



Electrochemical noise from oxygen reduction on stainless steel surfaces

Helmuth Sarmiento Klapper*, Joachim Goellner

Otto von Guericke University Magdeburg, Institute of Materials and Joining Technology, P.O. Box 4120, Magdeburg 39016, Saxony Anhalt, Germany

ARTICLE INFO

Article history:

Received 16 July 2008

Accepted 10 October 2008

Available online 18 October 2008

Keywords:

A. Stainless steel

B. Electrochemical noise

B. Potentiostatic

C. Oxygen reduction

ABSTRACT

Oxygen reduction occurring at the passive layer is probably the most important cathodic reaction involved in corrosion processes on stainless steel. Furthermore, the influence of the surface state on the oxygen reduction reaction is a key point for the understanding of the mechanism of localized corrosion on stainless steel. In this study, electrochemical noise measurements under cathodic polarization were carried out to obtain new information about this influence. It has been confirmed that the surface state of stainless steel plays a very important role in the kinetic of this cathodic reaction. Oxygen reduction kinetics was significantly reduced on passivated surfaces and improved on pre-reduced and ground surfaces. In addition, electrochemical current noise measurements allowed to differentiate between the electrochemical activity produced by the oxygen reduction reaction and that due to the reduction of the passive layer, in direct dependence on the characteristics of the different surface states investigated.

© 2008 Elsevier Ltd. All rights reserved.

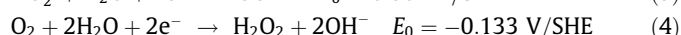
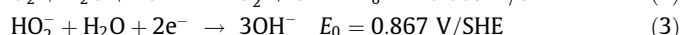
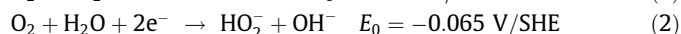
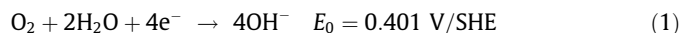
1. Introduction

Rather than merely an electrochemical method for corrosion studies and monitoring, the electrochemical noise (EN) primarily is a phenomenon based on spontaneous departures of a system from the equilibrium state in which electrochemical reactions normally occur. Therefore, it will be happening naturally even when not recorded [1]. Starting from early studies carried out by Tyagai et al., and by Iverson, the use of the EN measurements have advanced greatly so that a better advantage can be taken of the valuable electrochemical information inherent to the recorded EN signals [2]. This in turn has led to a clearer understanding of many complex corrosion processes, in which fluctuations of potential and current, (EN signals) are related to the electrochemical processes occurring at the metal (oxide layer)/electrolyte interface.

The oxygen reduction reaction is one of the most relevant cathodic processes in different fields of the electrochemistry. Regarding to corrosion, the electrochemical reduction of oxygen dissolved in aqueous media is probably the most important cathodic reaction. Depending on how this reaction consumes the electrons liberated by the metal dissolution it may inhibit or leave unaffected the development of the corrosion process which in many cases is the rate-determining process. On the other hand, passivation as a phenomenon of technical relevance to the practical use of many metals and alloys requires a cathodic process, i.e., oxygen reduction to proceed so as to guarantee that metals such as stainless steel are able to reach the passive state and, just as importantly, that they will be able to reach it once again after the passive

layers breakdown (to repassivate). In fact, this close relationship between the cathodic process, i.e., oxygen reduction and the passivation of stainless steel shows clearly that the corrosion processes do not depend solely on the anodic dissolution process. Every electrochemical corrosion process involves at least two partial reactions, anodic and cathodic, and either can exert a decisive influence on the kinetics and mechanism of the overall process as well as on the EN signals obtained from this process [3].

Several studies were focused on the electrochemical reduction of oxygen. It is well known that in neutral and alkaline solutions, this process can yield OH^- following a four-electron pathway (Eq. (1)), or it can yield OH^- via hydrogen peroxide following a two-electron pathway (Eqs. (2) and (3)), or it can produce H_2O_2 as a final reduction product (Eq. (4))



Investigations summarized in Table 1, carried out in many environments and under different conditions on iron [4–13], carbon steels [14–17], stainless steels, and iron–chromium alloys [18–25], have shown that generally, the mechanism and kinetics of oxygen reduction strongly depend on the material (chemical composition, state of the surface), the electrolyte (pH, chemical composition), and the conditions under which the reaction proceeds (hydrodynamic, temperature, polarization). In the specific case of stainless steel, the presence of passive layers is a very important factor affecting the oxygen reduction reaction [22]. As regards localized corrosion of stainless steels, it is well known that

* Corresponding author. Tel.: +49 391 6714566; fax: +49 391 6714505.

E-mail address: Helmuth.sarmiento@mb.uni-magdeburg.de (H.S. Klapper).

Table 1
Oxygen reduction investigations on iron and ferrous alloys.

| Material | Surface state | pH | Electrolyte | Reaction order | Pathway |
|---|---|--------------------------------------|--|---|--|
| Iron | Bare | Alkaline | [4] NaOH (pH 11.1) | | [4] via H ₂ O ₂ |
| | | | [5] KOH (pH > 11) | | [5] Direct to OH ⁻ |
| | | | [6] Borate and bicarbonate buffer solutions (pH 9.8) | [6] O ₂ = 1, OH ⁻ = -0.5 | [6] Direct with little H ₂ O ₂ |
| | | [7] NaCl 0.005 – 1 M (pH 10 ± 0.2) | [7] O ₂ = 0.5, OH ⁻ = 0 | [7] Direct to OH ⁻ | |
| | | Neutral | [7] NaCl 0.005 – 1 M (pH 7 ± 0.2) | [7] O ₂ = 0.5, OH ⁻ = 0 | [7] Direct to OH ⁻ |
| | | | [8] Phosphate buffer solution (pH 6.9) | | [8] Direct with little formation of H ₂ O ₂ and via H ₂ O ₂ |
| | [10] Borate buffer solution (pH 8.4) | | [10] O ₂ = 1, OH ⁻ = 0 | [9] Direct with little H ₂ O ₂ [10] Direct with little H ₂ O ₂ | |
| | Acid | | [4] H ₂ SO ₄ (pH 4.25) | | [4] Direct to OH ⁻ |
| | | | [7] NaCl 0.005 – 1 M (pH 4 ± 0.2) | [7] O ₂ = 0.5, OH ⁻ = 0 | [7] Direct to OH ⁻ |
| | | | | | |
| | Passive | Alkaline | [6] Borate and bicarbonate buffer solutions (pH 9.8) | [6] O ₂ = 1, OH ⁻ = 0 or -1 | [6] via H ₂ O ₂ |
| | | | [10] Borate buffer soln. pH 8.4–9.8 | [10] O ₂ = 1, OH ⁻ = -0.5 | [10] via H ₂ O ₂ |
| | | | [11] O ₂ = 0.5, OH ⁻ = -1 | [11] Direct with little formation of H ₂ O ₂ | |
| [12] NaOH 0.01 – 1 M | | | [12] O ₂ = 0.5, OH ⁻ = 0 or -1 | [12] via H ₂ O ₂ | |
| | | [13] NaOH (pH 12–13.8) | [13] O ₂ = 1, OH ⁻ = 0 or -1 | | |
| Neutral | | [13] Borate buffer solution (pH 7.4) | [13] O ₂ = 1, OH ⁻ = 0 | | |
| | | | | | |
| Carbon steel | [17] Covered with oxide layers | Alkaline | [17] NaOH 1 M | [17] O ₂ = 1 | [17] via H ₂ O ₂ |
| | | Neutral | [14] 3%-NaCl [15] 3%-NaCl [16] KCl 0.5 M | | [14] Direct with little H ₂ O ₂ [15] Direct to OH ⁻ [16] Direct and via H ₂ O ₂ |
| Stainless steel and iron–chromium alloys: | [18] Pre-reduced, pre-corroded, and pre-anodized | Alkaline | [18] NaOH 0,01 – 1 M (pH 12–13.8) and borate buffer solution pH 9.8 | [18] OH ⁻ = -1 | [18] Direct and via H ₂ O ₂ |
| | | Neutral | [22] NaCl 0.5 M pH 10 [18] NaCl 0.5 M and borate buffer solution pH 7.4 | [22] O ₂ = 1 [18] OH ⁻ = -1 | [22] Direct to OH ⁻ [18] Direct and via H ₂ O ₂ |
| [18] Duplex steel | [18] Pre-reduced, pre-corroded, and pre-anodized | | [19] Borate buffer solution (pH 8.4) | | |
| [19] FeCr | [20] Passive | | [20] NaCl 0.5 M | [20] O ₂ = close to 1 | [20] Direct |
| [20] AISI 316 SS | [21] Passive | | [21] Borate buffer solution (pH 8.4) | [21] OH ⁻ = -1 OR 0.6 | [21] Direct |
| [21] FeCr | [22] Pre-reduced | | [22] Seawater | [22] O ₂ = 1 | [22] Direct |
| [22] AISI 304 SS | [23] Polished, pre-reduced, passive and chem. treated | | [23] Seawater | | [23] Polished: direct and via H ₂ O ₂ , pre-reduced: direct with little H ₂ O ₂ |
| [23] AISI 316L and 904L SS | | | [24] Natural and artificial seawater (pH 8.4) | [24] O ₂ = 0.5, OH ⁻ = -1 | [24] Direct with little H ₂ O ₂ and via H ₂ O ₂ |
| [24] AISI 316 and 420 SS | [25] Polished, pre-reduced, passive and chem. treated | | [25] 3 g/l NaSO ₄ | | |
| [25] AISI 316 SS | [22] Pre-reduced | Acid | [22] NaCl 0.5 M (pH 4) | [22] O ₂ = 1 | [22] Direct to OH ⁻ |

oxygen reduction occurs in locations different from those where anodic dissolution takes place, i.e., at or across the passive layer. For this reason, the structure, the chemical composition and the conductivity of the passive layer play a very important role on this process. In fact, Le Bozec et al., concluded in their study about the effects on oxygen reduction of the surface condition of stainless steel (resulting from different treatments such as pre-reduction, passivation, or chemical treatment) that the mechanism of this cathodic reaction is influenced by the properties of the surface [23]. On pre-reduced surfaces for instance, oxygen reduction was observed to proceed mainly through the 4e⁻ pathway. In contrast, the two-electron and four-electron pathways were involved on polished surfaces. In both these cases there was little formation of hydrogen peroxide. Likewise, Le Bozec and co-workers suggested the existence of a relationship between the oxygen reduction kinetics and the chemical composition of the different surfaces investigated. Based on their experimental results, they deduced that surfaces covered with layers having a high concentration of Fe(II) ions, which is the case for pre-reduced and pol-

ished surfaces, are bound to exhibit higher oxygen reduction kinetics, whereas passive layers enriched in chromium species (which includes the cases of passivated and chemically treated surfaces) can be expected to inhibit the oxygen reduction reaction.

The importance of Fe(II) ions at the electrode surface that, due to their coordination geometry, constitute active centers for oxygen reduction on iron was considered by Gojkovic et al. [13] based on the redox surface catalyst Model proposed by Presnov and Trunov [26]. According to Calvo and Schiffrin, the reduction of the oxide layers yielding Fe(II) ions can influence the oxygen reduction because the reduction of these layers occurs over the same potential range [12]. Zecevic et al. outlined the presence of a Fe(III)/Fe(II) equilibrium within the mechanism of O₂ reduction on passive iron [6]. In addition, Fabjan [11] considered that oxygen reduction on passive iron is mediated by a reduction process taking place on metal centers within the oxide. This is in agreement with the mechanism of oxygen reduction on stainless steel proposed by Kapusta [24]. Based on studies of oxygen reduction on iron oxide layers, Stratmann and Müller proposed that this cathodic process

Download English Version:

<https://daneshyari.com/en/article/1470878>

Download Persian Version:

<https://daneshyari.com/article/1470878>

[Daneshyari.com](https://daneshyari.com)