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On the use of instantaneous impedance for post-electrochemical treatment analysis

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Abstract

For many electrochemical treatments, surface modifications and processes occurring during the relatively short post-treatment time are difficult to monitor using traditional surface analysis techniques. Instantaneous impedance, i.e. time-resolved impedance calculated from an in situ odd random phase multisine electrochemical impedance spectroscopy measurement, may allow for monitoring of these surface modifications. In this work, the AC electrograining process is used as a case study to investigate the possibility of post-electrochemical treatment analysis. It is found that the expected surface changes are indeed found in the instantaneous impedance data. The technique described in this paper can be used to monitor a variety of post-electrochemical treatment surface modifications in situ.

Keywords: ORP-EIS, instantaneous impedance, AC electrograining, aluminium, smut layer

1. Introduction

For many electrochemical treatments, such as the charging of batteries, electrolysis, and continuous processing, many processes occur during the relatively short post-treatment time \cite{1, 2}. These processes usually involve changes in the surface properties of the substrate. Often, it is difficult to gather information on
these different processes occurring during this period of time. Vacuum based techniques, which are commonly used for surface analysis, cannot be used to investigate these surface modifications as the substrate will have evolved compared to the substrate submerged in the solution. Due to the constantly changing nature of the substrate, regular electrochemical impedance measurements are also inadequate, as the process is not stationary [3].

In contrast, using odd random phase multisine electrochemical impedance spectroscopy (ORP-EIS), each excited frequency is applied continuously. Therefore, it provides continuous information on the system. This information can be extracted from the frequency spectrum by fitting the so-called “skirts” found in the frequency spectrum. Resolved in the time domain, this fitting provides the instantaneous impedance of the system [4].

The AC electrograining process of aluminium provides an excellent case study for post-electrochemical treatment analysis, as the process uses several electrodes in series for increasing the hydrophilicity and surface area of the substrate [5]. During the interval time between the electrodes, the electrochemical treatment is temporarily halted, and the substrate is subjected to the acidic electrolyte.

The electrograining process entails the removal of the native oxide layer, promotion of pitting corrosion, and the formation of a gel-like smut layer [6–9]. This smut layer is reported to obtain up to 90% water by mass [8]. In situ SAXS studies confirmed the presence of retained gas in the gel-like smut layer [10, 11], and the formation of temporary and permanent water passageways [2]. As the process is halted, besides the dissolution of the smut layer, the temporary water passageways close [2] and the retained gas is released from the system [10, 11].

In this work, the possibility of monitoring the fast changing surface properties post-electrograining using the instantaneous impedance technique is examined. First, the electrochemical influence of the short intervals between the electrodes is examined. Afterwards, an ORP-EIS signal is applied to the system immediately after the electrograining and the instantaneous impedance is calculated. The results are interpreted using electrical equivalent circuit fitting.
2. Experimental

The set-up used consists of an AA1052 aluminium working electrode, facing a Pt grid counter electrode with a spacing of 2 cm in a solution of 0.34 M HCl at 37 °C. A surface of 2.01 cm$^2$ of the working electrode was exposed, while the remainder of the surface was covered with insulating tape. A Bank HP 400 potentiostat/galvanostat is used to impose an AC graining current with an amplitude of 1.2 A cm$^{-2}$ (rms) to the working electrode at 50 Hz at six intervals of 1 s, with a dead time of 1 s. After this measurement, an ORP-EIS signal with an amplitude of 0.1 mA cm$^{-2}$ (rms) and a frequency range of 1 Hz – 50 kHz is imposed at the electrode. The dead time between the application of the electrograining current and the impedance signal is 0.03 s. The working electrode potential is monitored with a Ag/AgCl (sat. KCl) electrode as a reference. The current and potential response is measured using a National Instruments PCI-4461 DAQ card. Because of a setup-related measuring artefact found at frequencies exceeding 10 kHz, only data below this frequency is considered.

3. Results and discussion

3.1. Anodic and cathodic potential variations

First, the influence of short intervals between the electrodes on the electrochemical response of the system is examined. Two measurements are carried out; a control experiment that emulates one continuous electrode and a procedure with five intervals, emulating six electrodes. The anodic and cathodic maximum potentials of these measurements are compared. Figure 1 shows the anodic (blue dots) and cathodic (red diamonds) maximum potentials as a function of the cycle number, which is the period of the applied sinewave signal. As the frequency of the signal equals 50 Hz, 50 cycles correspond to 1 s of graining time. The continuous electrode procedure (figure 1a) shows the typical potential evolution of the electrograining process found in [6], while the five interval procedure (figure 1b) shows that both the anodic and cathodic maximum potentials drop significantly between the different electrodes. The maximum potentials show a
transient behaviour for each of the emulated electrodes. This is an indication that the smut layer is indeed changing during the intervals.

FIGURE 1

3.2. Instantaneous impedance

To find out whether the changes in the smut layer can be observed by using the instantaneous impedance technique, an ORP-EIS measurement is performed immediately after the five interval procedure. The measurement is performed for 10 s and has a frequency resolution of 1 Hz, resulting in 10 measuring periods. The results of this measurement are displayed as the Bode plots in figure 2. Aside from the modulus, also the stochastic noise, and the non-linearities and non-stationarities are shown in figure 2a. These noise parameters are indicators of the quality of the measurement data.

As the stochastic noise levels at the two lowest excited frequencies drop below one decade, only data exceeding 10 Hz will be discussed. It is clear that the system behaves non-stationary: the noise including the non-stationarities, indicated by the green markers, exceeds the stochastic noise at all frequencies. As the smut layer is being chemically altered by the electrolyte, this non-stationarity is expected. The detection of non-linearities, depicted by the red markers, can also be explained by the non-stationarity, as the impedance measured at the non-excited frequencies differs from the noise level [12].

FIGURE 2

The non-stationary behaviour of the impedance response can be determined by calculation of the instantaneous impedance [4]. The results of this calculation are displayed in figure 3. This figure shows the amplitude (a) and phase angle (b) of the calculated instantaneous impedance at the start of the measurement, and at each second of the measurement. The biggest change in the amplitude is seen at frequencies below 300 Hz. This change is most likely due to the chemical modification of the smut layer. In this frequency interval, the amplitude increases in the first seconds and then decreases rapidly. A second range of changing
amplitude is found at frequencies exceeding 7 kHz, where the impedance values drop over time. This change is most likely related to changes in the electrolyte resistance. These frequency domains are in line with the amplitude of the non-stationarities found in figure 2. The phase angle and characteristic frequency of the impedance response also changes over the course of the measurement. This change could be due to the change in the capacitance of the smut layer [13], and the change in smut layer resistance.

FIGURE 3

3.3. Instantaneous impedance fitting

The fitting results of the instantaneous impedance are shown in figure 4. The fitting is done using the electrical equivalent circuit shown in the inset of figure 4a. The model accounts for the electrolyte resistance and the smut layer. The smut layer is represented by a charge transfer resistance in parallel with a constant phase element (CPE). As all fitted values follow a logical trend with no big variations, no additional constraints are added to the fitting parameters, which is sometimes needed for a proper fitting result [14]. The error on the fitting, i.e. the standard deviation, is displayed as error bars on the graphs. The error bars on the electrolyte resistance $R_e$ and the smut layer resistance $R_{smut}$ are not visible due to the very low value of the relative errors. For the parameter with the highest variation, $Q_{smut}$, the standard deviation never exceeds 2.4 % of the total value, which means the fitted values are reliable.

As depicted in figure 4a, the electrolyte resistance ($R_e$) is not constant over the course of the measurement. Although this behaviour appears atypical, it can be explained by the change in the gas fraction in the electrolyte [15], which decreases after the gas-evolving electrograining process. The smut layer resistance $R_{smut}$ also changes over the course of the measurement, as displayed in figure 4b. This resistance encompasses the charge transfer resistance at the interface, and the resistivity of the smut layer itself. As expected based on figure 3, $R_{smut}$ increases during the first 1.5 s, from 463 $\Omega$ cm$^2$ to 547 $\Omega$ cm$^2$. It then decreases to a value of 133 $\Omega$ cm$^2$ at 10 s. As the smut layer is dissolving in the acidic
electrolyte, the decrease in $R_{\text{smut}}$ is a logical result. The initial increase may be due to the closing of the temporary water passageways observed in [2], which provide easier access to the surface for charge transfer.

The change in the Q-parameter of the CPE of the smut layer over time is shown in figure 4c. Its value decreases as a function of time, especially during the first two seconds. However, due to the change in the $\alpha$-value (see figure 4d), these results are difficult to interpret directly: any slight change in $\alpha_{\text{CPE, smut}}$ will result in a large change in $Q_{\text{CPE, smut}}$ [16]. Due to the limited knowledge regarding the entrapped gas inside the smut layer, its resistivity profile and dielectric property distribution is unknown. Therefore, the effective capacitance cannot be determined according to the power law model described by Hirschorn et al. [17, 18].

The change in $\alpha_{\text{CPE, smut}}$ can be interpreted to a greater extent. Its values range from 0.957 at the beginning of the interval to a maximum of 0.993 near the end of the interval. As $\alpha$ represents the dispersion of the capacitance over the smut layer, it can be concluded that the smut layer becomes more uniform over time. $\alpha$ is increased in two steps, one occurring during the first two seconds, and the second one occurring after 5.5 s. The first increase coincides with the closing of the temporary water passageways, also observed in $R_{\text{smut}}$. The second increase is harder to explain, however it may be related to the release of retained gas entrapped in the smut layer.

Because of the limited physical meaning of the CPE parameters, it is useful to consider the time constant of the system to investigate the materials properties. The time constant is determined in two separate ways, via a graphical interpretation of the imaginary impedance [19] and via equation 1.

$$\tau = 2\pi(R_{\text{smut}}Q_{\text{CPE, smut}})^{\alpha_{\text{CPE, smut}}}$$

The results are plotted in figure 4e. It is found that the two analysis methods overlap mostly, and the difference in the beginning could be due to noise in the instantaneous impedance results. The initial increase in time constant could again be due to the closing of the water passageways, and the later decrease
to the dissolution of the smut layer and possible retained gas release. Further research is required to identify this process more rigorously.

FIGURE 4

4. Conclusions

Using the instantaneous impedance calculated from an ORP-EIS measurement, it is possible to monitor surface modifications occurring immediately after an electrochemical treatment. In the case of AC electrograining, the impedance provides information on dissolution of the smut layer, closing of temporary water passageways and possibly the release of retained gas. This technique could be used to monitor surface processes occurring during the post-treatment time of a variety of electrochemical treatments.

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References


Figures

Figure 1: Anodic and cathodic potential variations during the AC electrograining. The anodic (•) and cathodic (♦) maximum potentials are shown as a function of the AC cycle number. (a) Continuous electrode; (b) five interval procedure.
Figure 2: Results of the galvanostatic ORP-EIS post-graining with six electrode intervals. (a) Modulus and noise levels; (b) phase angle.
Figure 3: Results of the instantaneous impedance calculation of the measurement shown in figure 2. The impedance during the entirety of the measurement (10 s) is shown. (a) Modulus, (b) phase angle.
Figure 4: Fitting results of the instantaneous impedance. The electrical equivalent circuit shown in the inset of (a) is used for fitting. (a) Electrolyte resistance; (b) smut layer resistance; (c) Q-value of CPE; (d) $\alpha$-value of CPE; (e) smut layer time constant determined graphically and through CPE parameters.