UNIVERSITY OF CAMBRIDGE

The Effect of Short Potential Pulses on 316L Stainless Steel.

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The effect of short voltage pulses.

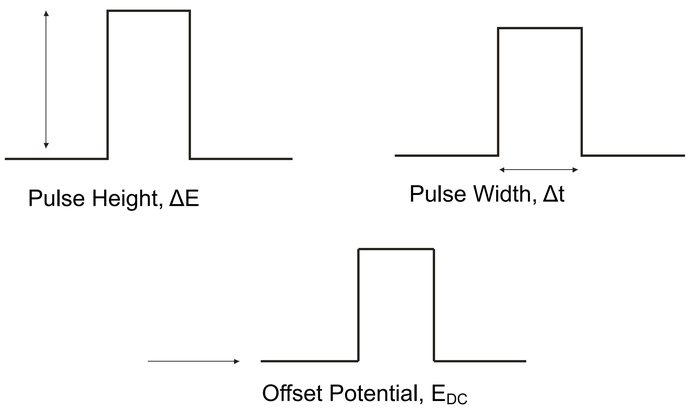
Many commonly used metals acquire corrosion resistance through the presence of a passive oxide film on their surface. However, this passive film is not inert. The metallic ions present in the oxide can still react, and so continuous dissolution and reformation of the film occurs, albeit at a very slow rate.

Pourbaix showed that the oxidation state of a metallic ion is dependent on potential [1]. However, this only takes into account thermodynamic factors. If a potential is only applied for a short period of time, will any reaction occur, and will this alter the passive behaviour of the metal? This can be investigated by the potentiostatic pulse technique—the potential of a sample is controlled, and the current response to a single potential pulse is measured.

Potentiostatic Pulsing.

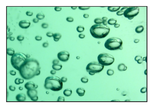
When a metal is polarised in an electrolyte, the excess charge on the metal surface is balanced by a build up of the opposite charge in the electrolyte. This is the electrical double layer, and essentially behaves as a capacitor. Hence, a component of the current response seen at the electrode during potentiostatic pulsing will arise from charging of the double layer— this is the non-Faradaic current. If a chemical reaction occurs, a Faradaic current will also be seen. The two components can be distinguished by integrating the current reponse to give the charge associated with a pulse. The non-Faradaic component rapidly decays to zero after the charging or discharging process is complete, meaning any remaining charge must result from Faradaic processes.

There are several parameters of the applied potential pulse which could affect the current response of the sample:



External parameters may also affect the current response. These include:

- Temperature



- Degree of Aeration

Method.

Figure 1 shows the experimental setup. A 316L stainless steel working electrode was potentiostatically controlled in an electrolyte of Ringer's solution (pH 7.4), with a platinum counter electrode. Ringer's solution is isotonic with body fluids. The temperature was held at 37°C, and air was continuously bubbled through the solution.

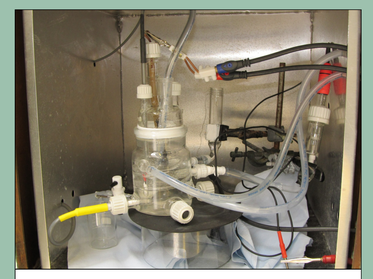


Figure 1: Cell setup for potentiostatic pulse experiment.

Figure 2: The working electrode: a 316L stainless steel sample encased in epoxy resin.

Results.

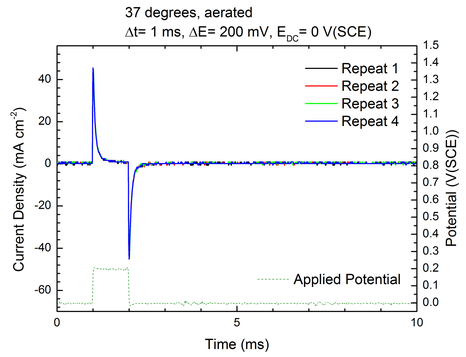
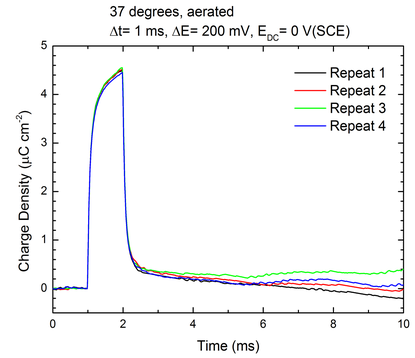


Figure 3: a) Current response of sample to potential pulse (pulse parameters: Δt= 1 ms, ΔE= 200 mV, E_{DC}= 0 V(SCE)). The sharp peaks at the start and end of the pulse result from capacitive charging of the electrical double layer.



b) Charge density response to the pulses in figure 3a). The range of values seen at t= 10 ms mean it is not possible to determine from this graph whether there is a Faradaic component of the charge. If there is, it is small: it takes around 0.5 mC cm^{-2} to oxidise a monolayer of ions by 1e$^-$.

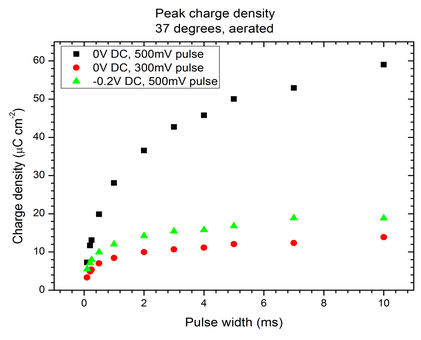
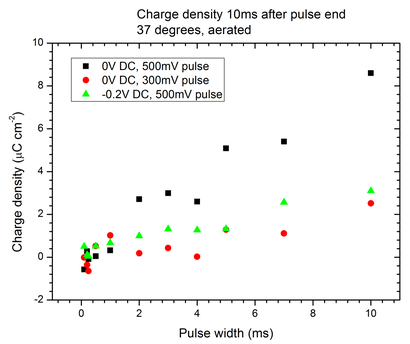


Figure 4: a) Variation in peak charge density with pulse width. This suggests that it is the maximum potential (E_{DC} + ΔE) which determines the current response rather than the individual values of E_{DC} or ΔE.



b) Charge density recorded 10 ms after the end of a potential pulse. Again, E_{DC} + ΔE determines the current response, and there is an increase in charge density with pulse width.

Why is this system of interest?

This project was begun to investigate the effect of TENS (Transcutaneous Electrical Nerve Stimulation) pulses on a fracture plate fixed within a human arm. In TENS therapy, electrodes are attached to a patient's skin and short, repetitive current pulses are passed between them. Typical pulse widths are up to 250 μs, at a frequency of around 100 Hz. However, it does not appear to be known if these pulses have any effect on any metallic orthopaedic implants which may be present, and hence whether use of TENS may alter the corrosion resistance of the implant, or cause metal ions to be released into the body. A further complication is that although the current output of the machine can be measured, the path of this current through human tissue is unknown. By combining the results of experiments designed to simulate the geometry and electrolytic conditions of a fracture plate inside an arm with the potentiostatic pulse results, it should be possible to determine the effect of TENS therapy.

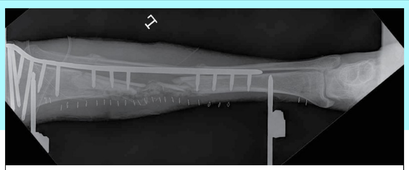


Figure 5: A tibial fracture plate. From Fayaz and Smith [2].

References.

[1] Pourbaix, M. *Atlas of electrochemical equilibria in aqueous solutions.* Pergamon Press, Oxford; New York, 1966.

[2] Fayaz, H.C. and Smith, R.M. *J Trauma Treatment* 1: 110, 2012.