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Development and application of the in situ radiotracer thin gap method for the investigation of corrosion processes. I. Adaptation of the thin gap method for the application of porous surfaces

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ABSTRACT

The electrode lowering method of the in situ radiotracer technique provides a unique opportunity for the understanding of both the kinetics and the mechanism of contamination, corrosion and electrocatalytic phenomena. The advanced version of the technique, the thin gap method was originally developed for the investigation of sorption phenomena on smooth metal surfaces. This fact greatly limits the applicability of the method both with species of low specific activity and in case of surfaces of industrial specimens. As the first part of an article series the adaptation of the original method for the investigation of compact, porous surfaces with high surface roughness is demonstrated. The basic equations of the improved method are described, with the help of which the description of sorption phenomena on rough surfaces can be characterized. The optimized preparation parameters of the porous platinum black layer for detection of ^{36}Cl labelled chloride ions are given. It is shown that the sensitivity of the in situ thin gap radiotracer method was substantially increased by the application of porous electrodes.

1. Introduction

In the last decades, various radiotracer methods have been applied for the investigation of the solid electrode/liquid electrolyte heterogeneous electrochemical systems. Due to the methodological and theoretical improvements, new in situ methods have been developed, which could be combined with conventional electrochemical methods and hence, they are capable for a complex investigation of the surface properties of different metal samples ([1–4] and the references cited therein).

With the in situ radiotracer methods, radiation originating from the labelled species adsorbed on the electrode surface can be measured continuously while the electrode is in contact with the solution. Then, the surface excess of the adsorbed species can be determined from the radiation intensity measured. All of the relevant procedures are based on the “thin layer principle” introduced by Aniansson [5]. By using isotopes that emit low- or medium-energy beta particles or gamma photons ($E < 20$ keV), the total activity of the system (i.e., the surface being tested and the solution) can be detected during the sorption process. In most of the cases when the thin layer method is applied, the background signal is minimal, while the radiation originating from the adsorbed species is significant. During the sorption process, the labelled species accumulate on the surface investigated; thus, the detector can measure an intensity increment proportional to the adsorbed amount of labelled species.

The in situ methods can be divided into three groups based on the cell arrangement. These are the “thin layer”, the “foil” and the “electrode lowering” methods [1–4]. The thin layer method applies a constant-thickness thin solution layer, in which the electrolyte is circulated with a solution flow system. In this cell arrangement, the close vicinity of the radiation detector and the working electrode provides a high detection efficiency. In the foil method, the detector is placed underneath the working electrode, and the detection efficiency is provided by the thin (primarily plastic) foil and the thin working electrode layer that covers the foil. In the foil method, unlike for the other methods, the radiation to be detected must pass the metal layer used as the working electrode. While in the above methods the working electrode is fixed, the electrode lowering method relies on the mobility of the working electrode

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[1] This paper is dedicated to the memory of Prof. K. Varga who passed away during the course of the present work.

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that can be either approached to or removed from the detector.

The electrode lowering technique combines the advantages of both the foil and the thin layer methods. The process was developed by Kazarinov and his co-workers in 1966 [6], and they improved it several times in the early 1970s [7]. The applicability of the original method is difficult and the measurement principles are not well developed, while the sensitivity is not satisfying in case of smooth, well-polished surfaces. To eliminate these disadvantages, significant methodological improvements were made in the last three decades. In 1987, Krauskopf and Wieckowski published their new thin gap method [8], in which the detector was replaced with a well-polished glass scintillator. It has been shown that the latter method can be used for the investigation of sorption processes on smooth, well-polished ($\gamma < 2$) single- or polycrystalline surfaces [1–4,9,10]. With the use of a well-polished scintillator and a smooth parallel sample surface, the sensitivity of the electrode lowering method could be increased by one order of magnitude. Therefore, the method elaborated by Wieckowski et al. plays an important role in the investigation of interfacial processes on well-defined electrode surfaces.

The modern version of the electrode lowering method (thin gap method) was developed for the investigation of polished compact metal surfaces [8]. Although the thin gap method was improved by various means in the past decades by Varga and co-workers ([1–4,9,11–15] and further works cited therein), it is still not suitable either for the investigation of species having low specific activity or for compact metal samples covered with porous layers. Therefore, the applicability of the thin gap method is greatly limited concerning both the isotopes to be used for labelling and the metal samples originating from the industry. The determination of the surface excess (Γ) is not possible by using isotopes of small specific activity and samples with low surface roughness ($\gamma < 2$). All above-mentioned problems can be solved when the previously developed measurement principles of the thin gap method are adopted for the investigation of compact metals with a high surface roughness ($\gamma > 10$).

The above-described aim of methodological development can be divided into three steps:

1. Deduction of the theoretical basis of the in situ radiotracer method for the investigation of sorption phenomena on compact metal samples covered with porous layers.
2. Validation of the relationships evaluated with the application of platinum black electrodes in the presence of chloride ions (labelled with ^{36}Cl) as adsorbate.
3. The investigation of various sorption, corrosion and contamination process on compact metal samples covered with porous layers (such as steam generator tubes covered with an oxide layer or a noble metal catalysts).

The aim of the present paper is to solve the equation system describing the radiation intensity that can be measured in the thin gap system for a porous electrode. Experimental validation of the theoretical approach to be provided below will be published separately.

2. Theory

2.1. Measurement principles of the thin gap method for the adsorption of pure beta-emitting isotopes on smooth surfaces

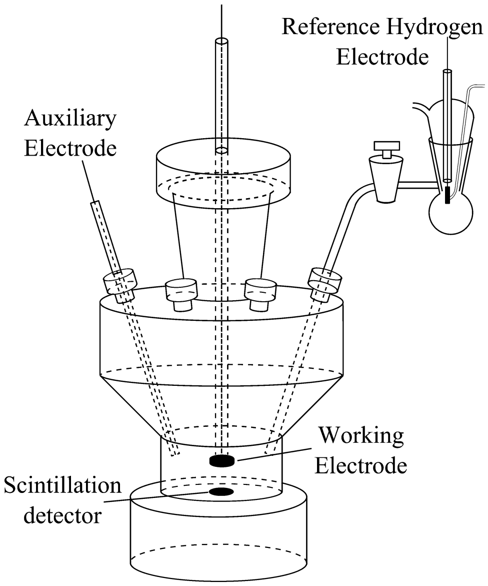

Fig. 1. The scheme of the improved cell used by Varga et al. [4].

Fig. 1 shows the radio-electrochemical cell made by Varga et al. for the in situ “thin gap” method [1,4,12]. The main part of the measuring system for the parallel radiation and electrochemical measurements is a glass–Teflon–austenitic steel cell. The reference electrode is a so-called reference hydrogen electrode (RHE), while the auxiliary electrode is a platinum or gold wire, depending on the measurement conditions. The Li-glass scintillation detector polished to optical quality is mounted in the ceramic bottom of the cell. For reference and auxiliary radiation measurements, similar plastic or silica (AMPTEX XR-100T type) semiconductor detectors can be used. During the electrochemical measurements, the working electrode can be adjusted in two positions, as can it be seen in Fig. 2.

In the lifted (upper) position, the adsorption of the labelled species can take place. In this position, the distance between the electrode and the detector is several times larger than the range of the radiation in the solution used.

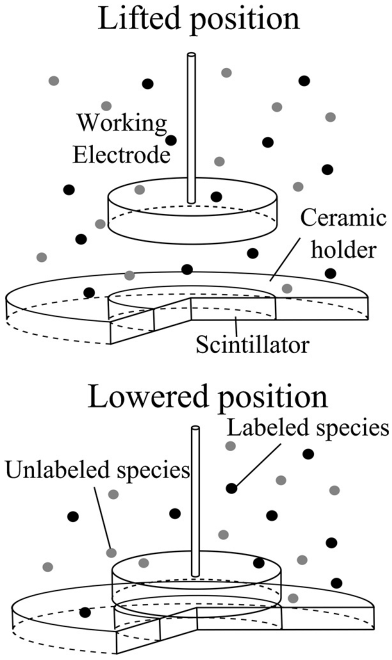

Fig. 2. The two positions of the electrode in the “thin gap” method: the lifted and the lowered one.