



# Micro-Potentiometry and Micro-Amperometry as Complements to SVET in Corrosion Research

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## Introduction

SVET has been used as sole technique or as complement to other techniques in many corrosion studies. It gives the distribution of cathodic and anodic regions in a corroding sample. The technique detects changes in the electric field in solution caused by fluxes of positive and negative ions. Regrettably, it is only sensitive to charged species and is unable to identify the species detected. Nonetheless, its information is unique and extremely useful in the description of many corrosion processes. This paper intends to show how micro-potentiometric and micro-amperometric measurements can help the interpretation of SVET data, complementing it.

The corrosion system analysed is AA2024-T3, an aluminium alloy for aeronautics applications, coated with a hybrid organic-inorganic film produced by the sol-gel route, with two small defects, immersed in 0.05M NaCl. Measurements were performed before and after a corrosion inhibitor, Ce(III) nitrate, was added to the solution.

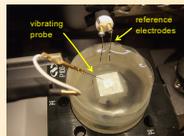
## SVET

### Scanning vibrating electrode technique

The measured potential differences in solution,  $\Delta V$ , can be related to the ionic currents that originate them,  $I$ , by a proper calibration or by equation

$$I = \frac{E}{\rho} = -\frac{1}{\rho} \frac{\Delta V}{\Delta r}$$

where  $E$  is the electric field between the two ends of the vibration amplitude,  $\Delta r$  is the amplitude of vibration and  $\rho$  is the solution resistivity.

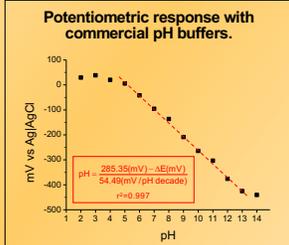
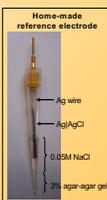
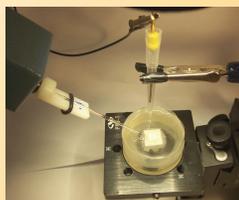


### Equipment

SVET, SIET and SPET measurements were performed using equipment from Applicable Electronics Inc. (USA) controlled by the ASET software developed by ScienceWares Inc. (USA).

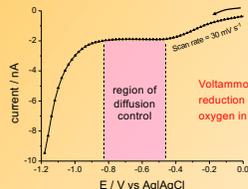
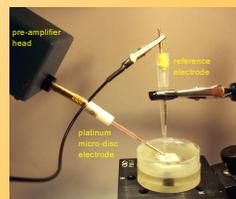
## SIET

### Scanning ion-selective electrode technique (Micro-potentiometry)



## SPET

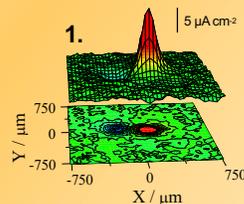
### Scanning polarographic electrode technique (Micro-amperometry)



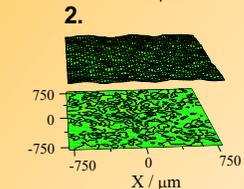
For the amperometric detection of dissolved O<sub>2</sub> the tip potential is fixed at -0.700 V vs Ag/AgCl, well inside the region of diffusion control. The diffusion-limited current is independent of small changes of applied potential and, for a disc microelectrode, can be calculated by  $i = 4nFD\sqrt{C}$  where  $n$  is the number of electrons for the reduction reaction,  $F$  is the Faraday constant,  $D$  is the oxygen diffusion coefficient,  $r$  is the micro-disk radius and  $C$  is the oxygen concentration in solution.

## Results

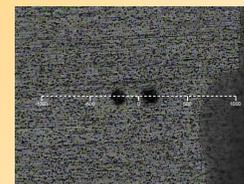
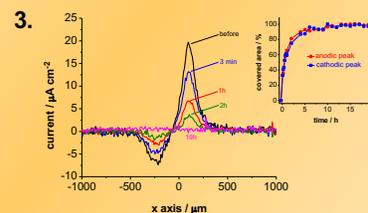
1. SVET current maps obtained in solution 100  $\mu\text{m}$  above the two defects after 24h of immersion in 0.05M NaCl. The corrosion activity is localized in the two defects, being one anodic and the other cathodic.



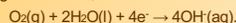
2. 24 hours after the addition of a corrosion inhibitor (cerium nitrate giving a final Ce<sup>3+</sup> concentration of 10 mM) no signs of corrosion are detected.



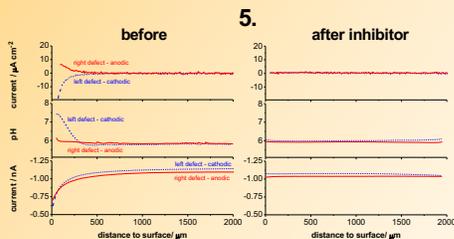
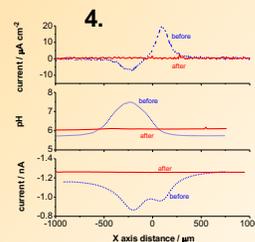
3. Ionic currents measured across a line over the two defects after the addition of inhibitor. The drop in corrosion activity is fast. Inhibition comes from the precipitation of cerium hydroxide in the cathodic regions. With time all exposed metal will be covered and protected by a layer of Ce(OH)<sub>3</sub> [1]. The covered area,  $\theta$ , can be estimated by  $\theta = 1 - i/i_0$  where  $i_0$  and  $i$  are, respectively, the currents before and after inhibitor [2].



4. Ionic currents, local pH and reduction current of dissolved oxygen obtained in parallel lines 50  $\mu\text{m}$  (100 for SVET) above the surface, before and after the addition of inhibitor. Before inhibition clear changes are observed near the defects. pH increases in the cathodic defect due to the oxygen reduction,



Oxygen is consumed in both defects indicating that reduction occurs in both, not just in the defect indicated as cathodic by SVET. After addition of inhibitor the measured values are the same as those encountered in the bulk solution. The metal becomes isolated from the solution and ceases to change the composition in its vicinity.



5. Ionic currents, pH and oxygen reduction current obtained in the z direction above the defects before and after inhibitor addition. The same trend described in 4 is observed.

- 1. B. R. W. Hinton, Metals Forum, 7 (1984) 211.
- 2. Shreir, Jarman, Burstein, Corrosion 3<sup>rd</sup> Ed, Vol. 2, Butterworth Heinemann, Oxford, 2000, p. 20:27

## Conclusions

- ◆ The corrosive process was addressed from the side of the solution.
- ◆ The measurement of ionic currents in solution permitted to follow the evolution of the corrosion process and the inhibition kinetics of a soluble inhibitor.
- ◆ The local distribution of pH and dissolved oxygen gave new insights into the corrosive process and the inhibition mechanism.
- ◆ Sensing microelectrodes can be very useful in studies of self-healing of coatings in defects.