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Gas film formation time and gas film life time during electrochemical discharge phenomenon

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ABSTRACT

The formation of a gas film around an electrode is at the origin of the electrochemical discharges in aqueous solutions and in molten salts. The study of the electrochemical discharge phenomenon from the current signal point of view is conducted to identify the gas film formations and the following discharges. This is performed using the wavelet analysis as a denoising tool with the discrete Meyer wavelet as base function. The proposed algorithm allows to measure experimentally the gas film life time and its necessary building time prior to each series of discharges. The accuracy of the algorithm is evaluated using generated signals and its application to real data is demonstrated. From the experimental data, it is concluded that the gas film is more stable at high terminal voltages whereas its formation time decreases with it. Electrochemical and thermal interpretations for the measured statistics are proposed.

1. Introduction

In a two-electrode configuration, the surface of the working electrode immersed into the electrolyte is seen to be covered by a thin gas film when the cell's terminal voltage is beyond a critical value, the critical voltage. Discharges across the formed gas film are generated. This later constitutes the origin of the so-called electrochemical discharges (ECD) phenomenon in aqueous solutions and in molten salts.

The discovery of the ECD goes back to the beginning of the 19th century with the work of the two French physicists, Fizeau and Foucault [1]. In 1899 the German physicist Wehnelt [2] developed a first technical application by presenting his high frequency current interrupter leading to multiple applications. ECD have been rediscovered in the middle of the 20th century with the works of Kellogg [3] about the anode effect in molten salts and the one of Hickling and Ingram [4] about the unconventional electrolysis process known as Contact Glow Discharge Electrolysis (CDGE). These contributions raised the interest of ECD in chemical applications. Investigations about the electrode wettability and the hydrodynamic parameters influencing the anode effect were done recently by Vogt [5,6]. The formation time of the gas film covering the electrode has been studied by Wüthrich et al. [7,8] who have also demonstrated its importance during micro-machining using ECD [9]. Latest application developed for ECD is the synthesis of metallic nanoparticles [10].

So far no quantitative studies about the gas film stability were done. In particular the mean life time of the gas film was never characterised. Increasing the knowledge in this field would have interesting applications in CGDE, micro-machining applications as well as nanoparticle fabrication. For example, it is known that discontinuities in machining and structure quality are correlated to the gas film instability [9]. Studying the statistical distribution of the gas film life time could as well give new insights in the processes responsible for its stability–instability behaviour.

To conduct such studies one needs reliable signal processing algorithms which would allow the proper identification of the various gas film formation peaks in the current signal. Due to the stochastic nature of the current response, it is primary to make sure that the signal's time and frequency views are not altered by the applied algorithmic steps. Furthermore, probability distributions of the time characteristics of the gas film, its formation time and its life time, are also of interest as they may contain valuable information about the physics behind the gas film formation mechanism. The aim of this paper is to present and characterise such an algorithm. Its reliability and efficiency are verified by firstly applying the algorithm to different simulated signals. Application to real signals is presented as well.

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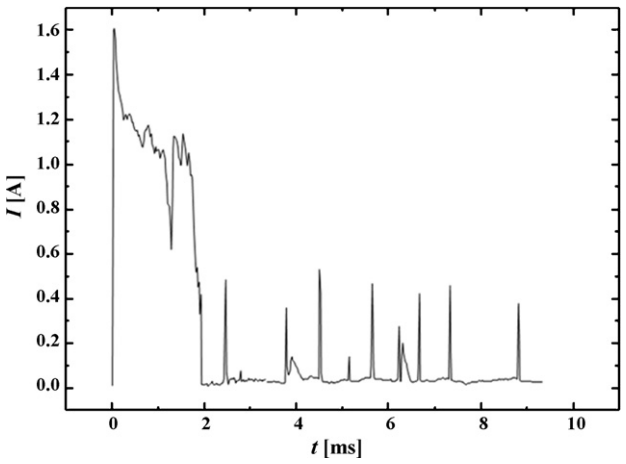

Fig. 1. A typical current signal for a 172 μm diameter stainless steel 316 L cathode for a voltage step input of 30 V at $t = 0$ ms. The large time period shape in the signal characterises the gas film formation while the high frequency pulses characterise the electrochemical discharges.

2. Algorithm

2.1. Current signal during electrochemical discharges

While acquiring the current in function of time during the electrochemical discharge phenomenon, one can identify the gas film formation prior to each series of discharges (Fig. 1) [11]. The signal is stochastic and therefore its description and interpretation becomes challenging. Indeed, the gas film formation and the ECD have non-constant magnitudes, formation times and frequencies. The aim is to present an algorithm able to determine the time period between each two successive gas film formations in the current–time signal. The analysis of the time duration that a gas film takes to be built is also of interest. Thus, a precise identification of the gas film formation should be preceded by filtering out the ECD pulses. The second constraint is to keep the low frequency part of the signal without the loss of information about the time- and frequency-based views. Descriptive statistics of the gas film formation time and life time can provide valuable information about its stability and instability so it should constitute a part of the presented algorithm.

Approximation using superposition of functions has existed since the early 18th century, when Joseph Fourier discovered that functions can be represented using the superposition of sinus and cosines. The bases of Fourier analysis are non-local functions and therefore are not very accurate in sharp discontinuities approximation. On the contrary, the wavelet analysis uses mother wavelets that are contained neatly in finite domain and one can look at the signal with large and small windows according to different scales or resolutions. Wavelet algorithms for temporal analysis are performed with a high frequency version of the base function, while frequency analysis is performed with a low frequency version of the base function. This property is the major point why to use the wavelet analysis in the algorithm knowing that the gas film formations will represent the low frequency part of the signal (typical formation times are about a few milliseconds [12]) while the ECD will represent its high frequency part (typically one to two order of magnitudes shorter than the gas film formation [12,13]). Other issues are that the gas film formation is subjected to large fluctuations and consequently applying simple low-pass filtering method will deform the original signal. ECD have various amplitudes which excludes the option of using a global threshold for the signal.

2.2. Wavelet transform of the current signal

Considering the family of functions $\mathbb{R}$ for wavelet analysis $g_{p,a}(t) = (1/a)\bar{g}((t-p)/a)$ where $p \in \mathbb{R}$, $a \in \mathbb{R}_+$ with $a \neq 0$ and $\int g = 0$, the wavelet transform of a function $p \in L^i(\mathbb{R})$, $i \in [1; +\infty[$, is defined by Eq. (1) [14,15]:

$$W_g s(p,a) = \langle g_{p,a} | s \rangle = \int_{-\infty}^{+\infty} dt \frac{1}{a} \bar{g}\left(\frac{t-p}{a}\right) s(t) \quad (1)$$

The numbers $W_g s(p,a)$ are the wavelet coefficients of s with respect to the basic wavelet function g. Suppose V_j to be a multi-resolution analysis over $\mathbb{R}$ with its associated wavelet spaces W_j. The orthogonal projections of V_j and W_j are called P_{V_j} and P_{W_j} respectively. Suppose $s \in V_0$ a function over $\mathbb{R}$. One may then decompose s without the loss of information into a sequence of functions according to [15]:

$$s_{LF}^{(j+1)} = P_{v_{-(j+1)}} s_{LF}^{(j)} \text{ and } s_{HF}^{(j+1)} = P_{w_{-(j+1)}} s_{LF}^{(j)} \text{ with } s_{LF}^{(0)} = s \quad (2)$$

At each step the low frequency part or approximation $s_{LF}^{(j)}$ is split into a part with lower frequencies or details $s_{LF}^{(j+1)}$ and a part with high frequencies $s_{HF}^{(j+1)}$ that have been dropped by passing from j to $j+1$. This is an orthogonal decomposition scheme of a one-dimensional function s. The reconstruction of the original signal from the different approximations and details obtained at each step of the decomposition procedure is obtained by addition (Table 1).

To avoid non-necessary large size data resulting from the continuous wavelet transform, the above algorithm has been conducted using the discrete wavelet transform and inverse transform using

Table 1
List of symbols.

Notation	Unit	Interpretation
A	m^2	Electrode geometrical surface
β	m^3/A	Coefficient of Faradic gas generation
$(\Delta t_b)^{-1}$	Hz	Mean detachment frequency of bubbles
$\hat{f}$		Fourier transform of the function f
j_{local}	A/mm^2	Local current density
HF		High frequency
$L^i(\mathbb{R})$		Set of signals of finite energy i.e. $\|\|s(x)\\| < \infty$ (infinite-dimensional Hilbert space)
LF		Low frequency
λ	ECD/ms	Poisson parameter
h_b	m	Mean bubble height
N	$1/m^2$	Mean number of nucleation sites per electrode surface
p		Position or translation
p_c		Percolation threshold
R^{bulk}	Ω	Inter-electrode resistance in the bulk region
$\mathbb{R}_+$		Set of positive real numbers
s		Cluster size
σ^2	ECD/ms	Variance of a random variable
$\langle s \mid s' \rangle = \int_{-\infty}^{+\infty} s(x)s'(x)dx$		Scalar product of s and s' over $\mathbb{R}$
$\sum_{s=0}^{s^{max}} s n_s(\theta)$		The fraction of nucleation sites covered on the surface by the growing gas bubbles able the leave the electrode
θ		Mean bubble coverage fraction of gas evolving electrodes
U_d	V	Water decomposition potential
V_b	m^3	Mean volume of a bubble growing on a nucleation site at the moment of coalescence with its neighbouring bubbles
$\langle x \rangle$		Mean value of the elements of the vector x
Δ	sec	Time interval between two successive gas film formation maxima
T_f	sec	Gas film life time
T_g	sec	Gas film formation time