



Short communication

Revealing onset potentials using electrochemical microscopy to assess the catalytic activity of gas-evolving electrodes



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ABSTRACT

Determination of the so-called onset potentials, i.e. the lowest (for the anodic reactions) or the highest (for the cathodic reactions) potentials at which a reaction product is formed at a given electrode and at defined conditions, is very important for the evaluation of the catalytic activity and even more for the comparison of different catalysts. We present an approach for the determination of the onset potentials based on scanning electrochemical microscopy (SECM) using the “substrate generation–tip collection” mode. In the proposed method, the potential applied to the catalyst sample is changed stepwise. A micro-electrode serving as SECM tip is positioned in known close proximity to the catalyst surface and is used to detect the onset of the formation of the product of the catalytic reaction, specifically gas generation at the sample surface. The oxygen evolution reaction (OER) at model RuO₂ and perovskite catalyst surfaces is used to evaluate the approach. The suggested method is supposed to provide a clearer and sensitive means for the detection of the onset potentials of electrolytic gas evolution reactions as compared to conventional procedures which mainly use cyclic voltammetry on stationary or rotating (ring) disk electrodes. Moreover, the detection of the reaction product at the SECM tip allows distinguishing between parasitic reactions at the catalyst surface and the true formation of the anticipated reaction product.

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1. Introduction

Electrolytic gas production is an important and constantly increasing class of industrial processes. It covers many critical reactions such as large-scale synthesis of Cl₂ [1], consuming more than 1% of the total generated electrical energy in the world, or the much smaller scale generation of high-purity AsH₃ [2], which is vital for semiconductor industry. While nowadays only 4% of H₂ is produced using water electrolysis [3], future requirements for a sustainable energy provision will without any doubt increase the value to deliver pure H₂ as fuel for cars [4–6] or potentially to accumulate D₂ for thermonuclear fusion reactors [7]. Additionally, there are reactions without any competitive alternative to electrolysis such as F₂ production [8].

Despite the fact that electrolytic gas evolution has been widely used in industrial applications, due to their distinctive features that complicate their detailed study these reactions stand slightly apart from other electrochemical processes. For instance, one complication arises from a continuous generation and growth of a new non-conductive

gas phase at the electrode surface. This causes stochastic, quasi-periodic [9,10] or permanent deactivation due to blockage of a large part of the electrode surface by the products imposing additional energy losses. Another, even more important issue, is related to the extreme conditions at which the electrolytic gas generation is performed. They can result in the initiation of background processes contributing to the overall current, changes in the composition and/or surface properties of the electrodes. This can drastically complicate the determination of key parameters of the catalytic processes, even when model electrode materials are used. The above-mentioned issues result in serious methodological difficulties in determining the onset potentials of gas evolving electrodes. To our opinion there are inherent limitations in the methodologies used to perform an affordable but accurate evaluation of the activity of gas evolving electrodes [9,11]. In addition, while laboratory experiments use voltammetric measurements at rotating (ring) disk electrodes to minimize the influence of bubbles, the results of the model laboratory measurements are not directly applicable to industrial gas-evolving electrodes.

An important parameter in the design and benchmarking of catalytic materials for gas evolving reactions is seen in the onset potential at which the gas evolution starts. However, classic voltammetry data are frequently ambiguous as the resulting direct current can originate from parallel parasitic Faradaic processes such as oxidation of the supporting material or even of the catalyst itself. For the search for

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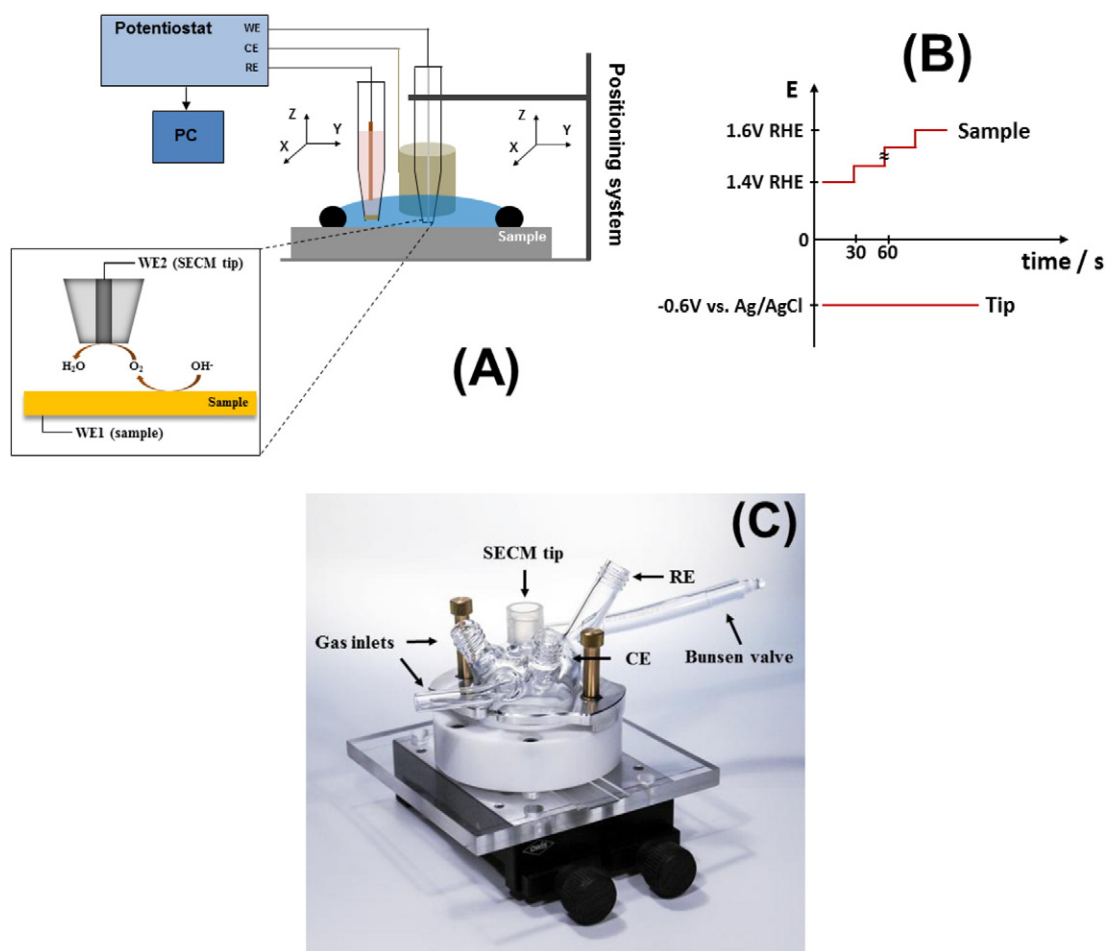


Fig. 1. Schematic representation of (A) the measurement setup, and (B) the experimental scheme (potential profiles applied at the catalyst sample and the SECM tip as a function of time). (C) Photographic image of the electrochemical cell.

new catalysts, these ambiguities in data interpretation are strongly unwanted.

In this work, we describe a relatively simple concept for a careful determination of the onset potential to assess the catalytic activity of gas evolving electrodes. The potential of the sample is increased stepwise with steps down to a few millivolts. At each of the steps, two parameters are measured simultaneously: (i) the anodic current at the sample and (ii) the cathodic current at the closely positioned microelectrode used as a sensor for the detection of the onset of gas generation at the catalyst surface. The oxygen evolution reaction (OER) at RuO_2 and perovskite electrocatalysts has been used as a model reaction to evaluate the approach.

2. Experimental

Glass-insulated Pt-disk microelectrodes (SECM-tips) were fabricated using borosilicate glass capillaries ($D_{\text{out}} = 1.5 \text{ mm}$; Hilgenberg) and a $10 \mu\text{m}$ diameter Pt wire (Goodfellow) following a procedure described in detail elsewhere [12]. Prior to experiments, the electrodes were polished with alumina pastes ($3 \mu\text{m}$, $1 \mu\text{m}$, $0.3 \mu\text{m}$ and $0.05 \mu\text{m}$, respectively; LECO) and subsequently ultrasonicated in acetone, 2-propanol and deionized water for 5 min.

The model samples were prepared by drop coating of $10 \mu\text{l}$ catalyst ink on the surface of clean FTO substrates. The catalyst ink was based on a 1:1 volume ratio of ethanol (VWR) and Siemens® UltraClear water containing 5 mg/ml of either RuO_2 (Sigma-Aldrich) or $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_3$

perovskite and 1 mg/ml of Nafion®117 (Sigma-Aldrich).¹ Prior to the sample preparation all components were mixed and homogenized in an ultrasonic bath for 3 h. To control the loading of the catalyst, an adhesive foil with a punched hole of 5 mm in diameter ($S_{\text{opening}} = 0.196 \text{ cm}^2$) was mounted on the FTO substrate. An aliquot of the catalyst ink was dropped into the punched hole leading to a final catalyst loading of $\sim 250 \mu\text{g/cm}^2$.

Determination of the onset potential of OER was performed using a SECM system (Sensolytics, Germany), as schematically shown in Fig. 1. To enable measurements under controlled atmosphere, a special glass cell was developed (Fig. 1A,C). It contains two gas tight inlets for the reference and counter electrodes (CE) while the gas tight inlet for the SECM tip was made using silicone tube enabling free movement of the tip above the sample surface. To control the pressure inside the cell a Bunsen valve made of a PVC tube was used.

SECM experiments were carried out in a four-electrode cell configuration with the catalyst sample as the first working electrode, WE1, and the SECM tip as the second working electrode, WE2 (Fig. 1). A large surface area Pt-mesh and a $\text{Ag/AgCl}/3 \text{ M KCl}$ electrode were used as the counter and reference electrodes (RE), respectively. To minimize the contamination with chloride ions, a double junction RE was used with the outer chamber filled with 0.1 M KOH (Sigma-Aldrich) solution. All

¹ This procedure is probably not optimal, especially in alkaline media due to possible effects on the Nafion properties. However, we use it on purpose, as it is widely utilized in the literature as a “common” procedure.

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