

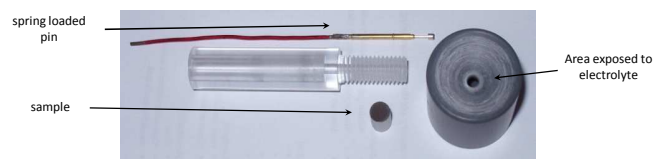
Introduction

The term thermammetry is derived from measurement (-metry) of current (-am-, from ampere) as a function of temperature (therm-) [1]. The technique records the current response to a cyclic linear temperature sweep for a potentiostatically controlled electrochemical reaction. The temperature dependence of electrochemical reactions is widespread, ranging from fundamental properties such as the activity of ions to the rate of oxide film growth, corrosion breakdown, batteries, fuel cells and electrocatalysis.

The aims are to validate the technique against well documented data on equilibrium potentials of reactions and investigate the thermal response of stainless steel in passive and aggressive systems.

Experimental

All experiments were carried out in a glass cell with a standard Calomel electrode (SCE) as a reference. A Platinum ring was used as a counter electrode. All the solutions used were de-aerated using N₂ or Ar gas. A novel method of mounting the sample was used by applying a pressure fit between a nut (PVC) and bolt (Perspex). The holder can accommodate various sample sizes and be assembled quickly.



Electrochemical cell under heating

The reference electrode is in a separate compartment on the right connected to the main cell by a luggin probe. Heating is carried out by an immersion heater with feedback control by a thermistor. Cold water cools the cell through PTFE cooling tubes circling the inside of the cell. The working electrode is in the rear with the platinum disc seen at the front of the cell. The system is able to cycle the temperature linearly up to 3 °C/minute.

Validating the method

These two ions form a highly reversible equilibrium on a platinum electrode, a length of platinum wire encased in a glass tube.



The potential of this equilibrium was measured against a SCE electrode for two ion concentrations (figure 1). This was done using a high impedance electrometer maintaining the current near zero. There is no hysteresis between the forward and reverse thermal cycles. The change of equilibrium potential with temperature is not linear. This arises due to the change of activity coefficients for the two ions with temperature. The equilibrium potential at all temperatures differs for the two concentrations. This is expected from the extended Debye-Hückel theory, which takes into account the unsymmetrical nature of the ions. The higher the concentration of the ions the greater the ionic interaction between them. The data follows other literature (figure 2) [2].

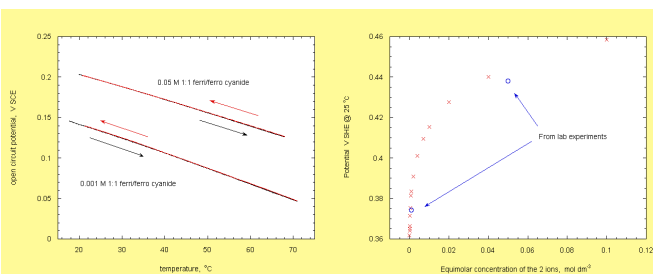


Figure 1: The change of the equilibrium electrochemical potential with temperature to 70 °C at a sweep rate of 30 mK s⁻¹

Figure 2: Equilibrium potential of the system potassium ferrocyanide potassium ferricyanide at various ionic strengths [2]

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Pitting Corrosion - Cyclic thermammetry in aggressive systems

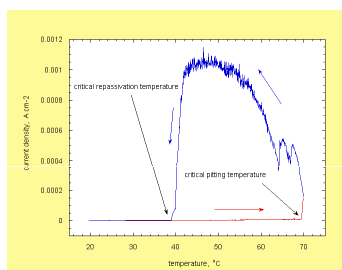


Figure 3a: 316L stainless steel in 1 M HCl, polarised to 0.05 V SCE and thermally cycled to 70 °C at a sweep rate of 40 mK s⁻¹

Figure 3a highlights the massive change in behaviour caused by Cl⁻ ions. There is a 100 fold increase in current density caused by the propagation of pits. A difference of 30.5 °C exists between the critical pitting temperature and the critical repassivation temperature. This means that once pitting commences it is harder to stop the corrosion process.

The pits were visible by eye after the experiment, illustrating the damage pitting corrosion can do in high temperature aqueous systems such as those in a steam turbine.



A Siemens steam turbine with the case open

Below the critical pitting temperature current transients can be seen due to the propagation of metastable pits. Pits grow initially in a metastable manner with a covering over the mouth. The cover maintains the aggressive environment in the pit. Metastable pits repassivate when the cover collapses. Stable pitting commences once the rate of dissolution of the metal is fast enough to maintain the pit chemistry without the need for a cover.

In figure 3b the frequency of these events increases with temperature. The passive current rises with temperature at a faster rate once metastable pits begin to form.

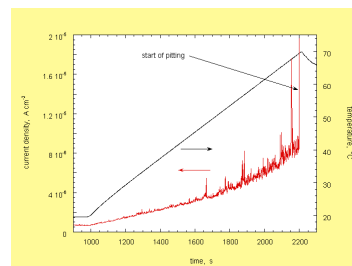


Figure 3b: Same experiment as in 3a but with expanded view of passive region before pitting

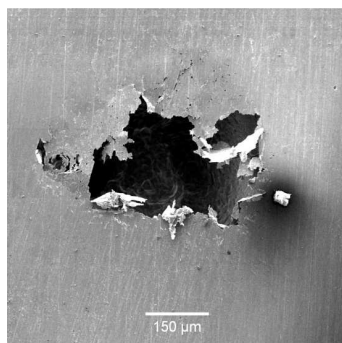


Figure 4: A view of a pit after a cyclic thermammetry experiment. Remains of the covering can be seen partially obscuring the bottom of the pit. The pit grows and gradually undercuts the passive film on the surface. The actual area of the pit mouth is approximately 0.25 mm².

Localised corrosion such as this pit is a disaster. Catastrophic failure results, with the subsequent huge loss of money from downtime and repair.

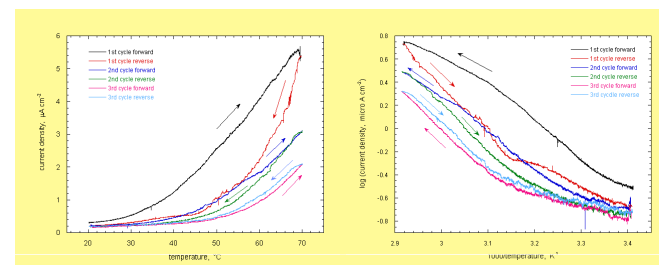
Cyclic thermammetry will help in the drive to understand corrosion and prevent future problems.

Pitting corrosion destroys the surface integrity unless engineered against as in the Thames Barrier.



River Thames Flood Barrier, opened 1982

Making metals more passive - Cyclic thermammetry in passive systems



Figures 5a and 5b: 316L surgical grade stainless steel in 0.1 M H₂SO₄, polarised to 0.3 V SCE and thermally cycled to 70 °C at a sweep rate of 30 mK s⁻¹, figure 5a is a cyclic thermammogram and figure 5b is an Arrhenius plot of the same data.

In figure 5a the current density increases with temperature indicating a thermally activated process. In the first thermal cycle an order of magnitude change in current density occurs over a 50 °C temperature change. The stainless steel is sensitive to the thermal cycle. The peak current density decreases for successive thermal cycles. The behaviour of titanium is similar to stainless steel in this system. A change in the gradient is observed at 45 °C (figure 5b) indicating a change in the mechanism of passivation. Cyclic thermammetry has revealed this new phenomenon.

The hysteresis loop shrinks from one thermal cycle to the next. The surface composition and topography of the stainless steel is becoming more stable the greater the number of cycles it is exposed to. This is a new form of surface treatment, which does not apply any coating. This treatment could be beneficial to sensitive devices such as implants in the human body. After three thermal cycles the corrosion rate at 37 °C body temperature has decreased by 75 %.



A titanium hip prosthesis, with a ceramic head and polyethylene acetabular cup

Summary

Cyclic thermammetry produces reliable and extremely accurate measurement of the electrochemical response to temperature.

Cyclic thermammetry enhances the passivity of metals under certain conditions. Thermal cycling reveals a change in the passivation mechanism.

Cyclic thermammetry reveals the critical pitting temperature and critical repassivation temperature of metals in aggressive electrolytes. The frequency of metastable events increases with temperature until the critical pitting temperature.

Cyclic thermammetry reveals several new phenomena, which are characteristic of the electrochemical system. These are not observable by any other technique.

Cyclic thermammetry can in principle be used in any electrochemical system such as fuel cell operation. Fuel cells are more efficient at higher temperature but the likelihood of breakdown increases. The technique can probe the limits of electrocatalysis in fuel cells to improve efficiency and durability. The technique can be used at higher temperatures to study solid state fuel cells.

References

- [1]: G.T. Burstein, J.J. Moloney, Electrochem. Comm., 2004, 6 (10), pp 1037-1041
- [2]: I.M. Kolthoff, W.J. Tomsick, J. Phys. Chem., 1935, 39, pp 945-954