Relaxation Kinetics of Plasma Electrolytic Oxidation Coated Al Electrode: Insight into the Role of Negative Current

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Abstract: Plasma electrolytic oxidation (PEO) is an advanced coating process based on high-voltage anodizing. Notwithstanding the anodic nature of the PEO process, it is known that negative polarization leads to synergetic effects in oxide formation efficiency and characteristics of resulting coatings. In this work, we used dynamic anodic voltammograms derived from polarization signal, combining working and diagnostic segments to evaluate in real time the effects of negative polarization on the formation of PEO on the coating on Al in the bipolar regime with a frequency of 50 Hz and a negative-to-positive charge ratio of 1.3. It was found that the hysteresis between ascending and descending branches of the voltammogram can be both caused by prior cathodic polarization and spontaneously generated under unpolarized conditions. This indicated the existence of a quasi-equilibrium in the chemical state of the coating material, which could be perturbed by the external bipolar polarization. The characteristic relaxation time for this system was found to be 40–370 ms. The quasi-equilibrium was attributed to a reversible hydration/dehydration reaction taking place in the active zone of anodic alumina layer (degree of hydration: 10–40%). Coating response analysis via kinetic hydration model allowed both explanations to be provided to a number of previous experimental observations and practical recommendations to be made for the design of efficient electrical regimes for intelligent PEO processes. The latter includes recommendations on avoiding long pauses during negative to positive switching.

1. INTRODUCTION

Electrochemical surface treatments are particularly well suited for smart manufacturing since they are driven by electrical signals that can also be used for the monitoring of the results of such treatments. On-demand fabrication of bespoke products tailored to a particular application, which lies in the core of modern smart factory concepts, relies upon a comprehensive model of the process and a bidirectional physical interface which can monitor and adjust processing conditions in situ to achieve the target functionality in accordance with Industry 4.0 strategy.

One of the most advanced examples of electrochemical conversion techniques is plasma electrolytic oxidation (PEO)—a high-voltage process utilized for anodic conversion of the surfaces of valve metals (Mg, Al, Ti, Zr, Nb, and Ta) into ceramic-like oxide layers. In contrast to conventional anodizing, anodic polarization between 300 and 700 V is typically employed in PEO. Together with enabling conventional anodic reactions, high energy density provided by the high-voltage polarization to the growing oxide layer causes its dielectric breakdown and thermal and plasma chemical effects, influencing the layer microstructure and phase composition. The resulting coatings are often hard, dense, crystalline, and well adhered to the metal substrate. They show promise as advanced antifriction materials, wear- and corrosion-resistant materials, supports and active components of catalytic systems, thermal management interfaces, electrically insulating and optically active layers, magnetic shielding, and so forth.

Although the primary electrochemical process in PEO is anodic oxidation of the metal substrate, it is now well documented that the interruption of positive polarization by negative (cathodic) pulses causes synergetic effects to the coating characteristics and properties as well as to the overall process efficiency, especially if a so-called “soft sparking” mode of the PEO process is established. Extensive overviews discussing implementation and results of empirical investigations and considerations for the mechanisms underpinning the role of the negative polarization in PEO can be found elsewhere. A wealth of evidence suggests that the key role in the transition to the soft sparking regime is played by switching from negative to positive polarization, leading to densification of the coating morphology and formation of high-temperature oxide polymorphs (such as α-Al₂O₃ in the case of PEO of Al) that provide coatings with excellent protective...
properties. However, the exact mechanism of such a transition is still unclear.

Despite high functional performance often demonstrated by PEO coatings in laboratory tests and a wide range of potential applications, industrial implementation of PEO technology is currently confined to several niche segments. One of the important problems in the industrial application of PEO processes is the high number of processing variables associated with bipolar polarization, which makes optimization of PEO treatments rather laborious and complicated. Some authors suggest developing a database which would include information about processing parameters and the resulting coating properties to find appropriate conditions for processing new articles using machine learning algorithms. However, to the best of our knowledge, no successful implementation of such big data strategies has so far been reported, with heuristic (e.g., trial-and-error) approaches remaining commonly used in the optimization of PEO processes, causing dramatic costs of research and development. In such circumstances, personal competence, including professional experience and sometimes intuition, play a major role in the design and engineering of PEO coatings, which cannot be directly implemented within the smart manufacturing concept because of difficulties in formalization of personal competence.

As an alternative approach to the tailored coatings, a few closed loop methods have been reported. Yang et al. suggested pulse shape monitoring to avoid current spike and associated detrimental discharge appearance. Hermanns et al. applied in situ image analysis of microdischarges acting on the sample surface to prevent large destructive discharges generation by automatic narrowing of the pulse width. However, most of the coating properties are unavailable for direct electrical or optical observations (porosity, thickness, hardness, wear resistance, etc.), and therefore a comprehensive model of the process is required to associate the desired coating characteristics with a measurable response of the system in situ. Such models are often referred to as a “digital twin” of the process, which allows modelling and prediction of the manufacturing process in the digital form.

It is expected that a detailed knowledge about process mechanism being embedded in the digital twin of the process will help in replacing preliminary experiments with real-time monitoring and prompt correction of the process in operando. In other words, this can be considered as a singularity of the “trial-and-error” method, when the trial happens every time the measurement is made and the error is “immediately” corrected at the next step. In contrast to the common trial-and-error approach, where quality criteria are known for the resulting coating only, the intellectual approach requires in situ understanding if the process goes the right or wrong way. This is why the adequate mechanistic model of the process is necessary.

However, because the typical potential difference in PEO can reach 700 V, standard equipment for electrochemical analysis of the PEO electrode becomes unavailable to perform the system identification in situ. Therefore, some specific features of charge and mass transfer under PEO conditions turn out to be hidden from observation and analysis. As a result, PEO is separated by a large gap from productive theoretical models developed for conventional electrochemical processes. At the same time, PEO is essentially an electrochemical phenomenon complicated by a number of side reactions and processes. A lack of basic understanding leads to the situation, when equipment developed for efficient coating manufacturing demonstrates low “informativeness” or ability to evaluate the system. In order to resolve this issue, a special high-voltage arbitrary waveform generator has been developed recently. Using this device, we proposed a high-voltage potentiodynamic voltammetry-based approach to real-time quantitative evaluation of the softening phenomenon induced by negative polarization in PEO processing of Al. This enabled various processes, including transient effects induced by reverse polarization, where the negative charge passing through the metal–oxide–electrolyte system acts as a stimulus for cathodically induced changes (CICs) in the growing oxide layer, to be instantly resolved and monitored.

In this work, the problem of understanding how to control the bipolar PEO process is addressed by means of kinetic analysis of the effects taking place during switching from negative to positive polarity. For this purpose, we analyze in situ a hysteresis charge, which appears in the dynamic anodic voltammogram. Particular attention in these experiments is paid to the lifetime of CICs in the PEO coating, which could be relevant to the practically important regimes with low duty cycles. Plausible mechanisms underpinning the effects of cathodic polarization are discussed. We expect that the information on kinetics of associated processes in the period between negative and positive polarization will bring us closer to the fundamental understanding of the PEO process. Such an in-depth understanding should allow steering the PEO coating process consciously, while avoiding the trial-and-error approach, as well as facilitating implementation of intelligent manufacturing processes based on the digital twin.

2. EXPERIMENTAL SECTION

2.1. General PEO Processing Arrangement and Characterization of Produced Coatings. The electrolyte was prepared by dissolving 0.01 mol/L potassium hydroxide (KOH, analytical grade) and 0.05 mol/L sodium silicate (Na2SiO3, anhydrous), purchased from Fisher Scientific, in distilled water. Substrates were cut from 0.3 mm pure Al foil (>99.9%) and installed into a round polystyrene electrochemical cell holder with an insulated electrical connector and an exposed surface area of 0.635 cm². PEO processes were carried out for 40 min in a 250 mL electrochemical cell made of stainless steel, which served as a counter electrode. Electrolyte temperature was kept constant at 30 ± 1 °C by a thermostat. These processing conditions were similar to those employed in our previous study; therefore, detailed characteristics of the coating microstructure and phase composition can be found elsewhere. Specific to this work, cross-sectional microstructure of PEO coatings was studied using a Carl Zeiss EVO-60 scanning electron microscope (SEM) operated in the backscattering electron mode. Glow discharge optical emission spectroscopy (GDOES) profiles of the main coating elements, Al and O, as well as H, were recorded using a GD-Profilier 2 (HORIBA Jobin Yvon) with an Ar pressure of 635 Pa during sputtering at a power of 35 W. Discharge appearance was taken with an Olympus C4000 digital camera.

2.2. Design of Intelligent Polarization Signal. A programmable power supply with an intelligent feedback loop based on in situ output signal analysis allowed us to design appropriate current waveforms and automatically perform measurements of the average currents, peak voltages, and charges passed, as well as synchronous acquisition of diagnostic
voltagograms. Details of supply operation and performance can be found elsewhere.37,39

Figure 1a illustrates schematically the basic cycle of polarization signal employed in this work. The primary element of the signal in both positive and negative directions is a trapezoidal current pulse depicted in Figure 1b. The working segment of the basic cycle was composed of a galvanostatically controlled pulse train with average current densities \(j_{\text{pos}} = 166 \text{ mA cm}^{-2}\) and \(j_{\text{neg}} = 216 \text{ mA cm}^{-2}\) and \(R = Q_{\text{Neg}}/Q_{\text{Pos}} = 1.3\) (where \(Q_{\text{Pos}}\) and \(Q_{\text{Neg}}\) are net charges passed in the positive and negative current pulses, respectively), frequency \(f = 50 \text{ Hz}\), and duration of 1 s. This was followed by a diagnostic segment which lasted for another 1 s and included the following five steps:

a) A positive “extracting pulse” below the breakdown voltage, which depolarizes the system and balances off residual chemical effects induced by the negative current in the working pulse train.

b) A negative “injecting pulse” with certain charge \(Q_{\text{inj}}\) passed through the metal—oxide—electrolyte system.

c) A variable delay \(\Delta T\) in the short-circuit state between 5 and 800 ms.

d) A diagnostic potentiodynamic pulse with voltage increasing and decreasing at a controlled rate.

e) A pause for the remaining period up to 1 s of the diagnostic pulse train.

The proper application of the extracting pulse was approved by the corresponding current response, the value of which was below 5% of the working pulse amplitude at the end of the extracting pulse, thereby confirming the absence of highly conductive states in the remaining coating after previous negative pulses.

Numerical values of elements of the basic cycle are collated in Table 1. The charge \(Q_{\text{inj}}\) passed during the negative injecting pulse in the diagnostic segment was related to charge \(Q_{\text{Pos}}\) passed by positive pulses in the working pulse train as \(R_{\text{inj}} = Q_{\text{Neg}}/Q_{\text{Pos}} = 0.96\). The hysteresis charge \(Q_{\text{H}}\) (Figure 1c) derived by voltammetric analysis of the potentiodynamic diagnostic pulse, as a difference between charges passed in ascending and descending voltage sweeps \(Q_{\text{Asc}} = Q_{\text{Pos}} - Q_{\text{Desc}}\), was employed as a characteristic response of the system. Detailed discussion of \(Q_{\text{H}}\) derivation and evaluation procedures can be found elsewhere.38

To minimize data scatter due to different sample sizes, positioning in the cell, electrolyte temperature, and other sources of experimental error attributed to individual runs in factorial \(n^2\) experiments, the polarization signal was arranged in a multistep sequence (Figure 1d) comprising \(n\) basic cycles (Figure 1a) with different levels of individual factors \(X\) associated here with the duration of delay \(\Delta T\) between injecting and potentiodynamic diagnostic pulses. Sequential implementation of various levels of experimental variables within the same run was both possible because the diagnostic segment does not contribute to the coating formation and is valid since, for \(n = 5\) levels, the overall sequence duration of 10 s is much smaller than the ergodicity interval of the PEO process (∼150 s38) during which the system can be considered time-invariant. Resulting sets of data points for every given level of experimental variable \(\Delta T\) can therefore be considered as discrete estimates of a continuous function \(Q_{\text{H}}(t)\) whose

![Figure 1](https://dx.doi.org/10.1021/acs.jpcc.0c07714/ pubs.acs.org/JPCC )

**Table 1. Parameters of the Combined Current Mode Pulses**

| segment | element | amplitude, mA or V | duration, ms | charge, \(\mu C\) |
|---------|---------|-------------------|--------------|-----------------|
| working | positive | \(A_0 = A_1\) | \(T_1\) | \(T_2\) | \(T_3\) | \(T_4\) | \(Q_{\text{Pos}}\) |
|         | negative | \(-A_0\) | \(0.5\) | \(8\) | \(0.5\) | \(1\) | 4250\(^a\) |
| diagnostic | extracting | \(0 \text{ mA} \) | \(300 \text{ V}\) | \(1\) | \(4\) | \(0\) | 5525\(^a\) |
|         | injecting | \(-A_0\) | \(-480 \text{ mA}\) | \(0.5\) | \(8\) | \(0.5\) | 4060\(^a\) |
|         | delay | short circuit cell terminals | \(5, 20, 50, 200, 800\) | \(0\) | 20 |
|         | potentiodynamic | adjusted to voltage envelope | \(\Delta T\) | \(\Delta T\) | \(\Delta T\) | \(\Delta T\) | \(\Delta T\) |

\(^{a}\)Evaluated as the mean average values over the whole working segment. \(^{b}\) Measured individually.
shape is independent of the timing of an individual measurement within the sequence of basic cycles. Resulting values of $Q_H(t)$ were plotted, together with corresponding anodic (UA) and cathodic ($-U_C$) voltages, in the form of time charts. Since the working pulse train has been set constant for all experiments, the voltage transients were nearly identical and depicted here mainly as an illustration of processing stages and coating formation reproducibility.

The applicability of the short-circuit cell state between pulses has been demonstrated earlier. Here, we verified this by alternating basic cycles featuring the same delay $\Delta T = 50$ ms but in open- or short-circuit states. The consistency between both cases and transition from arcing to soft sparking regimes can be clearly seen in Figure 2a.

3. RESULTS

3.1. Effect of Delay on Residual Hysteresis. Figure 2a illustrates the typical evolution patterns of the two peak cell voltages during the PEO treatment, with transition to soft sparking manifested in the noticeable drop in the anodic voltage magnitude $U_A$, which is usually observed between 20 and 30 min into processing. Figure 2b shows a typical microstructure of the produced coating and distributions of the chemical elements of interest, that is, Al, O, and H, across the surface layer, indicating a local increase in hydrogen content at the metal–oxide interface, which might be associated with the development of CICs in the active reaction zone of the growing oxide layer.

To find out for how long CIC can remain after external cathodic polarization is terminated, the hysteresis charge $Q_H$ has been measured at delay periods $\Delta T$ between the negative injecting and positive potentiodynamic diagnostic pulses varied in five levels between 5 and 800 ms (Figure 1d and Table 1). Figure 3a shows the evolution hysteresis charges $Q_H$ at different $\Delta T$ designated by color-coded data-point symbols. Initial stage of the process ($t < 7$ min), which is usually attributed to conventional anodizing up to the breakdown voltage and earlier sparking at constantly increasing voltages, shows a slight growth in the hysteresis charge independent of the delay period. Then, once the cathodic voltage starts decreasing at $t \approx 7$ min, the behavior of hysteresis charge splits depending on $\Delta T$. It can be seen that data points attributed to shorter delays are situated higher than those for longer delays, up to the maximum values established just before the transition to the soft sparking ($\sim 26$ min). This demonstrates that, before transition to the soft sparking, CIC undergoes relaxation within
the unpolarized period \( \Delta T \). Then, after the transition, \( Q_4 \) exhibits similar decreasing behavior for all studied delay periods as if it were independent of \( \Delta T \) in the soft sparking conditions, which will be clarified later.

In order to evaluate the contribution of negative charge \( Q_{\text{inj}} \) to the hysteresis, the next experiment was carried out without injecting pulse \( (R_{\text{inj}} = 0.0) \), with all other conditions being the same as in the run presented in Figure 3a. Results of this experiment are depicted in Figure 3b indicating that even at \( Q_{\text{inj}} = 0 \), the system provides a non-zero response which evolves with the processing time. This means that in addition to the well-known hysteresis in the anodic current–voltage characteristic promoted by cathodic polarization, the hysteresis can also be generated during the unpolarized state, in other words, by some sort of “nonelectrical” (HNE) phenomenon, in contrast to changes induced by cathodic polarization. However, unlike hysteresis assisted by \( Q_{\text{inj}} \) which tends to decrease with delay \( (\text{Figure 3a, black arrow}) \), the hysteresis \( Q_{\text{HNE}} \) developed without injecting pulse demonstrated an increasing trend with \( \Delta T \) \( (\text{Figure 3b, black arrow}) \). The appearance of this hysteresis should therefore be attributed to a cause other than residual polarization due to cathodic current passing through the system in the working pulse train.

The fact that \( Q_{\text{HNE}} \) originates without external polarization, the same processes can be expected to take place on the polarized electrode as well. It would therefore be reasonable to assume that the response \( Q_4 \) obtained with the negative injecting pulse \( (\text{Figure 3a}) \) includes two components: (i) the hysteresis induced by cathodic injection \( (Q_{\text{CIC}}) \) and (ii) the hysteresis induced due to nonelectrical effects \( (Q_{\text{HNE}}) \), altogether forming the detected response: \( Q_4 = Q_{\text{CIC}} + Q_{\text{HNE}} \). Finally, assuming a monotonic nature of all functions \( Q(t) \), it becomes possible to establish the fraction of hysteresis charge associated only with CIC: \( Q_{\text{CIC}} = Q_4 - Q_{\text{HNE}} \). Derived in such way, the hysteresis charge \( Q_{\text{CIC}} \) is presented in Figure 4, from pulse, it follows that the hysteresis charge derived from the asymmetrical part of current response to the anodic potentiodynamic diagnostic pulse could be caused by (i) CIC generated by prior negative polarization and (ii) an asymmetry generated due to exposure of unpolarized coating to the solution for a relatively long period of time (tens to hundreds of milliseconds that is much longer than the pulse period \( \sim 10 \) ms). It is worth noting that the hysteresis \( Q_{\text{HNE}} \) increases gradually up to the transition to the soft sparking, and after that, its value increases steeply, reflecting the transition of the coating material to a new state \( (\text{Figure 3b, } \Delta T = 800 \text{ ms}) \). In contrast, the hysteresis charge associated with the negative current \( Q_{\text{CIC}} \) \( (\text{Figure 4}) \) reduces sharply after the transition. The opposite trends in the described phenomena led us to the assumption that nonelectric generation and decay of CICs, while occurring simultaneously, are independent of each other and/or involve different species. Although it is still unclear how to identify the mechanisms underlying both the phenomena, it is possible to compare the shapes of current response to potentiodynamic diagnostic pulses with similar \( Q_4 \) but generated \( \tau \) different mechanisms.

Since the comparison has to be carried out at delays providing maximum levels of both types of hysteresis, the data of \( Q_{\text{HNE}} \) and \( Q_{\text{CIC}} \) was taken at the maximum \( (\Delta T = 800 \) ms) and minimum \( (\Delta T = 5 \) ms) delay periods, respectively. Time points of the PEO process were selected so that they provide similar levels of the hysteresis charge. Figure 5 depicts the results of voltammetric analysis applied to potentiodynamic diagnostic pulses of PEO processes carried out without \((a,b)\) and with \((c,d)\), negative injecting pulses as well as corresponding voltammograms of hysteresis currents \((e,f)\) before \((a,c,e)\) after \((b,d,f)\) transition to the soft sparking mode. It can be seen that before transition, the shape of voltammograms is identical for both generation mechanisms \( (\text{Figure 5e}) \). However, a shift of the hysteresis current to a lower voltage range with increased maximum value can be observed at the soft sparking stage of the process with injection \( (\text{Figure 5f}) \). Such a shift can be attributed to different kinetics associated with a lower activation energy for the charge-transfer process \( \tau \) states \( \text{(species)} \) induced by cathodic current rather than by those generated nonelectrically.

### 3.3. Temporal Evolution of Hysteresis.

In order to evaluate the transient behavior of the hysteresis charge attributed to CICs, the values \( Q_{\text{CIC}} = Q_4 - Q_{\text{HNE}} \) \( (\text{see Figure 4}) \) were averaged within 1 min intervals \((6 \) points\) and plotted against corresponding delay periods in Figure 6a,b. Evaluation of nonelectrically generated hysteresis was depicted as \( Q_{\text{HNE}} \) \( (\text{see Figure 3b}) \) against the delay period in Figure 6c,d. It can be seen that the experimental points of \( Q_{\text{CIC}} \) decrease and those of \( Q_{\text{HNE}} \) increase with increasing delay. It is reasonable to assume that dependency \( Q(\Delta T) \) reflects relaxation of the coating material after negative \( (\text{injecting}) \) and positive \( (\text{extracting}) \) polarization pulses. An attempt to fit kinetics data with the exponential decay or growth functions with a constant bias yielded satisfactory results \((R^2 > 0.96, \text{except for } S \text{ and } 10 \text{ min curves}) \)

\[
Q_i(\Delta T) = Q_i + q_i \exp \left( -\frac{\Delta T}{\tau} \right)
\]

(1)

where subscript \( i \) designates either CIC or HNE, \( q_i \) is the preexponential factor, \( \tau \) is the characteristic time constant \( (\text{lifetime of the generated state}) \), and \( Q_i \) is the offset \( (\text{the hysteresis charge at infinite time}) \). From Figure 6, it is evident

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**Figure 4. Temporal evolution of the difference between hysteresis charges in the PEO process \((Q_4 - Q_{\text{HNE}})\), indicating a fraction of hysteresis \((Q_{\text{CIC}})\) caused by negative charge \( Q_{\text{inj}} = 4060 \mu C \) at different delay times.**

which it follows that, after the transition to the soft sparking mode \((\sim 26 \) min\), the plots continue demonstrating distinct splitting with \( \Delta T \) in the same order as that observed before transition \( (\text{i.e., the smallest hysteresis at the longest delay period}) \). Therefore, the decay of CIC is a characteristic feature of the entire PEO process.

**3.2. Voltammetric Analysis.** From the comparison of experiments carried out with and without the negative injecting
that dynamic eq 1 of hysteresis charge as a function of delay \( Q_i(\Delta T) \) is applicable to the whole PEO process regardless of its phenomenological stages.

4. DISCUSSION

4.1. General Considerations. The observed behaviors of the studied metal–oxide–electrolyte system can be accounted for in the following way. Within the diagnostic segment, the PEO coating is affected by one of the two polarizations (Figure 7a) following the positive extracting and negative injecting pulses that lead to two states of the coating material characterized by a reduced and increased \( Q_{H} \) with respect to that straight after relaxation (see Figure 6, at \( \Delta T \rightarrow 0 \)). At the beginning of the delay period, those states were designated as A and B, respectively (Figure 7b). Relaxation during the unpolarized delay period brings the system into new states, C and D, in such way that \( Q_{HNE} \) spontaneously increases during transition to state C and \( Q_{CIC} \) spontaneously decreases during transition to state D. Since we consider the same coating material, but with different local history, we can assume that spontaneously increased \( Q_{HNE} \) (approaching C-state) is in essence equivalent to the B-state with increased \( Q_{CIC} \), which, in turn, is cathodically induced. Similar considerations can also be applied to the relation between states A and D. Therefore, states A and D represent state X and B and C represent state Y achieved by various routes (Figure 7c).

Moreover, according to the general chemical kinetics, a simple exponential decay in the amount of component can be associated with quasi first-order reactions. In this case, the presence of a bias in eq 1 can be associated with approaching an equilibrium state. Therefore, negative and positive polarizations of the coating can be considered as external...
perturbations acting in opposite directions with regard to the local quasi-equilibrium state of the system within the time frame of the diagnostic segment (solid colored arrows, Figure 7c). Once the sample is nonpolarized, the system spontaneously reaches an equilibrium (Figure 7c, solid black arrows). In general, we have to consider that electrical polarization of the system would affect not only the equilibrium by mutual transformation of two components ($X + Y = \text{const.}$) but also the ability of currents to change the quantities of active species because of electrode reactions ($X + Y \neq \text{const.}$). Hypothetical processes affecting the total amount of active species are illustrated in Figure 7c by dashed arrows. It should be noted that Figure 7c illustrates the most general case, whereas certain paths can be unrealizable because of specific characteristics of the real system studied here. Considering the behavior of the PEO coating on Al, reactions including cathodic deposition (+$\delta Y$) or cathodic reduction ($-\delta X$) are unlikely. Conversely, the anodic oxide formation ($+\delta X$) and anodic dissolution ($-\delta Y$) are known as typical reactions in the course of PEO on Al.

4.2. Formal Kinetics. In formal chemical kinetics, the problem of approaching an equilibrium is well known.\textsuperscript{41} For a homogeneous chemical system, where reversible reaction $X \rightleftharpoons Y$ started with initial values $x_0$ and $y_0$, respectively, the rate of formation $Y$ when approaching the equilibrium can be expressed as

$$\frac{dY}{dt} = k_{XY}X - k_{YX}Y$$

(2)

where $k_{XY}$ and $k_{YX}$ are the rate constants of forward and reverse reactions. Moreover, taking into account the mass balance

![Figure 6](image-url)  
Experimental data (points) describing relaxation of hysteresis charge and its corresponding exponential approximations (lines) during the delay period: (a,b) relaxation of $Q_{\text{CIC}}$ following negative injecting pulse with $Q_{\text{inj}} = 4060 \, \mu\text{C}$, ($R_{\text{inj}} = 0.96$); (c,d) relaxation of $Q_{\text{HNE}}$ without negative injecting pulse ($Q_{\text{inj}} = 0$, $R_{\text{inj}} = 0.0$); before (a,c) and after (b,d) transition to the soft sparking mode.

![Figure 7](image-url)  
Schematic diagram explaining the behavior of the PEO coating on Al under bipolar polarization: (a) effect of polarity on hysteresis charge; (b) relaxation evolution of different states A–D; (c) mass relations between two coexisting species ($X, Y$). $k_{ij}$—rate constants for $i \rightarrow j$ reaction.
\( X = (x_0 + y_0) - Y \) and the condition of dynamic equilibrium
\( (dY/dt = 0) \)
\[
\frac{\dot{X}}{\dot{Y}} = \frac{k_{YX}}{k_{XY}}
\]
where \( \dot{X}, \dot{Y} \) are amounts of \( X \) and \( Y \) at equilibrium; integration of 2 after variable separation gives the solution in following form
\[
Y(t) = \dot{Y} - (\dot{Y} - y_0) e^{-(k_{XY} + k_{yx})t}
\] (4)

It can be clearly seen that the form of eq 4 obtained using formal kinetics considerations represents the same exponential law 1 used for fitting of experimental data points, when \( \dot{Y} \) represents the quasi-equilibrium value of hysteresis charge (\( Q_i \)), the pre-exponential factor \( -(\dot{Y} - y_0) = q_i \) represents the maximum deviation of the initial state from the equilibrium, the time constant \((k_{XY} + k_{yx})^{-1} = \tau_i \), and \( t \) represents \( \Delta T \).

From fitted functions 1, it is possible to evaluate the values of initial hysteresis charge at the very beginning of the delay period (Figure 8a): \( Q_i = Q(\Delta T = 0) = \dot{Q}_i + q_i \). This exercise provides a much smaller value of \( Q_i \) for the PEO coating polarized without injecting pulse, confirming that extraction takes place reproducibly during the studied process. For the regime with the negative injecting pulse, initial hysteresis charge \( Q_{CIC} \) shows induction period \((t < 7 \text{ min})\) at the level similar to that of initial hysteresis without injection (\( Q_{\text{INE}} \)). Furthermore, continuous growth of \( Q_{CIC} \) is observed up to the soft sparking transition, beyond which it gradually decreases till the process is terminated.

The evolution of constant bias term \( Q_i \) in exponential fitting 1, representing the quasi-equilibrium state of the PEO coating, is illustrated in Figure 8b. It can be seen that up to the soft sparking transition, curves obtained both with and without injection follow similar increasing trends. From similar behavior of \( Q_i \) for the two initial states, we can conclude that both negative and positive pulses only shifted the equilibrium \( X \approx Y \) without noticeable changes in the total amount of active species, so that \( X + Y = \text{const.} \) (Figure 7c, solid colored arrows). Therefore, relaxations from both the initial states led to nearly the same quasi-equilibrium state (Figure 8b, \( t < 26 \text{ min}) \). However, once the soft sparking transition is initiated, an unexpected behavior can be observed. The quasi-equilibrium level of hysteresis charge \( Q_i \) demonstrates considerably higher level for the coating under polarization conditions without the injecting pulse (HNE) with respect to those with it (CIC). As the final quasi-equilibrium state after the positive extracting pulse (without injection) is characterized by a higher level of residual hysteresis; this cannot be associated with a shift in equilibrium since we expect a decrease in hysteresis charge after the positive pulse is applied (see Figure 8a, \( Q_{\text{HNE}} < Q_{i} \)). However, this can be attributed to an increased amount of the total number of active species, which can be introduced by the positive current. The latter can be associated with the path denoted +6X (Figure 7c) toward accumulation of anodic oxidation products. An alternative path of reducing \( Y \) species (−6Y) is in contradiction with the increased hysteresis charge for the case without injection.

In addition, it can be seen that the time constant describing relaxation of PEO coating following the negative injecting pulse was in the range 65–265 ms with the average value of about 160 ms (Figure 8c). The variation of time constant for relaxation without injecting pulse was much higher (40–370 ms), probably because of smaller absolute values of \( Q_i \) that increased the fitting error; the average value was found to be 220 ms. It is worth noting that even the smallest of these time constant values (40 ms) is much larger than the typical duration of the off period in most PEO processes, including those carried out at low AC frequencies \((T = 20 \text{ ms at } f = 50 \text{ Hz})\).

In accordance with the previous result, the estimation of rate constant can be done only for the sum of \( k_{XY} + k_{yx} \). In order to evaluate these rate constants separately, additional information (e.g., a total amount \( X + Y = x_0 + y_0 \)) is required. For the system under consideration, the quantity of only one component can be evaluated from the experiment, and therefore, a separate estimation of the rate constants could be performed only approximately. Assuming that at the beginning of the delay period following injecting pulse, one of the components significantly dominates, \( y_0 \gg x_0 \) and taking into account that \( y_0 \approx (1 + k_{yx}/k_{xy})\dot{Y} \), eq 4 can be rewritten in an approximate form as follows
\[
Y(t) \approx \dot{Y} \left( 1 + \frac{k_{yx}}{k_{xy}} e^{-(k_{YX} + k_{yx})t} \right)
\] (5)

Therefore, comparison with 1 gives \( q_i \approx Q_i k_{yx} / k_{xy} \), where from the rate constants can be found taking into account \( \tau = (k_{XY} + k_{yx})^{-1} \). Unfortunately, without information about the total uncertainty.
amount of species $X + Y$, it is impossible to separate the rate constants for charge transfer in the case without injection, wherein neither species prevails.

Figure 9 illustrates the evolution of estimated rate constants for a hypothetical reversible reaction (Figure 7c, black arrows) during the growth of PEO coating on Al. Gray areas designate periods, where the exponential fitting was less accurate because of initial instabilities and a small signal-to-noise ratio, or a fast drop of $U_A$ during the transition to the soft sparking mode, which caused an additional error in the evaluation of $Q_A$. A more detailed discussion of this chart will be more productive if given after the analysis of chemical species involved (see Section 4.3).

### 4.3. Chemical Species

Based on the above experimental results and discussion, we proposed a hypothesis of an unstable chemical equilibrium established in the metal–oxide–electrolyte system under PEO conditions. Of cause, the discussed kinetics parameters represent only effective values of rate constants attributed to the rate-determining steps, whereas the mechanisms of elementary reactions are expected to be more complex. Nevertheless, it is evident that the metal–oxide–electrolyte system exhibits two-fold behavior (Figure 6), wherein the hysteresis charge depends on electrical polarization ($a,b$) and is affected by the residence time in the unpolarized state, facilitating chemical relaxation ($c,d$). Moreover, certain interconnections exist between electrically and nonelectrically induced chemical states of the coating attained during polarization and relaxation periods.

Earlier, we considered that although alkali metal cations are important for conductivity under cathodic polarization, hydrogen species seem to be the most plausible candidate to play the main role in the softening phenomenon under cathodic polarization, mainly due to the much smaller size of protons and their abundance in the solvent (water). We conjectured that injection of protons into oxide under negative polarization became possible after the electronic conductivity of the coating was reduced with coating growth, which inhibited hydrogen evolution and decreased electrolyte pH in the vicinity of the oxide surface. This appears to take place in the studied process 7 min into the treatment (Figure 4). Subsequent recombination of $[H^+]_{OX}$ with electrons that can be injected from the metal–oxide interface because of valve effect would result in the formation of neutral hydrogen complexes $[H]_{OX}$ stabilized by surrounding oxygen in amorphous alumina. Similar phenomena are characteristic as well for some other metal oxides such as TiO$_2$ which charging by hydrogen under cathodic polarization is accompanied by a noticeable drop in the electrical resistance and changes in color (known as electrochromism). In other words, we assumed formation of hydrogen-intercalated alumina under cathodic polarization of PEO-coated Al in alkaline solutions to be the main source of hysteresis. Moreover, the decrease in hysteresis charge with delay period (relaxation) could be introduced to that model as an escape route for neutral hydrogen complexes, for example, forming gaseous hydrogen (Figure 10, “self-decay”).

![Figure 9. Evolution of rate constants for forward (XY) and reverse (YX) reactions during the PEO process on Al at R = 1.3.](https://dx.doi.org/10.1021/acs.jpcc.0c07714)

Although from our experiments it follows that relaxations are bidirectional (see Figure 6), it seems unlikely that gaseous hydrogen evolution would have a noticeable rate of reverse reaction because of negligible $H_2(gas)$ concentration in water and uncertain driving force for this process (Figure 10, question mark). Therefore, the mechanism presented in Figure 10 needs to be adjusted, which can be done by considering different chemical species participating in electrochemical stimulation (injection) and chemical relaxation processes. Regardless of polarization-induced effects, relaxation of amorphous oxide layers on aluminum can be associated with their hydration/dehydration process approaching equilibrium

$$\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} = 2\text{Al(OH)}_3$$

However, it is necessary to consider additional steps within such a relaxation mechanism since the hydration/dehydration reaction does not change the oxidation states of species involved and cannot therefore be directly associated with the electrochemical steps of the process. It is known that anodic films on aluminum tend to dehydrate under anodic polarization. As a result, the following three key processes can be considered: (a) incorporation of hydrogen in oxide under cathodic polarization, (b) chemical equilibrium of aluminum oxide and hydroxide, and (c) dehydration of hydrated anodic oxide under positive polarization. A plausible mechanism including all three reactions can now be formulated (Figure 11a–c), including only one additional step of transition from hydrogen-intercalated alumina to hydroxide under positive polarization (d), to close up the process loop.

![Figure 10. Reactions of hydrogen complex formation/depletion.](https://dx.doi.org/10.1021/acs.jpcc.0c07714)
The beginning of anodic pulse (A3a) is accompanied by an increase in the hydration level of anodic oxide (reaction 11). It is reasonable to assume that hydration would significantly increase the local electrical conductivity of the anodic oxide film.\textsuperscript{47,48} The appearance of a hydrated layer (A3b) in the forming oxide can both narrow down the part of oxide with low conductivity and facilitate formation of new hydroxide (reaction 14). Moreover, the route designated by reaction 15 (A3c) accounts for a well-known fact that the application of anodic polarization to anodic alumina promotes dehydration in both acidic and alkaline solutions,\textsuperscript{47} regardless of the exact mechanism. As a result, the evolution of hydrogen-intercalated oxide in the alumina layer during the anodic period (A3 in Figure 12) can be considered as a sequential transformation via at least one intermediate [Figure 13, Al(OH)\textsubscript{3}], which may contribute to the asymmetry in current response to the potentiodynamic diagnostic pulse.

Now it becomes possible to link the chemical behavior of PEO alumina to the above kinetics considerations. It can be seen that species X and Y, introduced earlier (Figure 7c), correspond to dehydrated and hydrated forms of alumina, including intercalated hydrogen species, because during anodic polarization imposed by the potentiodynamic diagnostic pulse, they are transformed into hydroxide and contribute to the measured \( Q_H \) value. Let us introduce an auxiliary function for the generalized characteristic of the coating as a degree of hydration established in the quasi-equilibrium state \( \Delta T \rightarrow \infty \) at a given time point

\[
\chi = \frac{\nu(\text{Al(OH)}_3)}{\nu(\text{Al}_2\text{O}_3) + \nu(\text{Al(OH)}_3)} = \frac{\tilde{Y}}{X + \tilde{Y}} \tag{7}
\]

which can be expressed via the rate constants (eq 3) estimated earlier (Figure 9) as

\[
\chi = \frac{k_{XY}/k_{YX}}{1 + k_{XY}/k_{YX}} \tag{8}
\]

The introduced hydration degree \( \chi \) estimates the average hydration ability of the coating, reflecting changes in its history. Evolution of the hydration degree during the PEO process is presented in Figure 14 demonstrating the average level about 0.2. A higher initial hydration degree can be associated with a thinner coating that provides less diffusion limitations, thereby signifying a decreasing trend with coating growth at \( t < 15 \) min. Moreover, initial stages of PEO processing are often characterized by a large number of relatively small discharges uniformly covering the treated surfaces, similarly to some soft phenomenon. A further increase in \( \chi \) observed after 15 min and up to the soft sparking transition (\( \sim 26 \) min) is associated with indirect hydration through hydrogen intercalate formation. During the soft sparking period (\( t > 28 \) min), the degree of hydration can be considered as fluctuating around a certain steady-state value.

### 4.4. Local Softening Phenomenon.

Although no detailed information about CIC generation/decay under alternating polarization could be derived from this study, a simplified qualitative modelling of the bipolar PEO process can...
be proposed. Figure 15 schematically illustrates current waveforms and corresponding evolutions for the coating hydration degree ($\chi$) in two characteristic cases, where the treatment is carried out in arcing ($R = 0.8$) and soft sparking ($R = 1.25$) regimes. In the first approximation, it is sufficient to take into account that negative and positive currents cause increases and decreases in hydration, respectively. Following this, we presented corresponding changes in $\chi$ as linear slopes that are proportional to current pulse magnitudes for negative (Figure 15,0−A) and positive (Figure 15,B−C) polarization for these two processes. Intervals between the pulses corresponding to $Q_H$ behavior in Figure 6 were approximated by exponential decays (Figure 15,A−B) or increases (Figure 15,C−D), depending on whether the initial hydration degree was higher or lower than that at the quasi-equilibrium level. The coatings were considered to be sufficiently thick to be affected by negative current (e.g., nearly soft sparking transition).

With both processes starting at zero level of hydration, it can be seen that the higher magnitude of negative current results in a higher $\chi$ at the end of the negative pulse (point A). Further, $\chi$ undergoes exponential relaxation up to the rising edge of the positive pulse (point B), ending up at a certain non-zero level. Since the magnitude of the positive pulse was taken identical, the linear dehydration slope during its period is constant, and starting with a lower level, the dehydration during the process with $R = 0.8$ will reach the minimum $\chi_{\text{min}} = 0$ earlier, at a point $C^*$, whereas at higher $R = 1.25$, the minimum ($\chi_{\text{min}} > 0$) will correspond to the end of the positive pulse (C). Between points $C^*$ and C, the coating formed under arcing conditions ($R = 0.8$) is exposed to the positive polarization in an "anhydrous" state. Subsequent pause after the positive pulse is characterized by spontaneous hydration toward the level of quasi-equilibrium, which is the final value $\chi$ at point D also depending on its initial value at point C. Thus, it can be pointed out that if the amount of negative charge passed through the metal–oxide–electrolyte system is sufficient to retain residual hydration at the end of the positive pulse, this
provides a condition to increase the average coating hydration degree with processing time. Contrary, if the negative charge is not enough and the coating is completely dehydrated by the end of the positive pulse, the next period will start at the same zero hydration and the average hydration level will remain the same throughout processing.

In the latter case, additional attention needs to be paid to the interval $C^+ - C$, where the oxide film is considered to be essentially anhydrous. Our main hypothesis was based on the ability of hydrogen species (and hydration) to extinguish microdischarges, which is a characteristic feature of the soft sparking regime in PEO processes. This ability was attributed to narrowing of the low conductive area within the active zone because of the presence of hydrogen species, as discussed in ref 27. Therefore, the initial period of the positive pulse (Figure 15, B–C$^+$) can be considered as a local softening, followed by complete dehydration within C$^+ - C$ interval, which can be considered as a local sparking regime. Indeed, such behavior is manifested as a lag between the rising edge of the anodic pulse and the appearance of light emission.$^{27,50}$ According to the proposed mechanism, the lag in microdischarge appearance can be associated with the kinetics of dehydration, which is in good agreement with experimental observations, indicating that it increases with both processing time and negative pulse magnitude.$^{49}$

4.5. Application-Related Cases. Finally, we are able to implement the proposed model to the analysis of a bipolar PEO process on Al in several characteristic situations including arcing ($R < 1$) and soft sparking ($R > 1$) regimes, as well as practical cases of especial importance, including PEO treatments of the same current ratio, but different relations between pauses $T_{\text{on}}$ and $T_{\text{off}}$. Since numerical parameters of the model are specific to particular substrate–electrolyte combinations, the following generic discussion will also be carried out in qualitative terms.

Figure 16 illustrates the evolution of oxide layer hydration degree for coatings grown under several practically important electrical regimes. For the arcing mode ($R < 1$), the positive pulse completely dehydrates coating at every cycle, facilitating microdischarges; thus, the average degree of hydration remains constant, always starting from zero level (Figure 16a). For the soft sparking conditions ($R > 1$), the falling edge of the positive pulse is characterized by certain residual hydration ($\chi > 0$), therefore the average hydration increases with processing time (Figure 16b). However, this increase is not infinite. Once the residual hydration at the end of the positive pulse becomes higher than the quasi-equilibrium level of hydration (dashed line), the relaxation within the following pause ($T_{\text{off}}$) changes sign and the degree of hydration becomes reduced, getting stabilized at a certain steady-state level. It is apparent that in the latter case, $\chi_{R=1.25} > \chi_{R=0.8}$ preventing the appearance of microdischarges.

Another important situation is when relatively short pulses are separated by long pauses in order to reduce average energy consumption in scaling up to industrial applications. Let us consider two extreme cases (Figure 16c,d), where the pulse current ratio is kept the same ($R = 1.25$) but pause durations vary: (i) "positive–negative–pause" ($T_{\text{on}} \ll T_{\text{off}}$) and (ii) "negative–positive–pause" ($T_{\text{on}} \ll T_{\text{off}}$). It is evident that the relative position of pulses does matter for the coating hydration degree. Despite the same $R$, a longer period between the negative and positive pulses ($T_{\text{on}} \ll T_{\text{off}}$) can facilitate oxide dehydration down to a level where residual $\chi$ at the end of the consequent positive pulse is zero (Figure 16c). Therefore, the onset of soft sparking conditions could be hindered or, in the worst scenario, blocked. Conversely, a shorter period between the negative and positive pulses ($T_{\text{on}} \ll T_{\text{off}}$) prevents dehydration, providing sufficient condition for current flow with no microdischarges in the soft sparking regime, which increases processing efficiency (Figure 16d). This explanation is in agreement with the experimental findings of Al Bosta and Ma$^{51}$ whose study into effects of bipolar pulse durations on the coating thickness clearly shows that the thickness increases with a decrease in the $T_{\text{on}}/T_{\text{off}}$ ratio (Figure 8 in ref 51).

The above example demonstrates that, although the current ratio $R$ can be easily measured, it could cause a confusion in the interpretation of experimental results if collateral processes taking place in the pauses between current pulses (when the coating is unpolarized) are neglected. This becomes particularly important when pulse durations and frequency are changed. For example, at a higher frequency, the contribution of capacitive current to the total current increases; however, this does not contribute to material changes in the surface layer, bypassing the electrochemical reactions. If it was not resolved in the current measured experimentally and is subsequently included in the corresponding current ratio $R$, this would not reflect the actual coating formation process, leading to results that are prone to misinterpretations. Moreover, other commonly used processing parameters, such as frequency and duty cycle, do not seem to be able to explicitly identify a bipolar PEO process alone because the relation between $T_{\text{on}}$ and $T_{\text{off}}$ remains hidden and the coating deposition process is not fully characterized (especially in the low duty cycle regimes).

5. CONCLUSIONS

In this work, we employed numerical evaluation of CICs in the PEO coating as a function of time to study the kinetics of the coating relaxation within unpolarized pauses following either negative or positive pulses. Summarizing the above study, the following concluding points can be drawn:

- From the fact that the relaxation of the coating response can be bidirectional, it follows that a quasi-equilibrium exists between the coating material and the electrolyte solution, which can be perturbed by application of external polarization.

- Since the characteristic time for establishing the quasi-equilibrium state (40–370 ms) is much longer than the typical period of polarizing signal in PEO (10 μs < T < 10 ms), the evolution of the coating state during PEO processing can be considered analogous to passage through a low-pass filter, where any fast changes in polarization affect the system as corresponding mean average values. This is in good agreement with known similarities observed in PEO processes carried out at low and high frequencies.

- A plausible explanation of chemical changes in the coating material is provided by the hydration/dehydration of anodic alumina, so that the evolution of coating composition during PEO processing can be characterized by a variable degree of hydration, directly determining the softening phenomenon in PEO.

- An important practical implication for utilizing benefits brought by the negative polarization to the overall oxidation process at a large scale consists in the
application of positive pulses straight after negative polarization (by minimizing $T_{off}$ period), while the overall duty cycle can be controlled by a duration of $T_{on}$ period. Moreover, since in many cases, the control of current pulse duration is more accurate (at least within the time region of the order of micro- to milliseconds which is of interest for PEO technology) than the control of its magnitude, it makes sense to control the coating formation process by adjusting the time intervals of pulsing polarization, especially when intelligent process control is considered, wherein a cycle-by-cycle analysis-feedback-control loop can be implemented.

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Notes
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