Microelectrochemical imaging of corrosion reactions

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Pécs, 2018
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1 Aims of research

Corrosion is one of the greatest industrial challenges of our days. Its treatment, the supplement of the degraded materials comes with serious expenses. Hence the corrosion research, the development of effective, anticorrosive treatments is an evergreen topic in science for centuries. Although the earlier used analytical methods provided a global picture of the ongoing processes on the corroding surfaces, the localized information could not be gathered. For this reason, the discovery of the scanning probe techniques, especially scanning electrochemical microscopy (SECM) that provides chemical information of different surfaces opened new ways in corrosion research. The scanning vibrating electrode technique (SVET) capable to image the temporal and spatial distribution of local anodes and cathodes is another powerful tool in corrosion surface analysis.

The prevailing operation mode of SECM is amperometric, nevertheless soon after its discovery, ion selective microelectrodes were applied as scanning probes that allows to selectively monitor the dissolving metal-ion distribution in instances where amperometric electrodes are of limited use. Besides, the pH changes accompanying both the anodic and cathodic half-cell reactions can be imaged in potentiometric mode.

The results discussed in the dissertation can be grouped in the two modes of SECM: I dealt with the development of potentiometric SECM and applied amperometric SECM for the investigation of magnesium corrosion.

I attempted to contribute the development of potentiometric SECM by the preparation of new, multiple ion selective electrode containing, multibarrel sensing probes. These devices are known in neuroscience; however they have not been utilized in SECM (except for a few early publications).
In potentiometric SECM, the main difficulty is the setting of the precise tip-sample distance. Ion selective electrodes do not possess the positive and negative feedback effect that is often invoked in amperometric measurements where the tip sample distance can be set based on the well-defined current-distance function. The currently used methods are often end with the break of the fragile tip – possibly this is the main reason for their limited use. In multibarrel arrangement, if an amperometric probe can be also found in the multielectrode body (i.e. the bifunctional antimony microelectrode), the problem can be easily resolved.

The possibility of simultaneous imaging of multiple species with multibarreled electrodes is obvious. In fact, there is an undoubted need for that since many simultaneously occurring reactions are going on the corroding surfaces and the concentration changes of many species can be detected in the adjacent solution and their concurrent knowledge can help to a deeper understanding of the corrosion phenomena.

With the aid of the multibarreled electrodes, a new evaluation method is available that helps to improve the reliability of measurements carried out in systems where the potentiometric signal comprises multiple ionic level changes – that is, the selectivity is not sufficient. This is relevant in alloy corrosion where the dissolution of several metal-ion species is expected.

I subdivided this problem into the time-dependent and equilibrium selectivity topics. Both of them can be found in the dissertation.

In my earlier studies, I often faced with the problem of potentiometric imaging of polarized samples of galvanic corrosion. This occurs in the literature, as well. The electrostatic field formed in these instances contributes to the potentiometric signal and eventually the results calculated based on the calibration curve can fall below expectations and suspiciously unrealistic activity values have been reported. The reason is that the ion selective microelectrode and the reference electrode sense different electric field potential and the difference will be added to the Nernstian
response. Multibarreled electrodes that contain a microreference electrode right next to the ion selective microelectrode help to minimize the problem caused by the electric field.

I used amperometric SECM to investigate the long time debated, anomalous feature of magnesium corrosion. Namely, the rate of the cathodic half-cell reaction (hydrogen evolution) is not decreasing with anodic polarization, as one would expect based on the Erdey-Grúz-Butler-Volmer theory, but increasing. Many theories have been worked out to explain this interesting phenomenon and there still is no consensus in the literature.

In my work, I aimed to study the two prevailing theories, using the sample generator tip collector mode of the amperometric SECM. That is, I detected the H$_2$ evolved on the Mg surface with the Pt microtip. For the investigation of the anodic and cathodic processes, besides the conventional electrochemical techniques, I used the scanning vibrating electrode technique.
2 Results

My results in the dissertation are discussed in 4 chapters based on the applications: two chapters are about the development of the potentiometric SECM and two focuses on the anomalous hydrogen evolution during magnesium corrosion.

Chapter 1 is related to the zinc and copper corrosion.

First, a new, Zn ISME and pH sensitive Sb ME electrode containing double barreled electrode is presented. The arrangement has several advantages. The bifunctional antimony microelectrode makes the tip-sample distance adjustment safer and easier utilizing the amperometric feedback effect. Moreover, simultaneous measurements can be done: I carried out measurements above the Zn-Fe galvanic couple and a real sample: the cut edge of the galvanized mild steel sheet. Cut edge corrosion is one of the main problems with the coil-coated, painted galvanized steels. The simultaneous measurements served supplementary information of the corrosion processes.

I have demonstrated an interesting phenomenon that has not been taken into consideration in potentiometric SECM so far: the appearance of transient signals in the presence of interfering ions. In general analysis this not a problem, however, in SECM where we make local measurements in the fraction of the second, the transient signals have to be taken into account.

A new, Cu ISME is also presented in the dissertation, along with its combination with Zn ISME in double barreled arrangement. Another advantage of simultaneous detection is demonstrated: in the presence of interfering ions the activity values determined with the ISME can be corrected by measuring with an electrode that is selective for the interfering ion.

Chapter 2 is still about potentiometric SECM, although the application field goes towards the magnesium corrosion. In the case of galvanic corrosion, the electric field formed due to the electric connection of the two metals can seriously affect the potentiometric
signal measured with the ISME. This unwanted contribution can be found in many instances in the literature where the tendency of the corrosion could be shown, however the quantitative evaluation often failed.

Double barreled, microreference electrode containing devices, this effect can be minimized, since the ISME and the microreference electrode will sense the same field potential, hence the undesired contribution can be mitigated.

The applicability of the new device is demonstrated with 2D Mg\(^{2+}\) and pH maps that are compared with the optical images.

In Chapter 3 and 4 amperometric SECM-related results are discussed obtained in the study of the anomalous hydrogen evolution on anodically polarized magnesium. The controversial behavior of magnesium is debated for decades. The two prevailing theories invoke the catalytic effect of the Mg(OH)\(_2\)/MgO layer, and the „noble” impurities to explain the hydrogen evolution. I carried out amperometric SECM measurements, where I used Pt microelectrode to detect the hydrogen evolved on Mg under different circumstances. I investigated the hydrogen evolution on prepolarized Mg (the layer formation is enhanced). I enhanced and hindered the layer formation chemically, as well, and studied the rate of the hydrogen evolution reaction. The experiments were carried out using 91 and 99% pure Mg to see the effect of the alloying metals. All my experiments suggest that the main role in the enhanced hydrogen evolution reaction in due to the oxide-hydroxide layer.

Chapter 4 investigates the role of the alloying metals further by separating the anode and cathode using Mg-Al galvanic couple. This way, the effect of the experimental conditions I applied in Chapter 3 can be investigated separately on the Mg and the Al. These experiments suggested that the contribution of the Al to the hydrogen evolution is negligible.
3 Theses

1. I have developed and characterized a new Cu\(^{2+}\)-selective microelectrode. It was found to be excellent for the potentiometric SECM mapping of Cu\(^{2+}\) distributions.

2. Combined double-barrel electrodes containing a Zn ISME and a pH sensitive antimony microelectrode were prepared. Using the double-barrel probes, the possibility of precise tip-sample distance determination and simultaneous detection of Zn\(^{2+}\) ions and pH could be achieved.

3. I studied the transient signals of ion selective microelectrodes. In quantitative analytical chemistry the long time selectivity coefficient dominates the applicability. It is different in SECM where relatively short time is available to take electrode response. In my experimental work the time dependence of the selectivity that has major importance in SECM was investigated for the first time. In the case of potassium interference of ammonium microtip, I clearly could show that in SECM care must be taken for finding the right scanning rate that is not disturbed by the time dependent selectivity coefficient.

4. A new evaluation method was introduced to enhance the selectivity of ion selective electrodes in SECM measurements for corrosion applications. It was demonstrated on the Zn\(^{2+}\)/Cu\(^{2+}\) selective microelectrode containing double-barrel tip developed in this work.

5. I developed and used double-barrel electrodes containing combinations Mg ISME/microreference and Sb/microreference electrodes to minimize the electric field effects in potentiometric mapping, and they showed superior performance over single-barrel electrodes previously reported in the literature. In addition,
a new triple-barrel electrode was used in SECM experiments to achieve more realistic simultaneous imaging.

6. I investigated the hydrogen evolution reaction on Mg under different conditions to get insight to the so-called negative difference effect. Interestingly, hydrogen evolution is happening at certain spots on Al/Mg alloy during anodic polarization. The mechanism has been long time debated. The hydrogen evolution reaction on AZ63 and 99% purity Mg was compared using the generator-collector mode of the SECM under different experimental conditions. The results provided new support for the enhanced catalytic activity of the MgO/Mg(OH)$_2$ containing bilayer on the HER.

7. Using the tools developed in my work, I investigated the events on Mg/Al galvanic pair to study the anomalous hydrogen evolution separately on the anodic and cathodic areas. My results could not support the so-called noble impurity theory proposed by several group.
4  Peer-reviewed publications

4.1  Publications related to the dissertation

   Novel dual microelectrode probe for the simultaneous visualization of local Zn$^{2+}$ and pH distributions in galvanic corrosion processes
   (IF: 5.245, D1)

2. D. Filotás, A. Asserghine, L. Nagy, G. Nagy
   Short-term influence of interfering ion activity change on ion-selective micropipette electrode potential; another factor that can affect the time needed for imaging in potentiometric SECM
   (IF: 4.396, Q1)

   Improved potentiometric SECM imaging of galvanic corrosion reactions
   (IF: 5.245, D1)
   Double barrel microelectrode assembly to prevent electrical field effects in potentiometric SECM imaging of galvanic corrosion processes
   JOURNAL OF THE ELECTROCHEMICAL SOCIETY
   165: pp C270-C277
   (IF: 3.259, Q1)

   An investigation of hydrogen generation from anodically polarized AZ63 magnesium alloy using scanning microelectrochemical methods
   JOURNAL OF THE ELECTROCHEMICAL SOCIETY (submitted)
   (IF: 3.259, Q1)
4.2 Publications not included in the dissertation

   New developments in scanning microelectrochemical techniques: A highly sensitive route to evaluate degradation reactions and protection methods with chemical selectivity

   Extended investigation of electrochemical CO$_2$ reduction in ethanolamine solutions by SECM
   (IF: 2.851, Q2)

3. A. Asserghine, D. Filotás, L. Nagy, G. Nagy
   Scanning electrochemical microscopy investigation of the rate of formation of a passivating TiO$_2$ layer on a Ti G4 dental implant
   (IF: 4.396, Q1)

   The effect of electric field on potentiometric Scanning Electrochemical Microscopic imaging
   (IF: 4.396, Q1)
Corrosion resistance and antibacterial activity of electrosynthesized polypyrrole
(IF: 2.435, Q2)

Highly sensitive potentiometric measuring method for measurement of free H$_2$S in physiologic samples
(IF: 5.401, Q1)

Combined amperometric/potentiometric probes for improved chemical imaging of corroding surfaces using Scanning Electrochemical Microscopy
ELECTROCHIMICA ACTA 221: pp. 48-55. (2016)
(IF: 4.798, Q1)

Capsaicin-sensitive sensory nerves mediate the cellular and microvascular effects of H$_2$S via TRPA1 receptor activation and neuropeptide release.
(IF: 2.229, Q3)
Imaging of concentration distributions and hydrogen evolution on corroding magnesium exposed to aqueous environments using scanning electrochemical microscopy
(IF: 2.851, Q2)

SECM investigation of electrochemically synthesized polypyrrole from aqueous medium
(IF: 2.235, Q2)

Electrochemical experimental study for the characterization of tetraferrocenyl-cavitand, synthetized in click-reaction
(IF: 2.471, Q2)

Synthesis and electrochemical properties of the tetraferrocenyl-cavitand in dimethyl formamide solvent using platinum and carbon working electrodes
(IF: 2.471, Q2)
13. L. Nagy, D. Filotas, M. Boros, G. Pozsgai, E. Pinter, G. Nagy
Amperometric cell for subcutaneous detection of hydrogen
sulfide in anesthetized experimental animals.

(IF: 1.576, Q2)