Multi-ion transport and reaction model used to improve the understanding of local current density measurements in presence of concentration gradients around a point current source

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A B S T R A C T

A departure from the theoretical current density distribution close to a point current source is observed in both Scanning Reference Electrode Technique (SRET) and Scanning Vibrating Electrode Technique (SVET) measurements. Here we report the use of a general multi-ion transport and reaction model, which accounts for micro-convection to point out the origin of the deviations that are experimentally observed. The validity of the model is proven by comparison against both analytical and measured (SRET and SVET) distributions of the current density in a typical calibration setup. Solutions with different conductivities and different impressed currents are considered.

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1. Introduction

The Scanning Reference Electrode Technique (SRET) was developed with the aim of investigating the distribution of the electric potential in the electrolyte solution near corroding metals [1–4].

The Scanning Vibrating Electrode Technique (SVET) was initially introduced to measure the resting potentials in biological systems [5–7], then adapted to localized corrosion investigation [8–11]. The working principles remain unchanged, although the design of the apparatus underwent several modifications since the first complete design specifications were published [6,7].

Both techniques measure the local electrolyte potential in the solution at two different points, which is then converted to a local current density in the solution, using Eq. (1),

$$\vec{J}_{loc} \approx -\kappa \frac{\Delta U}{\Delta r} \vec{1}_r \approx -\kappa \vec{\nabla}_r U \qquad (1)$$

in which $\vec{1}_r$ the unit vector in the direction of r, κ ($\mathrm{S\,m^{-1}}$) is the local electrolyte conductivity, ΔU (V) the electrical potential difference between the points at the distance Δr (m). This provides a good approximation of the gradient of the electric potential in solution in the direction of Δr. In SRET, Δr corresponds to the vectorial distance between two probing points. In SVET, Δr corresponds to the peak-to-peak vibration amplitude in the direction of the measurement. In both techniques a uniform conductivity of the solution is assumed.

Due to their resolution down to the micrometer range, these techniques are used to investigate localized corrosion, such as pitting, crevice and intergranular corrosion [12–19], or to evaluate the quality of organic and inorganic coatings [20–22].

A number of theoretical and experimental studies have been dedicated to improve the understanding and the performances of these methods. Soon it was experimentally found that the sensitivity of SRET is increased in solutions with lower conductivity [2,4,23]. Studies on the effect of the convection loops induced by the vibrating electrode on the measured current densities are available [24,25], as well as on the effect of the operating parameters, like the probe height and the ratio between probe height and the size of the current source [26,27], the ratio between probe height and

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vibration amplitude [26], the angle of probe vibration [28] and the probe tip inclination relative to the studied sample [29], the vibration amplitude [30], or the calibration procedure [31]. The shielding effect of the tip of the probe at distances from the current source lower than 1.5 times the tip diameter is briefly treated in [27,32]. However, due to the variety of devices in use, no universal working protocol can be defined; the one available in literature refers to a particular setup [33].

All the above-mentioned applications of SRET and SVET to corrosion present results at about 100 to 150 μm away from the current source. In order to further improve the accuracy of these methods, it would be very interesting and necessary to go closer to the current source. But what is measured? The practice shows that the recorded current density deviates from the theoretical one when the probe is close to the source. In literature examples of discrepancies from the analytical distribution close to the source are found, but they are not explicitly treated, as they are outside of the scope of those works [34–36].

Also the use of numerical models to simulate the SVET response of several corrosion systems of industrial importance lead to a somewhat astonishing conclusion: the simple potential model gives better simulation results than the more complete transport and reaction model that considers convection, diffusion and migration of each species [34,35,36] and that in fact includes the potential model.

An explanation of the divergence from Ohm's law was given by Ferrier and Lucas [24,25]. In their theory they assume that at steady state and close to the source, the current in solution is transported only by diffusion and migration of the reacting ion. Convection, including that one generated by the SVET tip, is neglected. The latter assumption will be discussed later but at least in the measurements presented in this work there is indeed no substantial difference between the SVET and SRET results (see below). In fact, for a point current source with current I (A), the expression giving, based on Ohm's law (Eq. (2)), the current density J (A m^{-1}) at a distance r (m), is not measured in all situations [24,25].

$$J(r) = -\kappa \overrightarrow{1}_r \cdot \overrightarrow{\nabla} U = \frac{I}{4\pi r^2} \qquad (2)$$

We extend this theory by proposing a formula to compute the mean diffusivity of the ions in the electrolyte solution. With this addition, the above-mentioned theory will be used in the postprocessing of our results to explain the predicted current density distribution inside the diffusion layer. Outside that layer the convection is mixing all ions. The formation of a hydrodynamic boundary layer is a direct consequence of the viscosity in an externally imposed flow. However, many SVET and corrosion studies are performed in quiescent conditions, without any source of forced convection. Nevertheless the settlement of a hydrodynamic boundary layer and consequently a diffusion layer is clearly observed. This means that a naturally, spontaneous occurring convection must be present. Some of the authors of the present work accounted for that natural convection by imposing very small convection loops [37]. This approach had laid to much more realistic simulations that were in fair agreement with the expected pH distribution close to the electrode and a proper bulk pH [37]. The current experimental conditions were carefully controlled, such that no intentional thermal and concentration gradients are expected. In the given conditions, the only source of convection remains the unsteady flow originating from small differences in temperature, concentration, vibrations, air movement, evaporation, etc. The direct simulation of these phenomena would be computationally hardly possible and as such almost unusable for electrochemistry simulations. Another way of accounting for these phenomena is to assign their effect to a space-dependent diffusion process [38]. This approach will be adopted in the present paper in order to extend the classical multi-ion transport and reaction model that will be used to simulate the current density distribution around a micropipette current source. The results will be compared with original SVET and SRET measurements performed in different conditions.

The paper is structured as follows. First the experimental setup and the corresponding electrochemical model will be described in detail. In a second part the theory is explained. Then simulations are compared with measurements. The discussion intends to provide an answer to the role of magnitude and sign of the applied current, the species distributions and related conductivity. Also the role of the vibration is discussed briefly.

2. Experimental

2.1. SVET measurements

Ionic currents in solution were measured with a SVET equipment manufactured by Applicable Electronics Inc. (USA) and controlled by the ASET program developed by Sciencewares (USA). The SVET microelectrode was prepared from Parylene C insulated Pt-Ir microelectrodes produced by Microprobes Inc. (USA). A 10 μm radius platinum black sphere was electrodeposited on the tip. The microelectrode vibrates in two directions but only the x vibration (the same as the approach direction) was considered in the present study. The frequency was 185 Hz and the amplitude of vibration was 10 μm. The measured potential differences were converted to ionic currents following a calibration routine performed with a point current source (microelectrode with a tip of ~2 μm) driving a current of 60 nA at 200 μm from the vibrating probe [6,7]. The calibration is valid for different solutions provided that the software is updated with the correct conductivity. The time of acquisition was of 0.2 s in each point with prior waiting time of 0.2 s to avoid translation effects from the previous position.

2.2. SRET measurements

The potential in solution was measured by SRET (scanning reference electrode technique) with a moving micro-reference electrode with respect to a fixed reference electrode. The microelectrode consisted of silanized borosilicate glass micropipette with a tip of 2 μm filled with the solution of measurement and an internal Ag|AgCl wire. The microelectrode was mounted in the 3D positioning system used for SVET via a pre-amplifier head (input resistance > 10^{15} Ω) which was connected to an IPA2 amplifier manufactured by Applicable Electronics Inc. A fixed Ag|AgCl electrode filled with the same solution of measurement was connected to the pre-amplifier head and worked as reference. The ASET program controlled the measurements and recorded the data.

2.3. Materials

The current source (point in space) was a glass micropipette with a tip of 2 μm and a platinized platinum wire inside. The solution both in the Petri dish and inside the capillary was 0.005 M or 0.05 M NaCl made with distilled water and p.a. grade reagent. The current flew between the wire located inside the micropipette and an auxiliary platinized platinum wire placed 2 cm away from the tip. Approach lines were measured from 2000 down to 10 μm by SRET and from 2000 μm to 50 μm by SVET. A picture of the experimental setup with the vibrating probe in the working position is given in Fig. 1a.