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Short Communication

The influence of vibration and probe movement on SVET measurements

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ABSTRACT

This communication describes a set of experiments performed to evaluate the influence of SVET vibration and movement of the probe on the obtained results. Both vibration and movement during scanning stir the solution with the risk of enhancing the oxygen transport to the surface thus increasing the measured currents and accelerating the corrosion process. It is shown that, for the SVET system used, due to its small probe, the effect of the vibration is negligible in normal operation. On the contrary, the movement of the probe during scanning increases the cathodic reaction and smaller excursions or slower movements just marginally reduce this effect. It is also shown that only the region of the sample under the probe is affect and for just brief instants. The overall corrosion in the long run is not influenced and the measured maps only scarcely show any evidences of artifacts introduced by the probe movement.

1. Introduction

The scanning vibrating electrode technique (SVET) has been applied to characterise a great variety of corrosion systems [1–11]. The visualisation of the corrosion progression in terms of the identification of anodic and cathodic regions with estimation of the respective currents and their evolution in space and time is usually sufficient. However, it may be important to go further and use the SVET data for modelling purposes or to estimate corrosion rates. When such quantitative information is necessary, the experimental data must be absolutely accurate which means that all experimental parameters must be well known and controlled at all times. In addition, it is assumed that SVET does not interfere in any way with the system under study. Usually the sample corrodes freely at open circuit potential with the probe scanning above it without any contact between the two. The probe vibrates in order to generate the sinusoidal signal required for the amplification and filtering in a lock-in amplifier.

The effect of the probe vibration in biological systems was analysed by Ferrier and Lucas [12] who showed that the convective loops produced by the probe do not affect the electrical current density but can significantly change the ion concentration gradients in the layer near a tissue or cell surface and, sometimes, even the electrical potential gradient. In the corrosion context, McMurray et al. [13] analysed the influence of the probe vibration on the transport of O_2 to the metal surface. Using a 25 μm Pt disk polarised as cathode they identified the probe-to-sample distance and the amplitude of vibration as critical factors and observed that, in some conditions, the vibrating probe was able to increase the oxygen reduction current by a factor of 3–4. The effect of probe vibration on the corrosion of cut edges of galvanized steel, where oxygen diffusion to the metal surface is the rate determining step, was also studied in the same work. It was observed that while an increase in amplitude increased the local cathodic currents beneath the probe, the vibration did not affect the overall measured total anodic current because it did not significantly alter the rate of oxygen reduction across the entire sample. An overestimation of the total cathodic current by up to an order of magnitude resulted from large amplitude vibrations ~25–250 μm. An optimum small amplitude vibration <25 μm was considered critical to the quality of the data obtained using SVET.

Different SVET systems and probes exist that may affect the measurements and the corrosion process in different manners and extents. In the case of reference [13] the tip of the vibrating probe was a glass disk of 250 μm in diameter with a central active Pt disk of 125 μm diameter. Another model of SVET, used by many groups and by the authors of this work, employs a probe with a tip of usually 20 ± 10 μm and vibration amplitude of the same order of magnitude, being the measurements performed typically in a plane 50–200 μm above the sample surface.

It is important to check whether or not this SVET system suffers from the same reported problem and identify the parameters most relevant to it. For that purpose, in this work the SVET measured the ionic currents above a platinum disk polarised at potentials where oxygen reduction is controlled by diffusion, while the current in the circuit was being simultaneously measured. This permitted to assess the level of alteration introduced by the SVET scans.

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Another experiment made use of a Zn–Fe galvanic couple with the galvanic current being recorded while SVET maps were being acquired. In this way it was possible to observe how a typical corrosion system was affected by SVET in normal operation.

2. Experimental

The SVET equipment was manufactured by Applicable Electronics Inc. (USA) and controlled by the ASET 2.00 program developed by Sciencewares (USA). The SVET microelectrode was prepared from polymer insulated platinum–iridium microelectrodes produced by Microprobes Inc. (USA). A 20 μm diameter platinum black sphere was electrodeposited at the tip. The microelectrode vibrates in two directions, one parallel (*x* axis) and another normal (*z* axis) to the sample surface, sensing the electric field in the two directions, but in corrosion the signals for the *x* vibration are seldom used. The *x* and *z* frequencies were 115 Hz and 69 Hz, respectively, and the amplitude of both vibrations was 10 μm. After arriving to a new point of measurement the probe waited 0.2 s and averaged for more 0.2 s before moving to the next point. The SVET measures potential differences which are converted to current densities after a calibration performed with a point current source (microelectrode with a tip of ~2 μm) driving a current of 60 nA at 150 μm from the vibrating probe [14–16]. The calibration is valid for a new solution provided the system is updated with its conductivity.

The two electrochemical cells used are depicted in Fig. 1. The first consisted of 1 mm diameter platinum disk electrode embedded in epoxy matrix, connected to Ivium CompactStat potentiostat (Ivium Technologies, The Netherlands) in a 3 electrode arrangement with the platinum disk as working electrode, a platinum wire as counter electrode and a homemade Ag|AgCl|0.05 M NaCl electrode as reference. A second cell consisted of 1 mm pure zinc disk galvanically coupled to 1 mm pure iron disk. The galvanic current was measured with the Ivium Compactstat. The surfaces of both samples were abraded to SiC 4000 grade before experiments. In all cases the solution was 0.05 M NaCl at 23 ± 1 °C (conductivity = 5.18×10^{-3} S cm^{-1}, at 23.0 °C).

3. Results and discussion

In the first experiment, the effect of SVET during scanning above a platinum disk where reduction reactions are taking place was analysed and the results are depicted in Fig. 2. Fig. 2(a) shows the current–potential curve of the platinum disk in 0.05 M NaCl at a scan rate of 1 mV s^{-1} with the region of diffusion control between −0.5 $V_{Ag|AgCl}$ and −0.9 $V_{Ag|AgCl}$, and the region dominated by H_2O reduction from −0.9 $V_{Ag|AgCl}$ to more negative potentials. The inset of Fig. 2(a) shows the chronoamperometric response of the electrode polarised at −0.75 $V_{Ag|AgCl}$. After a Cotrellian behaviour in the first ~3 min the current stabilised around 500 nA due to natural convection. The chronoamperometric measurement was repeated at different fixed potentials with SVET maps being acquired 100 μm above the surface. The chosen potentials were 0 $V_{Ag|AgCl}$, where almost no reaction occurs, −0.5 and −0.75 $V_{Ag|AgCl}$, in the region of diffusion control, and −1 $V_{Ag|AgCl}$, where H_2O reduction is the predominant reaction. The SVET measurements started only after a stable reduction current was attained. Each map comprised 20 × 20 points and in Figs. 2(bx) they correspond to the interval 100–388 s of the chronoamperograms. The records of the current clearly display the influence of the SVET measurements in the form of periodic variations. These coincided with the passage of the probe above the Pt disk while scanning left–right and right-left, line after line. Each scan line produces a rise and a fall in the current, with the maximum being coincident with the middle of the disk. The movement of the probe enhances the transport of dissolved oxygen from the bulk of solution to the cathode increasing the reduction current. The process is fast, with a sudden increase when the probe enters the area above the cathode followed by a rapid decrease as soon as it moves away.

The highest current variations occurred during the first lines of the scan whereas in the last lines just small variations were observed. This is related to the position of the probe. The SVET probe is basically a ball shaped platinum microelectrode tip at the end of an insulated wire inclined over the surface (Fig. 1c). The maps are acquired with the tip going from top to the bottom of the image. In the first lines the tip is over the insulating matrix but the wire is above the Pt disk. This induces the largest convection and produces the maximum disturbance. As the scan progresses, less Pt area is under that "moving wire". In the middle of the scan only half of the Pt disk is affected and in the last lines the probe is no longer above the disk and the effect vanishes.

The hydrodynamics induced by the probe is a subject to be investigated in future work.

Fig. 2(b2) compares the perturbation introduced by the probe when it scans at 100 μm with and without vibration and when it scans vibrating at 200 μm. The measurement performed at 200 μm had smaller impact on the current, leading to a maximum increase of 10% compared to 20% at 100 μm. The currents with the probe scanning at 100 μm with and without vibration were nearly the same, with a difference of only 15 nA. This means that it is the movement of the probe during scanning that creates most of the disturbance. The vibration just adds a limited contribution.

The effect is more important when the process is controlled by the diffusion of O_2 (−0.5 $V_{Ag|AgCl}$ and −0.75 $V_{Ag|AgCl}$). The relative

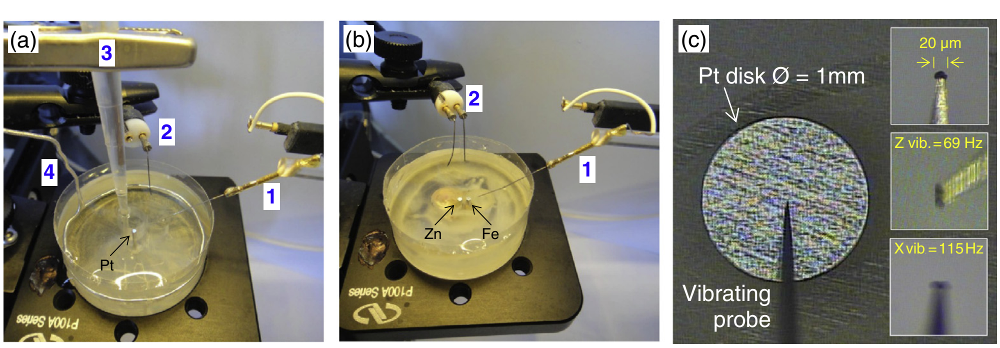

Fig. 1. Electrochemical cells used: externally polarised 1 mm diameter platinum disk (a) and galvanically coupled 1 mm diameter zinc and iron disks (b) where 1 – vibrating electrode, 2 – pseudo-reference electrode and ground (ground electrode removed in (a)), 3 – homemade Ag|AgCl reference electrode, 4 – platinum wire counter electrode. Also shown is the size, shape and vibration of the SVET probe (c).