



Quasi-simultaneous measurements of ionic currents by vibrating probe and pH distribution by ion-selective microelectrode

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ABSTRACT

This work reports a new methodology to measure quasi-simultaneously the local electric fields and the distribution of specific ions in a solution via selective microelectrodes. The field produced by the net electric current was detected using the scanning vibrating electrode technique (SVET) with quasi-simultaneous measurements of pH with an ion-selective microelectrode (pH-SME). The measurements were performed in a validation cell providing a 48 μm diameter Pt wire cross section as a source of electric current. A time lag between acquiring each current density and pH data-point was 1.5 s due to the response time of pH-SME. The quasi-simultaneous SVET-pH measurements that correlate electrochemical oxidation–reduction processes with acid–base chemical equilibria are reported for the first time. No cross-talk between the vibrating microelectrode and the ion-selective microelectrode could be detected under given experimental conditions.

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1. Introduction

The SVET measures extremely small potential differences in a solution due to the fluxes of ionic currents originated by the electrochemical reactions occurring at the active surface. The measured potential difference is converted into an electrical current density ($\mu\text{A cm}^{-2}$) at the point of measurement. Developed by biologists [1,2] the SVET is currently applied in several fields of biology, including studying pollen germination, fertilization, growth, functioning of ion channels and tissue regeneration [3–5]. In materials science, SVET has become a useful tool for studying various forms of localized corrosion [6–14], anti-corrosion coatings [14–16] identifying their self-healing ability [11,17,18] and testing the effectiveness of corrosion inhibitors [19,20].

A platinised platinum vibrating probe (VP) used for SVET has not been considered capable of differentiating chemical concentrations whereas ion-selective microelectrodes (ISMEs) are unique tools that sense specific ions *in-situ*. Coupled to either Scanning Ion-Selective Electrode Technique (SIET) [21,22] or Self-Referencing Ion-Selective probes (SERIS) [23] or Microelectrode Ion Flux Estimation (MIFE) [24] or Scanning Electrochemical Microscopy (SECM) in potentiometric mode [25–28] ion-selective microelectrodes are used for biomedical applications, materials and corrosion research. The non-invasive

measurements of H^+ , Ca^{2+} , K^+ , Mg^{2+} , Na^+ , NH_4^+ and Cl^- fluxes are of interest for biologists [4,22–25,29].

Corrosion processes are generally associated with anodic oxidation (metal dissolution followed by hydrolysis of formed $\text{Me}^{\text{n}+}$ producing H^+) and cathodic reduction (with oxygen reduction or hydrogen evolution accompanied by formation of OH^-). Hence, corrosion processes involve not only electrochemical reactions but also ionic equilibria and acid–base interactions in particular. Cations of alkaline and alkaline-earth metals, that are difficult for amperometric detection, can be quantified by ISMEs. The same applies for Cl^- and H^+ that play a crucial role in the processes at the surface of corroding metals. For example, when modeling the galvanic coupling in aluminum alloys Murer et al. [30] concluded that the blocking step for the application of numerical mass transport models is the lack of input data on the local dissolution rate of the aluminum matrix as a function of the chemistry, namely, pH and Cl^- concentration.

Undoubtedly, both SVET and micro-potentiometry provide important complementary information for studying mechanisms and kinetics of electrochemical processes in localized sites. Sequential use of both techniques, SVET and micro-potentiometry, was demonstrated by several groups in the field of corrosion and biology [10–13,29,31,32]. Despite the useful information extracted, there is always a considerable time lag that cannot be neglected and that may induce misinterpretations. To the best of our knowledge no simultaneous assessment of net ionic current density (CD) and distribution of specific ions have been reported until now.

In this study SVET and micro-potentiometric measurements were undertaken correlating values of local current density and activity of H^+

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in space and time. The details of the experimental setup are disclosed. The absence of any significant influence of the VP on the readings of the pH-SME and vice versa was verified.

2. Experimental

Commercial equipment manufactured by Applicable Electronics and controlled by ASET software was used to perform SVET and SIET measurements. A dual head stage manipulator (Biomedizinische Geräte, Germany) was used for precise positioning of two measuring electrode tips of a VP and a pH-SME. The dual head stage was mounted on the 3D step motors which moved with a lateral resolution of 0.8 μm .

The SVET vibrating probe was an insulated Pt–Ir microelectrode (Microprobe) with Pt black deposited on the exposed metal tip, making a $15 \pm 3 \mu\text{m}$ diameter spherical sensor. The probe vibrated in the vertical (Z) and horizontal (X) planes relative to the cell surface with amplitudes of 17 μm . The vibration frequency of the probe was 210 Hz (Z) and 128 Hz (X). The SVET is designed to respond to the potential gradients in the ionic solution associated with the flow of current. The vibrations of the probe tip convert the dc potential gradients it detects along the vibration direction into an ac signal with a frequency of the vibrations. The signal is fed into a phase sensitive detector that filters out other ac frequencies enabling measurement of the current components in the X- and Z-directions to be made and improves the signal detection by orders of magnitude compared to a dc measurement.

Localized pH measurements were performed using glass-capillary ISMEs. The silanized capillaries were filled with a selective ionophore-based oil-like membrane and back-filled with an inner reference solution. The column length of the membrane was about 60–70 μm . An Ag/AgCl wire was inserted into the electrolyte to provide the reference electrode.

The membrane of the pH-SME consisted of 6 wt.% ETH 1907 4-nonadecylpyridine, 12 mol% (relative to the ionophore) potassium tetrakis(4-chlorophenyl) borate, and a membrane solvent 2-nitrophenyloctyl ether. The pH-SMEs were calibrated using commercially available pH buffers. The linear range of pH response was 2–10, and the Nernstian slope was $-54.6 \pm 0.6 \text{ mV/pH}$.

All reagents for the membrane of pH-SME were Selectophore grade products from Fluka. The aqueous solutions were prepared with salts of the highest purity available using Millipore purified water ($\rho > 18 \text{ Mohm cm}$). All experiments were performed in a Faraday cage at room temperature ($26 \pm 2 \text{ }^\circ\text{C}$).

A Ag/AgCl mini-electrode with an agar stabilized 0.05 M NaCl salt bridge was used as the reference electrode. A ring shaped platinum black wire was used as an auxiliary electrode.

The pH-SME was positioned 30 μm ahead of the SVET probe to avoid breaking the glass microelectrode due to the vibration of the probe, to minimize possible cross-talk effect and solution stirring by the vibrating probe. In the ASET program, a “Flyback” mode rather than “Zig Zag” mode of scanning probe movement was always used to keep the SVET probe behind pH-SME during measurements. A “move-wait-measure SVET-wait-measure pH” scheme was employed for mapping and profiling above the surface. Time for acquisition for each SVET and pH data-point was 0.4 s and 1.5 s respectively. For the presented SVET–pH measurements, the VP and pH-SME were at a fixed height 50 to 100 μm above the surface, as these are the usual settings used in our lab for sole SVET and SIET measurements. However, two probes can be positioned at the same height if required. All measurements were carried out in a 0.05 M NaCl neutral solution.

3. Results and discussion

Quasi-simultaneous SVET–pH measurements and verification of the mutual influence of the VP and the pH-SME were carried out in a

validation cell, Fig. 1. The cell comprised a needle-shaped platinum wire of 48 μm diameter. A positive or negative current of 50 nA was injected into the wire making it a source of current. The cathodically polarized (-50 nA) Pt current source caused local alkalization recorded by pH-SME. When negative currents are passed oxygen or water is reduced generating OH^- . The positive current ($+50 \text{ nA}$) induced anodic oxidation of water with the evolution of gaseous oxygen and the acidification of the solution around the Pt wire:



The results of the SVET–pH measurements over the Pt wire are shown in Fig. 2. The line scans were taken through the middle of the current and pH source as shown in Fig. 2a. Direct comparison of sole and quasi-simultaneous SVET and pH measurements is presented in Fig. 2b and c for anodic and cathodic currents. It confirms that the signals of the pH-SME and VP operating by themselves are similar to the signals when two probes operate together. For the negative and positive polarizations, the standard deviation between the line scans taken in quasi-simultaneous and sole modes is 0.68 and 1.00 $\mu\text{A cm}^{-2}$ for CD and 0.031 and 0.038 for pH measurements. For comparison, parallel sole CD and pH measurements are also presented. Average standard deviation in this case is very similar: 0.83 and 1.02 $\mu\text{A cm}^{-2}$ for CD and 0.027 and 0.041 for pH. This comparison proves that the deviation between combined and sole SVET and pH measurements are within the expected experimental variation indicating that there is no cross-talk between the VP and the pH-SME under given experimental conditions.

An example of application of quasi-simultaneous SVET–pH measurements is shown in Fig. 3. The CD and pH distribution were simultaneously recorded over the oblong pieces of pure Zn and Fe coupled and embedded in epoxy resin. The optical image of the scanned area is shown in Fig. 3a. The cathodic reduction results in formation of an alkaline area over the Fe, anodic dissolution and consecutive hydrolysis of Zn^{2+} lead to slight acidification over the Zn foil detected by VP and pH-SME.

Neither SVET nor micro-potentiometry by themselves, individually, is able to detect complex electrochemical processes at the metal/

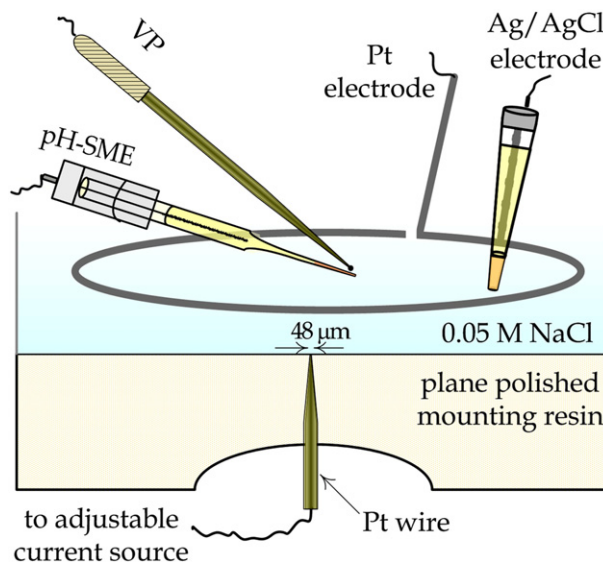


Fig. 1. A schematic drawing of the validation cell for quasi-simultaneous SVET–pH measurements.

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