BATTERIES, IDENTIFIED FRACTAL OBJECTS

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Summary

We interpret the dependence of a battery's capacity upon the rate of discharge (Peukert's law) as the consequence of the fractality of the cell electrodes characterized by their fractal dimension. The exponent in Peukert's equation may be obtained using several experimental procedures, one of which is a method of renormalisation of galvanostatic discharge curves.

Introduction

It is well known that the efficiency of electrochemical batteries at different rates of discharge depends on both chemical processes and the geometry of the electrodes. These two factors are intimately connected and their effects are not easily separated. Several advanced models are available to describe the coupling between them.

These models currently pertain to a simple reaction which takes place in ideal porous electrodes and requires several empirical parameters. The profusion of these parameters and the need to adjust them in order to obtain convergent solutions necessitates the use of a computer. These models are useful for predicting the discharge behaviour of idealised systems but are of limited value for practical cells.

It can be shown that the application of the TEISI model (Transfert d'Energie sur Interface à Similitude Interne) [1 - 3] in the framework of the fractal geometry [4] to this problem — see also ref. 10 — allows the coupling between the discharge curves and the geometry of the electrodes to be described in a relatively simple manner.

Fundamental properties of galvanostatic discharges

The discharge of an electrochemical cell may be carried out in several ways (*i.e.*, constant load, constant current, constant power). In this note we focus our attention on constant current discharge.

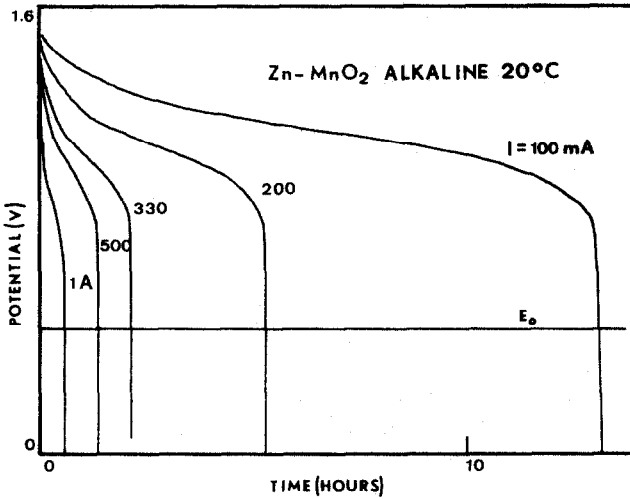
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Fig. 1. Galvanostatic discharge of alkaline commercial R6 batteries at 20 °C.

The temptation to treat the galvanostatic response of an electrochemical system as the linear response to a step of current is strong. An examination of standard discharge curves under constant current conditions (potential *versus* time), however, renders such a proposal untenable, as may be seen from the typical discharge curves shown in Fig. 1.

A discharge curve generally exhibits three distinct regions:

— an instantaneous potential drop;

— a smooth potential decrease;

— a final rapid potential drop.

The last potential drop represents a non-linear process (crystallization, species depletion ...) and is of particular interest to battery makers since it signals the end of the useful discharge.

It is also clear that no single transfer function — connecting the voltage (or output of the system) to the current (or input) — can lead to this characteristic voltage. In consequence, responses to two different current densities may not be deduced from each other in a simple way. One concludes that the system is not linear in terms of current (I) and voltage (E) and, although they are the parameters usually measurable, they cannot be used in linear theories. We show, however, that a way exists of applying linear system techniques to this problem in order to break away from the local kinetic parameters of the medium. The irreversible kinetics in porous media display, especially in their electrochemistry, some invariants to which a meaning must be found.

An example of an experimental invariant is given by the well-known Peukert's law [5], that capacity is inversely proportional to the current density to a power n. Let C designate the total capacity obtained under cur-

rent I from time $t = 0$ to the time $t = t_0$ where the potential reaches a given value E_0 (Fig. 1). We have:

$$C = It_0$$

The quantity C is a decreasing function of the current density and is known to behave according to Peukert's law [5]:

$$C = C_{st}I^{-n} \tag{1}$$

where C_{st} is a parameter of the battery depending on E_0. In the case of lead–acid batteries, several studies [5 - 7] have shown that n is close to 0.4. With $n = 0$, the battery behaves ideally according to the Faraday balance; with $n = 1$, eqn. (1), known as Sand's law, is characteristic of diffusion limited discharge on a planar interface. Figure 2 shows that the data of Fig. 1 fit eqn. (1) with $n = 0.38$, E_0 being taken equal to 0.
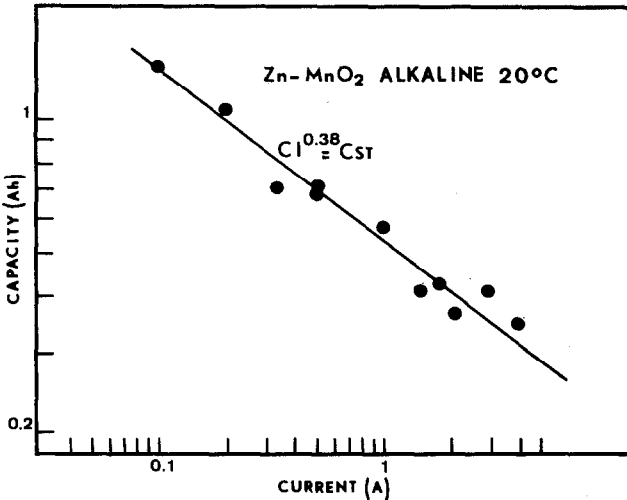

Fig. 2. Peukert's law ($E_0 = 0$) for discharges obtained in Fig. 1.

Moreover, it may be shown that Peukert's exponent, n, is insensitive to the cut off value, E_0, provided that the discharge curves have been corrected for ohmic voltage drop. Equally, a particular constant current discharge curve (I_1) may be superposed on another curve at constant current (I_2) by a transformation of the t axis in the ratio $(I_1/I_2)^n$, together with a translation along the E axis to take the instantaneous potential drop into account. One may also plot E versus $\log(t)$ for different current densities and check that the curves are translated from one to another by a factor along the t axis of $n[\log(I_1) - \log(I_2)]$.

Figure 1 was transformed in this manner by using the $I = 100$ mA curve as a reference; the result is shown in Fig. 3.
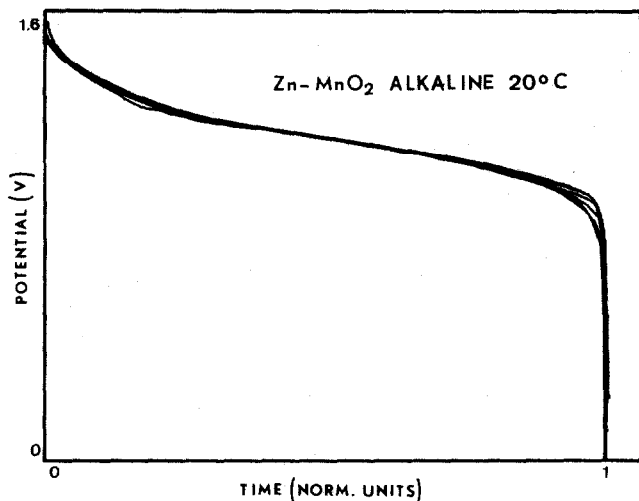
Fig. 3. Normalized discharge curves from Fig. 1.

By using a particular curve as a reference, one may take the complexity of the reaction into account without any knowledge of it. We may even totally disregard chemical kinetics, since it can be shown that n does not depend on them.

The easiest way to prove the accuracy of this assumption is to modify the kinetics of the chemical reactions. Consider the discharge curves of batteries identical to those of Fig. 1 when lowering the temperature from 20 °C to −40 °C. We thereby alter the various reactions and/or mass transport kinetics, as evidenced by a comparison of the shapes of the discharge curves. The superposition principle, however, still applies with a roughly unchanged Peukert's exponent (Figs. 4 and 5).
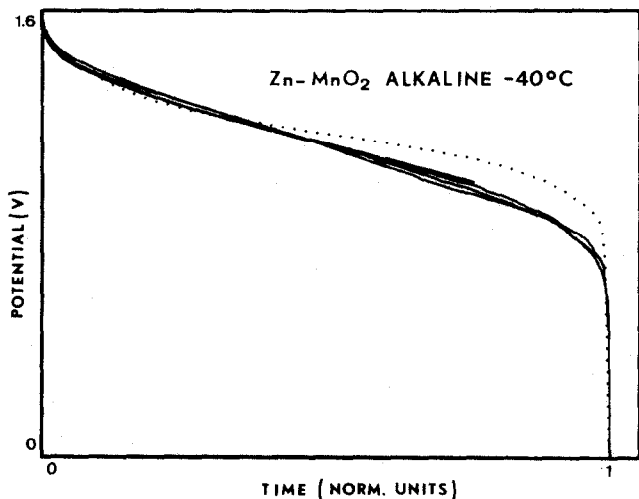

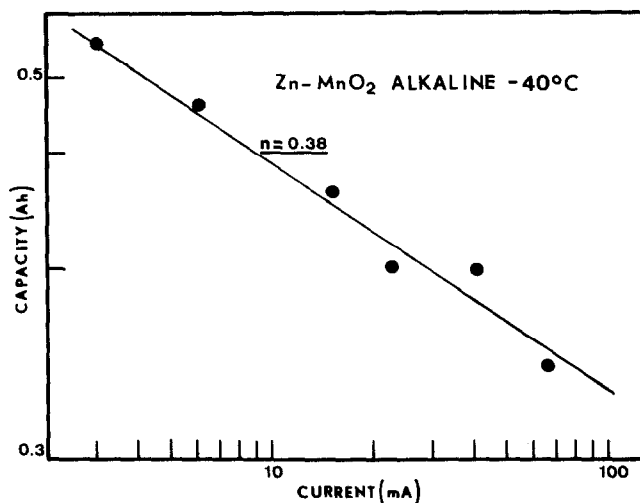Fig. 4. Normalized discharge curves of alkaline R6 batteries at −40 °C.

Fig. 5. Peukert's law ($E_0 = 0$) for R6 alkaline batteries at −40 °C.

These facts are general and were checked on various electrochemical systems (either macro or micro, organic or mineral, solid or liquid ...). The experimental conclusion is that the origin of Peukert's law should be found in the invariance of the geometry of the system.

It might be thought that we observed diffusion in a porous media, although one would expect n to be larger than 1 (the planar diffusion case). Most of the systems, however, exhibit, at higher rates of discharge, a second slope much larger than the first one, corresponding to a second exponent $m > 1$. The shapes of the discharge curves are also distorted and one can only superimpose curves associated with the same exponent. The capacity diagrams are then composed of three domains (Fig. 6). At the lowest
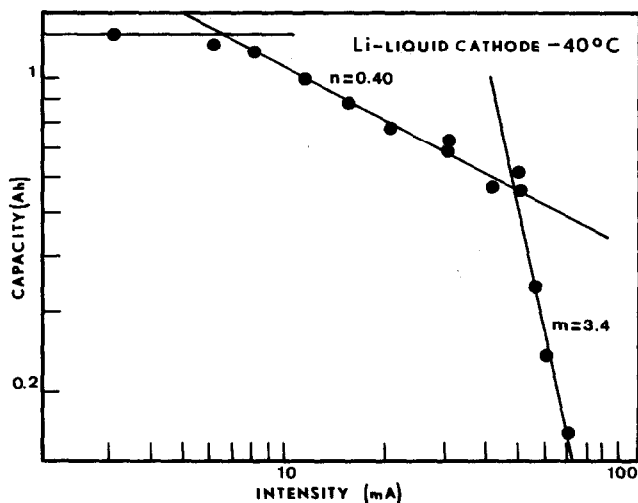

Fig. 6. Capacity diagram ($E_0 = 0$) for commercial Li–liquid cathode batteries at −40 °C.

regimes, the capacity is nominal and independent of current density but, at intermediate regimes,

$$CI^n = C_{st} \qquad (0 < n < 1)$$

and, at highest regimes,

$$CI^m = C_{st} \qquad (1 < m)$$

We demonstrated, in the same manner as for n, that m is independent of the local chemical kinetics.

A fractal interpretation for Peukert's law

We give here arguments according to which n is related to the non-integer dimension of the electrode and determined only by its fractal character.

Let us consider a linear charge transfer upon an Euclidian interface controlled by a change of the electrochemical potential of the reactive species $\mu(t)$.

It is well known that the linear thermodynamic transfer function, determined by the double layer and the exchange current, is given by:

$$F(\omega) \propto \frac{1}{1 + i\omega\tau} \tag{2}$$

The thermodynamic response to a pulse excitation $\delta(t) = 1$ for $t = 0$, is then given by:

$$\Phi(t) \propto \exp(-t/\tau)$$

Le Méhauté has shown [1 - 3] that porous electrodes may often be considered as fractals, that is to say characterized by a non-integer fractal dimension d $(2 \leqslant d \leqslant 3)$. The thermodynamic response of the electrode is then written as a convolution product between fractal geometry and the local kinetics. As a result, the following thermodynamic transfer function is found in place of eqn. (2):

$$F(\omega) \propto \frac{1}{1 + (i\omega\tau)^{1/d_a}} \qquad d_a = d - 1 \tag{3}$$

where the constant 1 in the denominator signifies some proximity with equilibrium or stationary state, as in the case of impedance measurements. According to these hypotheses, the response to a pulse is given by [8]:

$$\Phi(t) \propto 1/\tau \sum_{n=0}^{\infty} \frac{(-1)^n \tau^{\alpha(n+1)} (t/\tau)^{\alpha(n+1)}}{\Gamma(1 + \alpha(n+1))}$$

Let us now consider the application of a constant current density I at the electrode. We shall hypothesise that the local thermodynamic intensive

parameter governing the electrode polarization (for instance, the electro-chemical potential) is related to the current by the mean of a transfer function such as eqn. (3), although one cannot use the measured I and E values which we found to be inadequate linear variables in our conditions. Equation (3) gives the relationship between I and the local potential $[I\Phi(t)]$. The electrical state of the electrode is determined by the step response through an unknown function Ψ of the local potential (Ψ being Nernstian or not):

$$E(t) = \Psi[I\Phi(t)] \tag{4}$$

On the other hand, the capacity under constant current conditions is proportional to the time:

$$C = It \tag{5}$$

We now choose a value E_0 for $E(t)$. From eqns. (4) and (5), and for all values of I we have:

$$E_0 = \Psi[I\Phi(C/I)]$$

that is to say:

$$I\Phi(C/I) = C_{st} \tag{6}$$

As pointed out above, the use of 1 in eqn. (3) implies some proximity to equilibrium. It expresses the existence of a transfer resistance. This resistance is not a constant for large current densities, but is an exponentially increasing function of it. For this reason, we shall hypothesise that the local kinetics of the electrode are no longer governed by eqn. (3), but by a transfer function of the form:

$$F(\omega) \propto \frac{1}{(i\omega\tau)^{1/d_a}}$$

then:

$$\Phi(C/I) \propto (C/I)^{1/d_a}$$

and, from eqn. (6):

$$CI^{d_a-1} = C_{st}$$

According to this analysis, the role of the fractal dimension may be recognised in the Peuckert's law (Figs. 2, 5) with:

$$n = d_a - 1 = d - 2 \tag{8}$$

Two comments should be made:
— Peukert's law is obtained whatever the relationship (Ψ) between the electrical and the chemical potentials of the electrode. The counterpart is that $\Phi(t)$ does not allow us to determine the polarization of the electrode directly.
— The analysis is based on the assumption that the local behaviour is linear and d_a is a constant. Such an hypothesis does not hold at very long

times, when non-linear processes (crystallisation, passivation, phase transition ...) can occur.

Larger current densities involve chemical diffusion. In the academic case of semi-infinite diffusion on a planar interface, the transfer function to be used is the classical Warburg one [9]:

$$F(\omega) \propto 1/(i\omega\tau)^{1/2}$$

For a fractal electrode, this becomes [2, 3]:

$$F(\omega) \propto 1/(i\omega\tau)^{1/d_b} \tag{9}$$

where $d_b = 2(d-1)/(3-d)$

In a manner similar to that of the previous paragraph, we obtain Peukert's law in the diffusion case:

$$CI^m = C_{st}$$

$$m = d_b - 1$$

$$m = (3d-5)/(3-d)$$

the exponents n and m are then related by:

$$m = (3n+1)/(1-n) \tag{10}$$

This last relation is in good agreement with experimental data on various systems, as shown in Fig. 6. The difficulty with experimental measurements in the diffusion regime must, nevertheless, be stressed (especially thermal effects at high rates).

Fundamental properties of non-galvanostatic responses

Galvanostatic discharge is only one particular type of transient response. Many other experimental electrochemical methods may be extended in the same way to heterogeneous materials. We give two examples.

(i) Current step relaxation

In the case of relaxation, one applies a current step for a time, t_1, and then allows the system to rest for a time, $t_r > t_1$; for a linear system, the relaxation curve is symmetric to the discharge curve. In our case, both curves are related through Peukert's exponent in a more complicated way, allowing a direct determination of the exponent. Let us denote E_d the potential for the discharge at time t_d and $E_{(r+1)}$ the relaxation one at time $t_1 + t_r$ (both corrected for ohmic drop: see Fig. 7). Using the linear properties of Φ, we can write:

$$E_d = \Psi[I\Phi_d]$$

$$E_{(r+1)} = \Psi[I\Phi_{(r+1)} - I\Phi_r]$$

When the potentials are equal, we get:
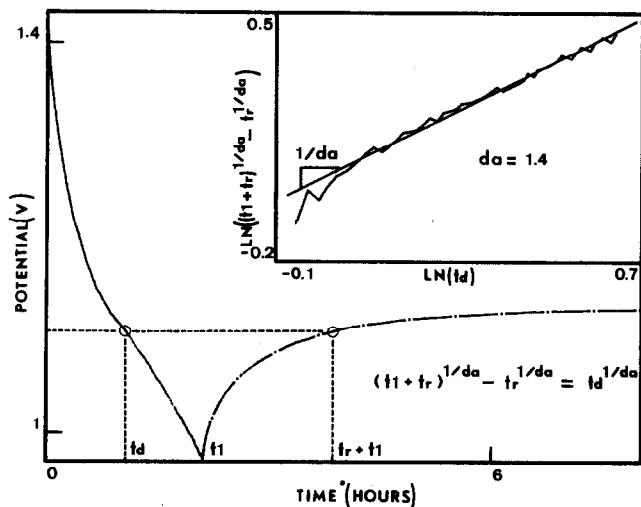
$$\Phi_d = \Phi_{(r+1)} - \Phi_r \tag{11}$$

Fig. 7. Discharge at $I = 300$ mA and relaxation (ohmic drop corrected) of an alkaline R6 battery at 20 °C. Inset: numerical determination of d_a using lower formula ($d_a = 1.4$ to be compared with $d_a = 1.38$ as determined by eqn. (8) and data of Figs. 2 and 5).

for both diffusion and transfer far from equilibrium:

$$\Phi(t) \propto t^{1/d_a - 1}$$

eqn. (11) then becomes:

$$(t_1 + t_r)^{1/d_a} - t_r^{1/d_a} = t_d^{1/d_a} \tag{12}$$

d_a was calculated in Fig. 7 by determining the best fit to this relation for large t_d and found to be compatible with Peukert's exponent value as found in Fig. 2. We stress that one should only use such a method when the ohmic drop is constant over the discharge.

(ii) Cyclic voltametry

The dependence upon the sweep rate voltage of the peak current for linear sweep voltamperometry on a planar interface is known to be quadratic:

$$I^2 \propto v$$

For a rough interface, we expect the result to be different.

Generally, the local parameter $\mu(t)$ is given by a convolution product:

$$\dot{\mu}(t) = i(t) * \dot{\Phi}(t) \tag{13}$$

where $i(t)$ designates the current sequence through the electrode. Under the same hypothesis as for eqn. (4):

$$\mu(t) = \Psi^{-1}[E(t)]$$

then, using eqn. (13):

$$\Psi^{-1}[E(t)] = i(t)^*\dot{\Phi}(t)$$

In the case of a linear potential sweep, $E(t) = E^0 + vt$:

$$\Psi^{-1}[vt] = i(t)^*\dot{\Phi}(t)$$

taking the Fourier transform of this last equation, we get:

$$\tilde{i}(s) = 1/v\tilde{\Psi}^{-1}(s/v)1/s1/\tilde{\Phi}(s) \qquad (s = i\omega)$$

taking Φ as $\Phi(t) \propto t^{1/d_a - 1}$

$$\tilde{i}(s)v^{1/d_a} \propto \frac{1}{v}\ \Psi^{-1}\left(\frac{s}{v}\right)\ \frac{s^{1/d_a - 1}}{v^{1/d_a}}$$

$$i(t) \propto [\Psi^{-1}(vt)^*(1/vt)^{1/d_a}]v^{1/d_a} \sim v^{1/d_a}$$

When Ψ is such that $i(t)$ is maximised, the amplitude of the maximum depends on v^{1/d_a}. Then the peak current and the sweep rate are related by:

$$I^{d_a} \propto v$$

It is then possible to get the value of the Peukert's exponent from potentiodynamic peaks. Figure 8 shows that the positive electrodes used by the batteries, Fig. 1, in alkaline media exhibit a sweep rate dependence in good agreement with $d_a = 1.38$ as found in Fig. 2.
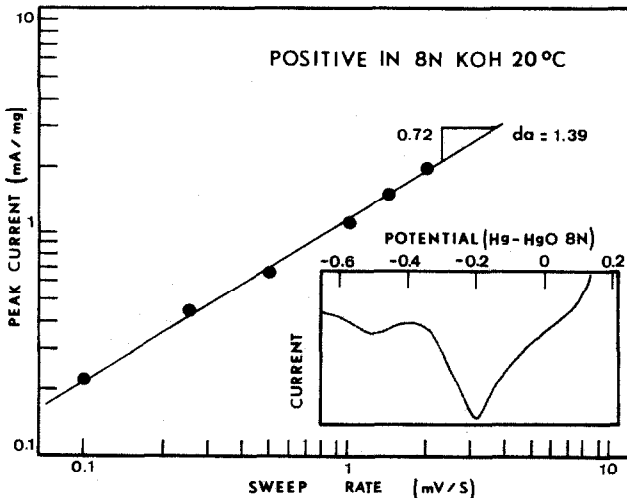

Fig. 8. Linear sweep voltamperometry on positive electrodes built with the manganese dioxide used in alkaline R6 batteries (free electrolyte).

Conclusion

Using the conclusions of the TEISI model, and assuming linear local behaviour during discharge, we have linked the Peuckert's exponent to the
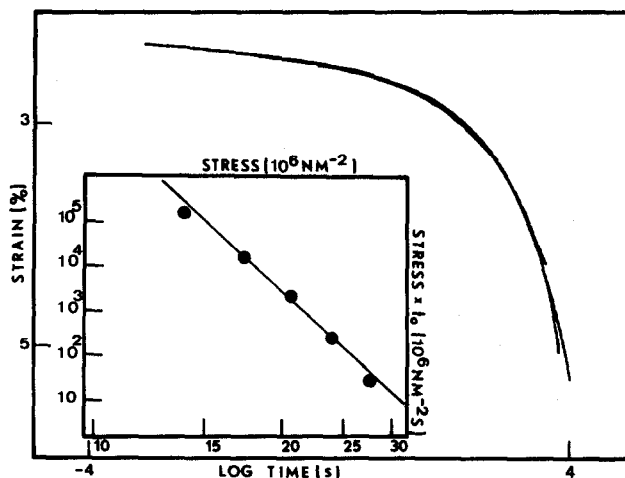
Fig. 9. Normalized creep curves for PVC. Inset: "Peukert's diagram" from these data. The results suggest diffusion of chains in a fractal media with $d = 2.8$. This value is consistent with the behaviour currently observed in linear viscoelasticity [11, 12].

heterogeneity of the electrodes. Various transient experimental procedures may be used to determine this exponent and bear out the linear hypothesis. This, and advanced theoretical aspects, are discussed elsewhere [10].

This procedure is not limited to electrochemical systems. Transfer functions such as eqns. (3) and (9) are currently observed in other fields of physics [11] and the conclusions may also apply to these systems as well, as shown in Fig. 9 for the case of polymer creep.

List of symbols

I	Intensity
E	Electrical potential
t	Time
t_0	Referenced time
E_0	Referenced potential
C	Faradic capacity
C_{st}	Constant depending on E_0
n	Peukert's exponent in the transfer regime
m	Peukert's exponent in the diffusional regime
I_1	
I_2	Referenced intensities
$F(\omega)$	Transfer function
ω	Frequency function (= $2\pi f$]
$\Phi(t)$	Relaxation function
d	Fractal dimension

d_a	Apparent dimension $[= (d - 1)]$
d_b	Diffusion index $[= 2(d - 1)/(3 - d)]$
τ	Characteristic time
Γ	Gamma function
Ψ	Thermodynamic function giving the electrical polarization of the electrode against thermodynamic local parameter
E_d	Potential during discharge
E_r	Potential during relaxation
t_d	Time during discharge
t_r	Time during relaxation
t_1	Duration of the current pulse
v	Potential sweep rate
μ	Thermodynamic local parameter (concentration, activity...)
$\cdot$	Time derivation
-1	Inverse function
E^0	Initial potential for linear voltametry
s	Laplace variable ($s = i\omega$)
$\sim$	Fourier transform

References

1 A. Le Méhauté and G. Crepy, *C.R. Acad. Sci.*, *294* (1982) 835.
2 A. Le Méhauté and G. Crepy, *Solid State Ionics*, *9 - 10* (1983) 17.
3 A. Le Méhauté, *J. Stat. Phys.*, *36* (5 - 6) (1984) 665.
4 B. Mandelbrot, *The Fractal Geometry of Nature*, Freeman, San Francisco, 1977.
5 W. Peukert, *Electrotech. Z.*, *18* (1897) 287.
6 P. E. Baikie, M. I. Gillibrand and K. Peters, *Electrochim. Acta*, *17* (1972) 839.
7 M. I. Gillibrand and G. R. Lomax, *Electrochim. Acta*, 8 (1963) 693.
8 A. Le Méhauté, L. Picard and L. Fruchter, *Philos. Mag.*, *52* (6) (1985) 1071.
9 A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York, 1980.
10 A. Le Méhauté, L. Fruchter and G. Crepy, Colloque sur les fractales, *Ann. Centre International de Rencontres Mathematiques*, Marseille, 1986.
11 G. Marin, *Thesis*, Univ. Pau, 1977.
12 L. Fruchter, *Rapport de D.E.A.*, Univ. Paris VI.