

## Efficiency of Pitting Corrosion Inhibitors on AA2024 T3 Quantified using Numerical Integrated SVET Data

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A numerically integrated scanning vibrating electrode technique (SVET) approach is used to quantify the influence of chromate ( $\text{CrO}_4^{2-}$ ) and the trivalent rare earth metal (REM) cations of cerium ( $\text{Ce}^{3+}$ ), yttrium ( $\text{Y}^{3+}$ ) and lanthanum ( $\text{La}^{3+}$ ) on the kinetics of pitting corrosion as it occurs on AA2024 T3 aluminium alloy immersed in 3.5% aqueous sodium chloride (NaCl).

SVET may be calibrated to map the normal current density distribution occurring at a fixed distance above a metal surface freely corroding in aqueous electrolyte<sup>1</sup>. Thus, in the case of pitting corrosion it has been shown that SVET may be used to determine the number of stable pits active at any point in time and to estimate the anodic current emerging from individual pits.<sup>1</sup> Furthermore, repeated scanning of the corroding surface with a similar technique has allowed the pit current-time profiles associated with the initiation, propagation and repassivation of individual pits to be obtained.<sup>2</sup>

Here we show that the total pitting current for a pit population may be estimated by numerically integrating anodic components of the normal current density distribution over the scanned area. Thus, repeated scanning of the corroding surface allows the pitting current-time profile to be obtained for the entire pit population under free corrosion conditions (Fig.1). Furthermore, numerical integration of the pitting current-time profile with respect to time estimates the total metal loss over the experimental period (Fig.2).

Using the numerically integrated SVET approach it is shown that  $\text{CrO}_4^{2-}$  present in concentrations between  $2.5 \times 10^{-5} \text{ mol dm}^{-3}$  and  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$  rapidly (within one hour) reduces the total pitting current to  $< 0.02 \text{ Am}^{-2}$ . In contrast, the inhibition of pitting current by the trivalent REM cations is found to depend strongly on inhibitor concentration. Thus REM cations present at  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$  reduce pitting current to  $< 0.02 \text{ Am}^{-2}$  within 10 hours. Whereas, when the same REM cations are present at  $2.5 \times 10^{-5} \text{ mol dm}^{-3}$  pits and significant levels of pitting current may remain detectable for much longer periods of time.

The total metal loss estimated through the numerical integration of pitting current with respect to time is used to calculate inhibitor efficiency. Thus it is shown that inhibitor efficiency increases in the order  $\text{Y}^{3+} \sim \text{La}^{3+} < \text{Ce}^{3+} < \text{CrO}_4^{2-}$ , although the efficiencies of  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  are comparable suggesting a similar mode of action for all the REM cations. Furthermore, it is shown that the principal reason for the lower efficiencies of the REM cations is the slower onset of inhibition observed with these species. That is to say, whilst the ultimate reduction in pitting current may be similar in the case of REM and chromate inhibitors the persistence of pitting current for longer periods in the case of REM cations gives rise to significantly higher levels of metal loss.

It is proposed that the slower onset of inhibition in the case of REM cations arises from the need for corrosion, and associated cathodic oxygen reduction, to proceed in order to allow the deposition of a REM (hydr)oxide cathodic film.<sup>3</sup> In contrast chromate may act as a cathodic depolariser, producing rapid surface passivation without the requirement for significant levels of corrosion to have occurred.

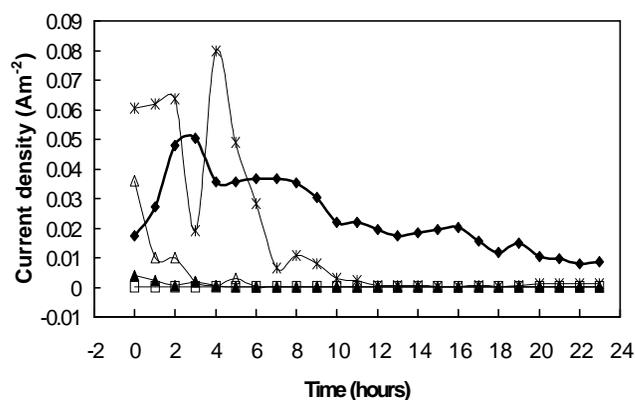


Figure 1: Plot of total anodic current density against time for AA2024 T3 immersed in 3.5% aqueous NaCl at 20°C.

Uninhibited sample  $\blacklozenge$ . Inhibitors at concentration  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ :  $\square$   $\text{CrO}_4^{2-}$ ,  $\blacktriangle$   $\text{Ce}^{3+}$ ,  $\triangle$   $\text{La}^{3+}$  and  $\times$   $\text{Y}^{3+}$ .

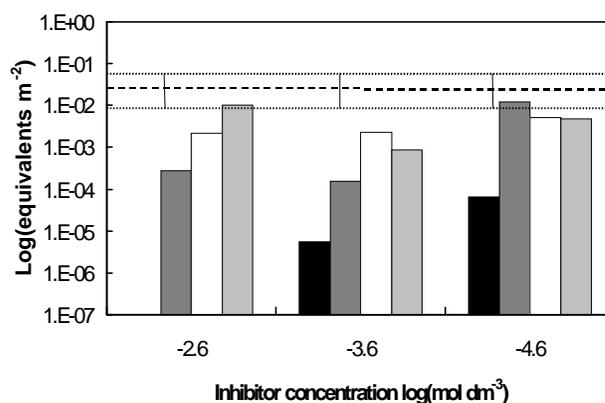


Figure 2: Metal loss in equivalents per square metre for AA2024 T3 in 3.5% aqueous NaCl for 24 hours at 20°C. Inhibitor concentration:  $\blacksquare$   $\text{CrO}_4^{2-}$ ,  $\blacksquare$   $\text{Ce}^{3+}$ ,  $\square$   $\text{La}^{3+}$ ,  $\square$   $\text{Y}^{3+}$ . Dashed line indicates corrosion of uninhibited sample  $\pm$  standard deviation,

## REFERENCES

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