Effect of positive and negative pulse voltages on surface properties and equivalent circuit of the plasma electrolytic oxidation process

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ABSTRACT

The paper discusses a methodology for the equivalent circuit design for the plasma electrolytic oxidation (PEO) process from the voltage and current waveform transients recorded during pulsed bipolar PEO treatment. Joint analysis of the coating morphology and the electric transients enabled the proposal of an equivalent circuit with elements corresponding to characteristic parts of the system — electrolyte, porous and dense coating layers, showing different behaviours at anodic and cathodic polarisations of PEO. Two thresholds based on the sparking voltage for a positive pulse and on the minimal resolved current for a negative pulse were introduced to draw the boundaries for the application of the circuit structures. The simplest equivalent circuit corresponds to lower positive and negative pulse voltages ($U_p < 526$ V, $U_n < 20$ V); it comprises a linear parallel RC branch corresponding to the thinnest coating in series with the electrolyte resistance. For higher negative voltages ($U_p < 526$ V, $U_n > 20$ V), the anodic and cathodic branches become separated due to different coating behaviour under positive and negative polarisations. The RC branch represents the anodic behaviour of a thinner porous single layer coating, and the RL branch describes the cathodic response. For higher positive and negative voltages ($U_p > 526$ V, $U_n > 20$ V), the PEO microdischarges become stronger, and the anodic branch evolves into two RC loops connected in series in order to represent heterogeneity developed in the coatings containing porous outer and dense inner regions. The fact that the equivalent circuit elements evolve with the coating growth enables assessment of the coating thickness *in-situ* during the PEO treatment. Finally, the equivalent circuit modelling methodology can contribute towards design of advanced PEO equipment with power supplies optimised to the electrolyser properties depending on the treatment conditions and with diagnostic instruments providing *in-situ* estimates of the coating properties.

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1. Introduction

Pulsed plasma electrolytic oxidation (PEO) technologies are promising processes for surface modification of light alloys [1]. Being more effective and environmentally friendly than their conventional electrochemical analogues, they suffer from lack of understanding of the process mechanism, which restraints the design of industrial scale technological equipment for PEO treatments. Despite the fact that industrial installations have recently become available, they comprise power supplies which are not optimised specifically for PEO since the equivalent circuit underlying the process mechanism has not been fully elaborated yet.

The major problem in this justification is caused by the application of high voltages (300–600 V) and high current densities (100–500 mA·cm^{-2}) [2]. Operation at these conditions leads to a generation of plasma microdischarges and vapour gaseous envelope in the vicinity of the treated surface; this makes the system's behaviour nonlinear and

requires careful control of the electric and thermal parameters required for the process [3]. In such a system, the majority of voltage drops across a thin oxide layer generally possessing *n*-type of conductivity; under anodic polarisation this leads to a reversely biased semiconductor barrier [4]. The resulting high field strength promotes a dielectric breakdown which initiates a plasma discharge within the oxide layer, facilitating its growth. Therefore, the mechanism of the plasma electrolytic oxidation involves a complex combination of electrochemical, electrophysical, plasma and metallurgical processes [5]. These can be modelled using an equivalent circuit analysis.

Several approaches can be considered when developing the equivalent circuit from experimental investigations. Firstly, DC analysis can yield a resistive network, being non-linear due to the current–voltage characteristic [3]. Early research into this topic provided series-parallel resistive equivalent circuits comprising the electrolyte resistance and conductivities of *N* individual discharges [6]. Also, a non-linear resistive circuit was proposed after current–voltage characteristic slope analysis [7].

Secondly, waveform analysis in the time domain, especially of the voltage and current transients, can yield a more advanced circuit

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Table 1
Experimental design with respect to positive and negative pulse voltages (U_p (V) — numerator, U_n (V) — denominator).

U_1 (V)	U_0 (V)			
	285	265	245	225
385	$\frac{587}{57}$	$\frac{567}{123}$	$\frac{547}{86}$	$\frac{527}{116}$
305	$\frac{525}{5}$	$\frac{505}{5}$	$\frac{485}{5}$	$\frac{465}{48}$
225	$\frac{462}{5}$	$\frac{442}{5}$	$\frac{422}{5}$	$\frac{402}{5}$

$^*U_0$ — DC bias of the voltage waveform, U_1 — implied sine wave amplitude.

because in this case the effects of interfacial double layer charging and discharging can be revealed. First attempts of a step response analysis yielded a series-parallel $R_0 + R_1 \| C$ circuit taking into account the electrolyte resistance R_0, the coating resistance R_1 and the coating capacitance C [8]. Also, AC analysis in the time domain helped to propose non-linear equivalent circuits containing resistors and capacitors for the electrolyte and the coating representations, and also diodes in order to separate different properties of the PEO electrolyte-coating system under anodic and cathodic polarisations [9]. In some cases the proposed circuit can be quite complex [10], and no techniques for identification of the circuit element values were supplied at that time.

Thirdly, frequency response analysis in the frequency domain helped to provide the electrochemical impedance spectroscopy tools for assessing the equivalent circuit [11,12]. However, the *in-situ* evaluations of the impedance spectra, even after linearisation, appeared quite complex, and a highly simplified series-parallel $R_0 + R_1 \| C$ circuit has been proposed so far, leaving this field open for further research [13, 14]. Despite yielding the simplified equivalent circuit, this approach provided a tool for estimation of the coating thickness during the PEO treatment, contributing to the development of advanced technological equipment for PEO processing [15].

As discussed above, it is clear that the waveform analysis in time domain could provide the most appropriate deconvolution of the electric signals, since it allows both charging and relaxation effects, as well as non-linearity of the process to be taken into consideration. The above ideas have been assessed recently, and it was shown that the

PEO equivalent circuit can be derived from the analysis of voltage and current transients appearing under pulse polarisation mode [16]. However, a variation of the circuit structure depending on the treatment conditions has not so far been assessed. Therefore, the aim of this work is to study the effect of pulse voltages on the structure of the equivalent circuit derived from the transient analysis of electrical characteristics of the pulsed bipolar PEO process of Al. The proposed analysis of the PEO process equivalent circuit evolution with respect to the process parameters, such as the pulse voltages and the treatment time, would contribute to development of the efficient industrial scale technological equipment, based on the deeper understanding of the coating growth mechanism and supported by *in-situ* diagnostics of the surface properties.

2. Experimental

The pulsed power supply setup for the PEO process included two Advanced Energy MDX II units for the positive and negative voltage levels, and one pulse unit SPIK 2000 which was used for combining the DC voltages into a bipolar waveform. A 2-litre water-cooled stainless steel tank with a specimen immersed into conventional silicate-alkaline electrolyte was used. The electrolyte was composed of 1 g/L KOH, 1 g/L $Na_2P_2O_7$, and 2 g/L Na_2SiO_3 dissolved in deionised water.

BS6082 aluminium alloy specimens 25 mm × 20 mm × 6 mm in size were used. Before the treatment the samples were polished to achieve the roughness $R_a = 0.15$ μm. The coating thickness was measured using an Elcometer eddy current gauge. The surface morphology was investigated using CamScan and JEOL 6400 scanning electron microscopes.

For the PEO process, bipolar pulses with positive voltages U_p ranging from 400 to 600 V and negative voltages U_n from 5 to 200 V were used according to the design of experiments [13]. The positive and negative pulses were separated with a zero pause lasting at least 5 μs. One positive and one negative pulse occurred during the period, both centred on the corresponding half-period, with duty cycle 45–55% and 20–30% respectively. To compact the experimental design, the pulse voltages and corresponding duty cycles were chosen so that the pulsed bipolar voltage $u(t)$ becomes a close approximation of an implied sine wave with a bias [12]:

$$u(t) \approx U_0 + U_1 \cdot \sin(2\pi \cdot f \cdot t), \tag{1}$$

where U_0 — DC bias of the voltage waveform and U_1 — implied sine wave amplitude.

The experimental design with respect to positive and negative pulse voltages is shown in Table 1. The details of the positive d_p and negative d_n pulse durations, pause d_0 and voltages U_p and U_n are given in Table 2.

For the data acquisition, a Tektronix digitising oscilloscope (TDS430A), high voltage (P5205A) and current (A6302) probes were used. Specially developed software *Oscope* allowed simultaneous frames of both voltage and current signals to be saved. The waveforms of length $N = 120{,}000$ samples were acquired in 8-bit resolution at sampling frequency $f_s = 250$ kHz every $\Delta t = 10$ s, in "slow" discrete time t_m, $m = 0 \ldots M$. With measurement ranges of 1000 V and 100 A, this provided 4 V and 0.4 A accuracy errors respectively, which is close to the stabilisation properties of the DC sources.

3. Results

3.1. Surface characterisation

Four conditions, corresponding to characteristic corners of the experimental design, were chosen for the analysis. They comprise higher positive and negative voltages ($U_p > 526$ V, $U_n > 20$ V), lower positive and negative voltages ($U_p < 526$ V, $U_n < 20$ V), and lower positive and higher negative voltages ($U_p < 526$ V, $U_n > 20$ V) as shown in

Table 2
Pulse parameters and coating thickness (h) for PEO of Al.

	Pulse voltages		Pulse and pause durations at frequency 50 Hz (ms)			t_m (min)	h (μm)
	U_p (V)	U_n (V)	d_p	d_n	d_0		
Higher U_p, higher U_n, fast coating growth	587	57	10.2	5.4	2 × 2.2	5	13.6 ± 1.0
						10	23.3 ± 1.6
						20	35.0 ± 2.5
						40	43.9 ± 3.1
						60	46.2 ± 3.4
	527	116	9.7	5.5	2 × 2.4	5	10.1 ± 0.7
						10	17.2 ± 1.2
						20	25.5 ± 1.0
						40	31.4 ± 1.6
						60	32.8 ± 1.2
Lower U_p, lower U_n, slow coating growth	525	5	10.9	4.1	2 × 2.5	5	3.9 ± 0.3
						10	6.3 ± 0.4
						20	8.4 ± 0.6
						40	9.3 ± 0.7
						60	9.4 ± 0.9
Lower U_p, higher U_n, slower coating growth	465	48	10.2	5.2	2 × 2.3	5	1.2 ± 0.1
						10	2.1 ± 0.1
						20	3.3 ± 0.7
						40	4.2 ± 0.8
						60	4.5 ± 1.0