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Simulation of the role of vibration on Scanning Vibrating Electrode Technique measurements close to a disc in plane

Olga Dolgikh[a], Andrei–Stefan Demeter[a,b,*], Sviatlana V. Lamaka[c,d], Maryna Taryba[c], Alexandre C. Bastos[e], Marcela C. Quevedo[e], Johan Deconinck[a]

[a] *Vrije Universiteit Brussel, Research Group Electrochemical and Surface Engineering, Pleinlaan 2, 1050 Brussels, Belgium*
[b] *Technical University of Cluj Napoca, Faculty of Electrical Engineering, 26-28 George Baritiu Street, 400027 Cluj Napoca, Romania*
[c] *Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa. Av. Rovisco Pais, 1049-001 Lisbon, Portugal*
[d] *MagIC, Magnesium Innovation Centre, Institute of Materials Research, Helmholtz-Zentrum Geesthacht, 21502, Germany*
[e] *University of Aveiro, CICECO, Department of Materials and Ceramic Engineering, 3810-193 Aveiro, Portugal*

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ABSTRACT

An elegant and accessible way to account for the local stirring created by the vibration of the SVET tip by adding a new diffusion–like term into the molar flux expression is proposed, in order to avoid solving the fluid flow. This term is maximal in the point of vibration and rapidly decreases with the distance. It is shown that the local mixing leads to a substantial increase of the migration current density in the vicinity of the probe with simultaneous decrease of the diffusion current contribution. This local mixing has no effect on the pH distribution, regardless the applied polarization, and increases under cathodic polarization the oxygen concentration only when the probe is close to the electrode surface which is confirmed by experimental observations. The proposed model is compared with the analytical current density distributions obtained from potential model and experimental data. All this indicates that local mixing might explain why the SVET technique, although based on the measurement of an ohmic current density, measures always the total current density.

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1. Introduction

Scanning Vibrating Electrode Technique (SVET) has become a widely used investigation technique in the field of corrosion [1–6]. It is used primarily for visualization of the corrosion process progression in terms of anodic and cathodic areas localization and evolution in time, as well as current magnitude monitoring.

An ideal analytical tool should not disturb the system under investigation. In practice, the local stirring of the electrolyte is a feature of SVET. This stirring was observed since the introduction of the modern vibrating probe [7]. The main effect of the stirring is the local mixing of the electrolyte, canceling out the concentration gradients. Even at small vibration amplitude (about one diameter of the SVET tip) and moderate vibration frequency, the mixing effect spreads over an area of few times the vibration amplitude. The reduction of the local concentration gradients increases the local

electrical potential gradient [8,9]. On the other hand, larger values of the vibration amplitude lead to important increase in the rates of the electrode reactions taking place under diffusion control, e.g the oxygen reduction reaction on cathode [10]. A deeper investigation of this phenomenon performed by one of the authors, proved that in normal operating conditions (SVET tip of diameter 10–20μm placed at more than 50 μm above the surface of the sample, vibration amplitude of the same order of magnitude as the tip radius and up to 200 Hz vibration frequency [11,12]) most of the stirring of the electrolyte solution is caused by the movement of the probe during scanning and less than 5% of the total increase of the cathodic current is caused by the vibration of the tip of the SVET probe [13]. Despite of these disturbances, the technique was experimentally validated long time ago and used to produce valuable analytical results ever since H. Isaacs has adapted SVET for corrosion research [14].

The technique is based on a simple idea: the electrolyte potential in the solution is measured at two different points and then converted to a local current density in the solution, using Eq. (1)

$$\vec{j}_{loc} = -\kappa \frac{\Delta U}{\Delta \vec{r}} \approx -\kappa \vec{\nabla} U, \tag{1}$$

where j_{loc} (A m^{-2}) is the local current density in the electrolyte, κ (S m^{-1}) is the local electrolyte conductivity, ΔU (V) the electrical potential difference between the points at the distance $\Delta \vec{r}$ (m). This provides a good approximation of the gradient of the electric potential in solution, $\vec{\nabla} U$ (V m^{-1}) in the direction of $\Delta \vec{r}$, which corresponds to the peak-to-peak vibration amplitude in the direction of the measurement. Conductivity of the electrolyte solution is assumed to be constant. Most often it is believed that SVET measures the total current in a measuring point. However, this is true only far from the electrode, outside the diffusion layer where migration is dominant. Most of the corrosion studies are performed at distances between 50 and 150 μm from the surface of the electrode, while the usual thickness of the diffusion layer in quiescent conditions is higher than 200 μm. It is expected that measuring in the diffusion layer would lead to significant discrepancies between the measured migration current and the total current and even to seemingly unbalanced anodic and cathodic currents [10,15]. This apparent imbalance could be explained either by the presence of a chemical redox reaction that influences the probe/solution potential [15] or by the enhancement of the dissolved oxygen transport by the moving SVET probe [13]. Further, deviations are observed between the measured and the simulated current densities above real corroding samples and these deviations are more pronounced in the case of a Multi-Ion model than of the Potential (electrostatic) model. This leads to an astonishing conclusion that the Potential model would be better suited for simulation of SVET measurements than the Multi–ion model [16]. The question arises: "Why is a Multi-ion model, which encompasses the electrostatic model, less accurate than a Potential model"?

The possible answer resides in the fact that none of the above mentioned models, however complex it is, accounts for the convection created by the movement of the SVET probe. At the same time, it is true that a proper, quantitative simulation of the SVET probe movement (translation and vibration) would be way too complex and time consuming for everyday electrochemical practice. In what follows, we will present a simplified approach to account for the mixing effect around the tip of the SVET probe, without actually solving for the convection created by its vibration in the electrolyte solution. The effects of the probe movement during scanning were omitted at this time, as they can be mitigated by a suitable set up of the scanning procedure. The proposed approach brings the simulated SVET response obtained with use of a Multi-ion model closer to the measured one. The validation is performed by comparing the results of the simulations with the analytical current density distribution and with a set of actual SVET measurements.

2. Theoretical approach

2.1. Potential model

The Potential model assumes perfect mixing of the electrolyte solution, therefore no concentration gradients:

$$div \left(-\kappa \vec{\nabla} U \right) = 0, \tag{2}$$

with κ being the electrical conductivity of the electrolyte:

$$\kappa = F^2 \sum_i z_i^2 u_i c_i = const. \tag{3}$$

Here $F = 96485$ C mol^{-1} is the Faraday's constant, c_i (mol m^{-3}), z_i and $u_i = D_i/RT$ (mol s kg^{-1}) are concentration, charge and mobility of species i respectively. Total current density in the solution is given by the gradient of the electrical potential only, Eq. (4).

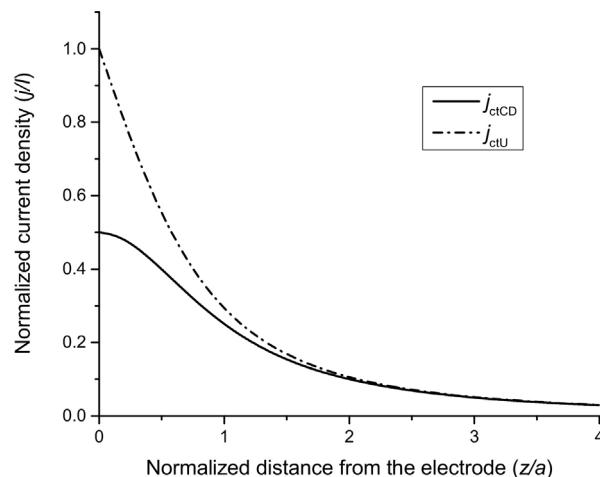$$j = -\kappa \vec{\nabla} U. \tag{4}$$

Fig. 1. Theoretical current density distributions, normalized to the total current I, above the center of the electrode for the limiting cases of equipotential (Eq. (5)) and constant current density (Eq. (6)) electrodes.

Two theoretical limiting cases are possible for the current density distribution above a disk-shaped electrode: an equipotential electrode and a constant current density electrode. If we restrict the analysis to the center of the electrode in polar coordinates, analytical expressions describing the current density distribution as a function of the distance from the surface of the electrode are available for these cases (Eq. (5) for the equpotential and Eq. (6) for the constant current density electrodes respectively) [17,18]. Since in corrosion studies mainly the vertical component of the current density is reported, in what follows we will consider only this z-component in the center of the disc:

$$j_{ctU} = -\frac{I}{2 \pi \kappa} \frac{1}{(a^2 + z^2)} \tag{5}$$

$$j_{ctCD} = -\frac{I}{a^3 \kappa \pi} \left(\frac{z}{\sqrt{1 + (z/a)^2}} + a \right) \tag{6}$$

with I (A) the total current, a (m) the radius of the electrode and z (m) the distance from the surface of the electrode. A graphical representation of these two extreme current density distributions is given in Fig. 1. The real (measured) current density distribution is expected to fall between the two theoretical ones.

2.2. Multi–ion model

The mathematical model for ion transport in dilute solutions based on balance equations provides concentration and potential distributions (Eq. (7)) and ensures the electroneutrality of the solution (Eq. (8)) [19].

$$\frac{\partial c_i}{\partial t} + \vec{v} \cdot \vec{\nabla} c_i = \vec{\nabla} \left(z_i F u_i c_i \vec{\nabla} U + D_i \vec{\nabla} c_i \right) + R_i, \tag{7}$$

$$\sum_i z_i c_i = 0. \tag{8}$$

The notations in the above equations have the following meaning: $\vec{v}$ (m s^{-1}) the velocity field of the electrolyte solution, D_i (m^2 s^{-1}) the diffusion coefficient of the species i and R_i (mol m^{-3}s^{-1}) the net production rate of species i due to homogenous reactions, given by Eq. (9)

$$R_i = \sum_i v_k s_{ki} \tag{9}$$