = c_L(1 - X),$$

$$c_L = \lim\left[\frac{(1 - Y)}{(1 - X)}\right]_{X\to 1} \qquad (B.7)$$

and the proportionality constant s

$$c_L = \frac{k_L^2}{(k_o^2 dk_a/dk_o)_{k_a=k_L}}$$

$$= \left[A_L + (1/k_c)(k_o^2 dA/dk_o)_{k_a=k_L}\right]^{-1}, \quad f_{cL} = (c_L - 1) \tag{B.8}$$

as k_a becomes indistinguishable from k_L for high, even if finite, values of k_o, the limit of $k_o^2 dk_a/dk_o$ for $k_a = k_L$ is often zero and c_L diverges, that is the function $Y(X)$ tends to the vertical $X = 1$.

Another parameter which can generally express the differences between Eqs. (B.3) and (B.4) is the size of the belly of the curve, as measured by the segment on the other diagonal $(Y = 1 - X; k_o = k_L)$ of the square, between the diagonal crossing and the intersection with the curve. The length $d_\#$ of this segment is

$$d_\# = \frac{(\sqrt{2}/2) f_{c\#}}{(2 - f_{c\#})} \tag{B.9}$$

where $f_{c\#}$ indicates the correction in Eq. (B.4) for $k_o = k_L$.

Obviously, when Eq. (B.3), that is Eq. (11), is correct, the constants assume the reference values corresponding to the principal diagonal Eq. (B.3):

$$c_o = 1, \qquad c_L = 1, \qquad d_\# = 0 \tag{B.10}$$

whereas when there is some shifting from the diagonal, the constants will, in most cases, be Eqs. (16) and (B.4):

$$c_o < 1, \qquad c_L > 1, \qquad d_\# > 0 \tag{B.11}$$

The low current constant c_o is particularly important for the proper characterisation of an electrode, as it directly modifies the linear current–voltage relationships of type (5).

Appendix C. Some examples

The real relevance of the asymptotic constants c_o and c_L can be illustrated by reporting some significant examples.

C.1. Stirred electrode

A first, very simple, example regards the behaviour of one well stirred electrode to which the reagent fluid is continuously fed, so that a unique value of concentration C_A is sufficient to describe its steady condition (open system with concentrate parameters, or continuous stirred tank reactor, CSTR). So, the local condition is described by C_A, while the inlet concentration is C_{Ao}, which is connected to the former by the balance equation

$$C_{Ao} - C_A = \frac{K}{k_f} C_A, \quad k_f = \frac{q}{S} \tag{C.1}$$

and the flow dynamic constant k_f, (volumetric flow rate supplied to the electrode per unit active surface).

In terms of the electrode concentration, according to Eq. (C.1)

$$C_A = \frac{C_{Ao}}{(1 + K/k_f)} \tag{C.2}$$

the apparent constant referring to the inlet concentration $k_a = KC_A/C_{Ao}$ is then

$$k_a = \frac{K}{(1 + K/k_f)} = \left(\frac{1}{k_o} + \frac{1}{k_c} + \frac{1}{k_f}\right)^{-1} \tag{C.3}$$

and corresponds to an averaging coefficient

$$A = 1 + \frac{K}{k_f} \tag{C.4}$$

Eq. (C.3) seems different from Eqs. (10) and (11), at least because of the flow constant k_f. In fact, if the discontinuous concentration drop from inlet C_{Ao} to internal C_A is taken into account, the electrode should be classified as "complex" and behavioural differences are to be expected when it is compared with the simple electrode at uniform C_{Ao}: the X–Y trends of a stirred electrode with the position $k_L = k_c$ typical for the simple electrode should be represented by a family of straight lines with increasing slope with increasing k_f. Nevertheless, from another point of view, the stirred electrode can be considered "simple" because all its surface points work at uniform concentration C_A.

In order to reconcile the two antithetic positions it is sufficient to observe that, in the absence of reaction resistances, the limit constant is

$$k_L = \left(\frac{1}{k_c} + \frac{1}{k_f}\right)^{-1} \tag{C.5}$$

which is equivalent to

$$A_L = 1 + \frac{k_c}{k_f} \tag{C.6}$$

and also depends on k_f; in such a way it is possible to re-obtain Eqs. (10) and (11) through the elimination of k_c in Eqs. (C.3) and (C.5).

Eqs. (C.3) and (C.5) come from definition (12). In other words, the validity of Eq. (11) is extended thanks to definition (12) of the apparent and limit constants, a definition that has been stated in direct agreement with the experimental evidence.

However, it is worth noting that the simple identity between the transport coefficient and the limit constant in the second equation in (9) is not adequate any more, while the valid position has become the more complicated Eq. (C.5), in which the "flow" constant k_f is also considered in order to take into account the limits imposed on the electrode current by the amount of reagent at its disposal. Obviously, only if the link between k_L and k_c is known, for instance the one in (C.5), Eq. (10) or (11) makes it possible to analyse the experimental results on the limit current (k_L) in order to achieve a reliable characterisation of the transport phenomena (k_c).

C.2. Longitudinal flow electrode

A second example, which is apparently just as simple as the preceding, but able to highlight the possible difficulties of the problem, regards a planar electrode in contact with a longitudinally flowing and transversally well mixed fluid: it is the system

characterised by a piston flow, that is the one defined as an ideal tubular reactor (or plug flow reactor, PFR) in the chemical reactor theory. Under stationary and constant flow rate conditions, the differential mass balance along the axial coordinate z, written in terms of the utilisation factor

$$k_f du' = K(1 - u')d\zeta, \qquad \zeta = 0 \quad u' = 0, \qquad \zeta = 1 \quad u' = u$$

$$k_f = \frac{q}{S}, \qquad\qquad \zeta = \frac{z}{L}, \qquad\qquad K = \left(\frac{1}{k_o} + \frac{1}{k_c}\right)^{-1} \tag{C.7}$$

allows the integral

$$K = -k_f \ln(1 - u) \tag{C.8}$$

and the limit condition

$$k_c = -k_f \ln(1 - u_L) \tag{C.9}$$

Moreover, it is

$$k_f u = k_a, \qquad k_f = u_L k_L \tag{C.10}$$

and, by combining Eqs. (C.8)–(C.10) with the last equation in (C.7) the variable X and Y are obtained in terms of the variable u used as a parameter

$$X = \frac{k_a}{k_L} = \frac{u}{u_L}$$
$$Y = 1 - \frac{k_a}{k_o} = 1 + u_L X \left[\frac{1}{\ln(1 - u_L X)} - \frac{1}{\ln(1 - u_L)}\right] \tag{C.11}$$

This time the similarity between the second equation in (C.11) and Eq. (11) is only very partial. Obviously both equations, thanks to the way they have been constructed, allow the limits where the reaction ($k_a = 0$ for $k_o \ll k_L$) or the transport ($k_a = k_L$ for $k_o \gg k_L$) is controlling, but the characteristic constants of the curve (B.4)

$$c_o = \left(\frac{k_L}{k_f}\right) \frac{(k_c + 2k_f)}{2k_c}$$
$$c_L = \left(\frac{k_L}{k_c}\right)^2 \left[\frac{k_f}{(k_f - k_L)}\right] \tag{C.12}$$
$$d_\# = \sqrt{2} \left[\frac{(2k_a - k_L)}{k_L}\right]_{k_o = k_L}$$

depend on the ratio k_c/k_f (see Figs. C.1 and C.2) and assume the values (B.10) only in the trivial case in which the flow constant is quite non-limiting, or non-influencing ($k_f \gg k_L$). Under such conditions the amount of the fed reagent is much more than that consumed (very low utilisation factors) and the reagent concentration is almost uniform along the length of the electrode, so that the whole electrode behaves as a simple electrode ($C_A = C_{Ao}$).

Under the contrary conditions, when the amount of the inlet reagent becomes controlling ($k_f \ll k_L$), the characteristic constants (C.12) approach the limit values $c_o = 1/2$, $1/c_L = 0$, respectively, and Eq. (C.11) tends to degenerate into $k_a/k_L = 1$, which is quite different from Eq. (11).

A first comment, of a reassuring nature, could be that a deliberate choice of flow-controlling conditions ($k_f < k_c$) is very unlikely, so that the values assumed by the asymptotic constants in (C.12) are almost always close to the reference ones in (B.10): in such instances Eq. (11) is substantially acceptable for all the values of k_o, that is the voltage, and the electrode behaves as a simple one.

Just this kind of consideration, on the other hand, diverts attention from the circumstances in which the Eqs. (C.12) are more pertinent, so impeding a full appreciation of their role in possible malfunctions, often not foreseen nor suspected, in a particular region of a cell or stack, at the commercial or laboratory scale. In fact, even if usually the operative conditions involve a current decidedly lower than the limit one in terms of average values, some section of a cell can really work under conditions very close to the limit current and the complete exhaustion of the reagents.
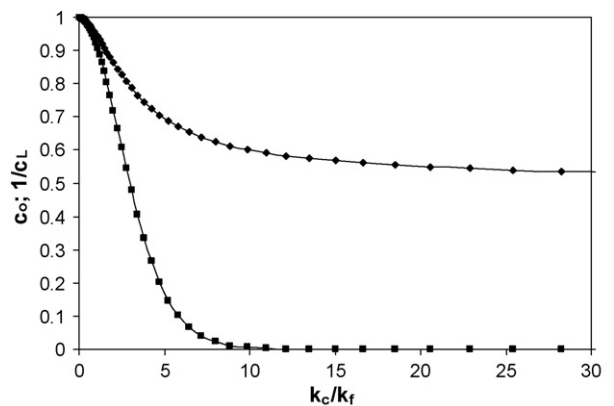

Fig. C.1. Longitudinal flow electrode. The asymptotic constants c_o and $1/c_L$ as a function of the rate k_c/k_f.
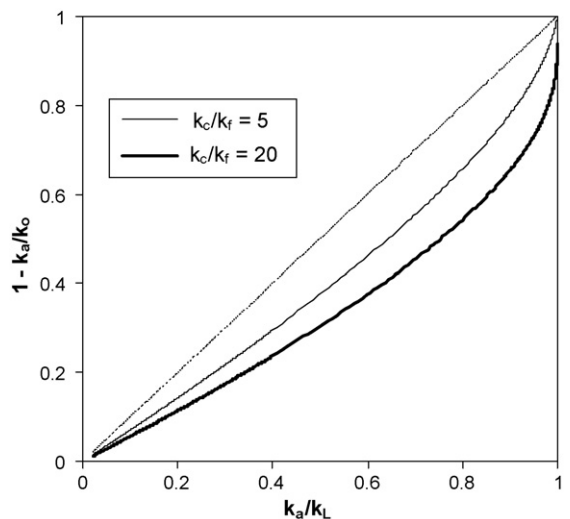

Fig. C.2. Longitudinal flow electrode. *XY* plot for different values of the ratio k_c/k_f. The diagonal represents the simple electrode.

Moreover, and it is perhaps the most important point, the first equation in (C.12) stresses the necessity of using a corrective c_o constant different from unity in the interpretation of many experimental results, even if they are obtained under low current conditions.

C.3. Diffusive electrode under uniform velocity

Another example, which is particularly relevant for polymeric membrane fuel cells in their special interdigitated or serpentine flow configurations [15], is the that of a planar electrode in contact with a fluid flowing over its surface with a uniform velocity field. This uniformity is typically due to a porous medium (Darcy flow) and the reagent can reach the electrode exclusively through a diffusive path orthogonal to the electrode direction. If v is the velocity, s the thickness of the porous medium and L its length and reference is made to the pellicular regime where the residence times L/v are much lower than the diffusion times s^2/D_A, the mean electrode current can be evaluated by integrating the partial derivative system

$$v\frac{\partial C_A}{\partial z} = D_A \frac{\partial^2 C_A}{\partial y^2} \tag{C.13}$$

$$z = 0, \qquad C_A = C_{Ao} \tag{C.14}$$

$$y = 0, \qquad -D_A \frac{\partial C_A}{\partial y} = k_o C_A \tag{C.15}$$

$$y \to \infty, \qquad \left[\left(\frac{D_A L}{v}\right)^{1/2} \ll y < s\right], \qquad C_A = C_{Ao} \tag{C.16}$$

In particular, the last boundary condition corresponds to the reference to a semi-infinite medium, which is fully coherent with the pellicular regime assumption.

The operations of integration and calculation of the mean flux towards the electrode, after having defined the flow dynamic and transport constant as

$$k_f = \frac{vs}{L}, \quad k_c = \frac{D_A}{s}, \quad \left(\frac{k_c}{k_f} \ll 1\right) \tag{C.17}$$

yield [16,17], for the apparent constant,

$$k_a = \left(\frac{4k_f k_c}{\pi}\right)^{1/2}$$
$$- \frac{k_f k_c}{k_o}\left\{1 - \exp\left(\frac{k_o^2}{k_c k_f}\right)\text{erfc}\left[\frac{k_o}{(k_c k_f)^{1/2}}\right]\right\} \tag{C.18}$$

When $k_o/(k_c k_f)^{1/2} \gg 1$ (transport controlling) the preceding Eq. (C.18) can be written

$$k_L = \left(\frac{4k_f k_c}{\pi}\right)^{1/2} \tag{C.19}$$

so that, by eliminating k_c between Eqs. (C.18) and (C.19)

$$k_a = k_L - \left(\frac{\pi k_L^2}{4k_o}\right)\left\{1 - \exp\left(\frac{4k_o^2}{\pi k_L^2}\right)\text{erfc}\left[\left(\frac{4k_o^2}{\pi k_L^2}\right)^{1/2}\right]\right\} \tag{C.20}$$

The characteristic asymptotic constant can so be obtained from Eq. (C.20) so that

$$c_o = \frac{8}{3\pi} = 0.849$$
$$c_L = \frac{4}{\pi} = 1.274 \tag{C.21}$$
$$d_\# = \left(\frac{\sqrt{2}}{2}\right)\left[1 - \left(\frac{\pi}{2}\right) + \left(\frac{\pi}{2}\right)\exp\left(\frac{4}{\pi}\right)\text{erfc}\left(\frac{4}{\pi}\right)^{1/2}\right] = 0.05$$

where the asymptotic solution with controlling kinetics $(k_o/k_c \ll 1)$ requires a series expansion of both the exponential and the error functions, while for the transport controlling solution $(k_o/k_c \gg 1)$ the well known approximation $\exp(x^2)$ $\text{erfc}(x) \approx 1/(\sqrt{\pi}x)$ for $x \gg 1$ is sufficient.

It is worth noting here that a non-controlling feed rate condition is encountered $(k_c/k_f \ll 1)$, where the reference values (B.10) should be expected to be correct, while Eq. (C.21) and Fig. C.3 show the necessity of a certain, non-negligible correction. In particular, the first equation in (C.21) indicates that the simple electrode solution needs a correction by means of a coefficient c_o less than unity even in the low current field.

Naturally, Eq. (C.18), as well as the other derived Eqs. (C.19)–(C.21), fail when the feed-rate limitations begin to act, that is the ratio k_c/k_f increases until it becomes comparable with or even greater than unity. The complete solution for all the values of $k_c/k_f = D_A L/vs^2$ can be found in specialised books [17]; here it is sufficient to note that for $k_c/k_f \gg 1$ the semi-infinite layer hypothesis is no longer realistic and the diffusion acts throughout all the layer thickness, so that other solutions become sufficiently accurate instead of the one presented in this section, for instance those discussed in [16] or that of the preceding section for a transversally well mixed flow. For instance, Eq. (C.18), just as in the preceding example, also tends to finally be reduced to

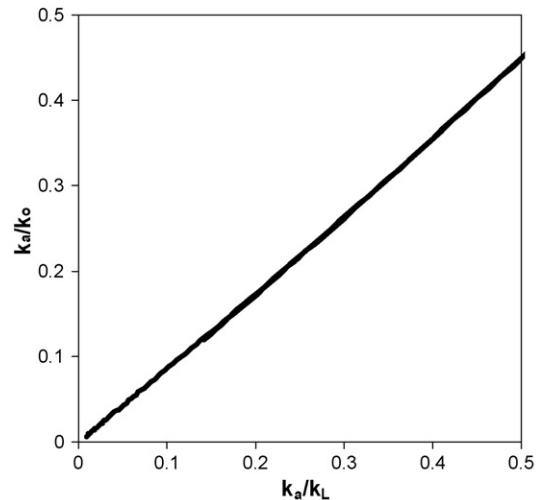$$k_c/k_f \gg 1, \quad k_o > k_c, \qquad k_a = k_L = k_f \tag{C.22}$$

Fig. C.3. Uniform velocity electrode. *XY plot for $k_c/k_f \ll 1$.*

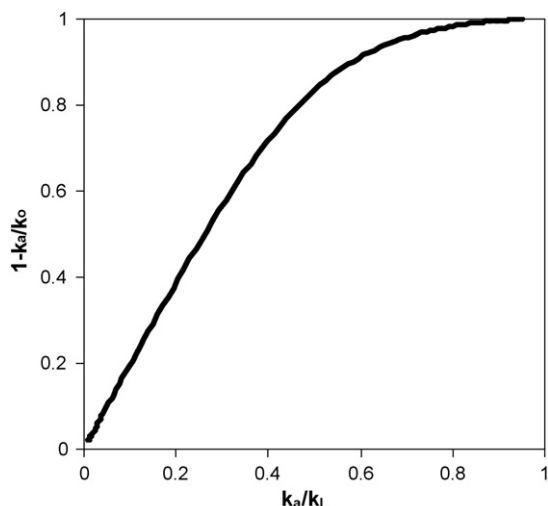Fig. C.4. Porous electrode, local behaviour. *XY* plot for $s_p D_{Aeff}/s_{ex} D_{aex} = 3$.

C.4. A local example

The examples in subsections C1 and C2 refer to effects at the electrode scale, for instance a "postcard" laboratory electrode. In subsection C3 attention is shifted to a level which is more properly classifiable as an aggregate scale: for instance, the considered flow pattern interests a small porous region, 1 or 2 mm in length and one or two tenths of a millimetre in thickness, between two adduction channels of an interdigitated PEMFC. However, in all these examples, the diffusion and reaction paths are considered to take place strictly in series.

On the other hand, from a local point of view, the porous structure of an electrode may act by combining diffusion and reaction in a series-parallel mechanism. Here the scale considered is the one of the thickness of an electro-catalytic layer, that is, typically, less than 100 μm.

In such instances, a rough and non-univocal local description can do reference to an external diffusive layer, corresponding to the external transport coefficient

$$k_{cex} = \frac{D_{Aex}}{s_{ex}} \tag{C.23}$$

and to an internal reaction affected by diffusion, which can be treated in terms of the effectiveness factor φ and the Thiele module Φ

$$k_{oeff} = k_o \varphi = k_o' a_p s_p \varphi, \quad \varphi = \frac{\text{tgh}\Phi}{\Phi}, \quad \Phi = s_p \left(\frac{k_o' a}{D_{Aeff}}\right)^{1/2} \tag{C.24}$$

The apparent constant is then

$$\frac{1}{k_a} = \frac{1}{k_o \varphi} + \frac{1}{k_L}, \quad k_L = k_{cex} \tag{C.25}$$

and, between the low current range, where kinetics is controlling ($k_a = k_o$), and the high current range, where the external transport is controlling ($k_a = k_L$), there may be an intermediate range where both internal diffusion and reaction act through the geometrical mean $k_a = (k_o D_{Aeff}/s)^{1/2}$.

Moreover, due to the series-parallel mechanism, the sum of the diffusive resistances decreases with increasing current, so that the *X–Y* plot lies over the square diagonal (see Fig. C.4).

Such effects will combine with the effects acting on the other scales, so that an exhaustive separation and identification of the various effects could prove to be extremely difficult.

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