



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.

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 [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 cm² 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

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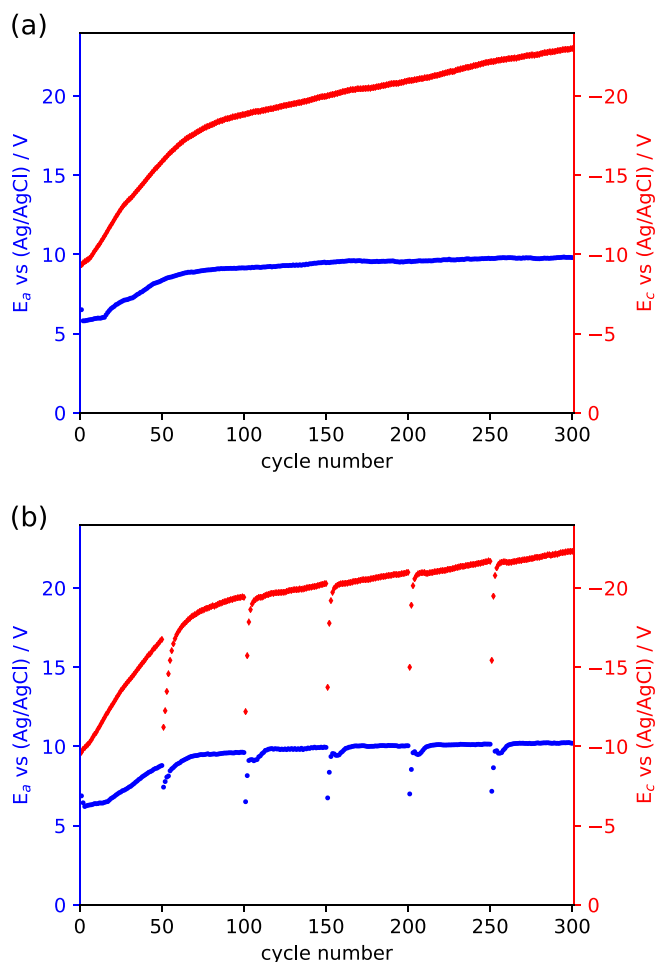


Fig. 1. Anodic and cathodic potential variations during the AC electrograining. The anodic (●) and cathodic (♦) maximum potentials are shown as a function of the AC cycle number. (a) Continuous electrode; (b) five interval procedure. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

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. Fig. 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 (Fig. 1a) shows the typical potential evolution of the electrograining process found in Ref. [6], while the five interval procedure (Fig. 1b) shows that both the anodic and

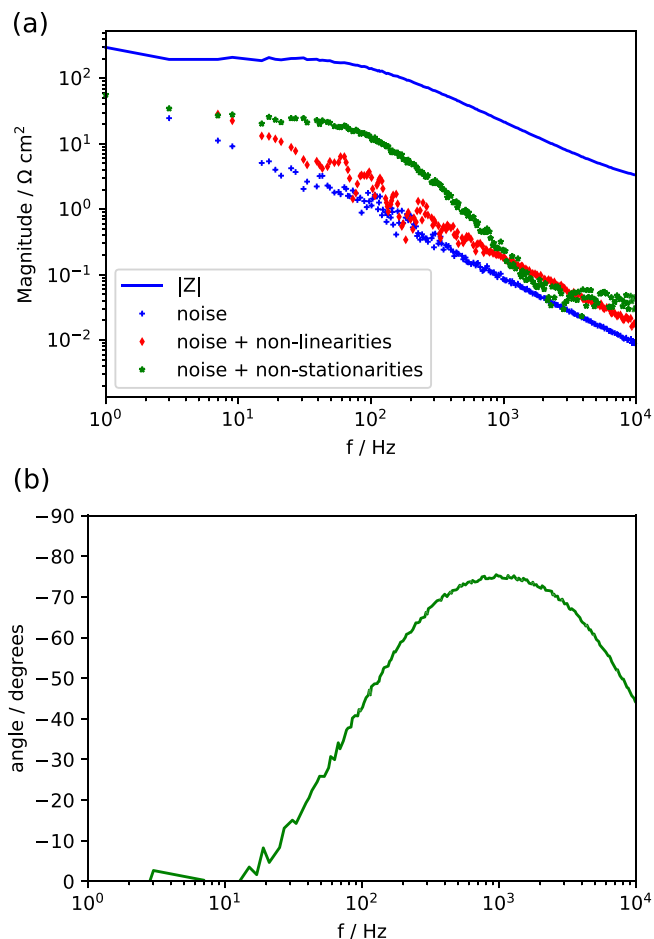


Fig. 2. Results of the galvanostatic ORP-EIS post-graining with six electrode intervals. (a) Modulus and noise levels; (b) phase angle.

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.

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 Fig. 2. Aside from the modulus, also the stochastic noise, and the non-linearities and non-stationarities are shown in Fig. 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].

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 Fig. 3. This figure shows the

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