



# A mathematical description accounting for the superfluous hydrogen evolution and the inductive behaviour observed during electrochemical measurements on magnesium

M. Curioni <sup>a,\*</sup>, L. Salamone <sup>a,b</sup>, F. Scenini <sup>a</sup>, M. Santamaria <sup>b</sup>, M. Di Natale <sup>c</sup>

<sup>a</sup> School of Materials, Corrosion and Protection Centre, Material Performance Centre, University of Manchester, M139PP, Manchester, United Kingdom

<sup>b</sup> Electrochemical Materials Science Laboratory, DICAM, Università di Palermo, 90128, Palermo, Italy

<sup>c</sup> Department of Mathematics and Applications, Università degli Studi di Milano Bicocca, 20125, Milano, Italy

## ARTICLE INFO

### Article history:

Received 13 February 2018

Received in revised form

12 April 2018

Accepted 16 April 2018

Available online 17 April 2018

### Keywords:

Magnesium

Inductive behaviour

Superfluous hydrogen evolution

Corrosion

## ABSTRACT

When electrochemical techniques are used to probe the surface of corroding magnesium with the aim of obtaining quantitative information on the corrosion process, two peculiarities are generally observed: i) with anodic polarization, the rate of hydrogen evolution increases instead of decreasing and ii) during electrochemical impedance spectroscopy measurements, an inductive contribution is often observed at the low-frequency end of the spectra. The presence of these two phenomena clearly has an impact on the methodology that should be applied to correctly estimate corrosion rates from electrochemical data. The aim of this work is to provide a general mathematical description of the corroding magnesium surface that, under minimal a priori assumptions regarding the reaction kinetics, can account simultaneously for both superfluous hydrogen evolution and inductive response. The mathematical results are consistent with the suggestion that the superfluous hydrogen evolution is mainly related to the increase of the surface of the active corrosion front during anodic polarization. Further, the obtained results show that the inductive response is expected when, at the corrosion front, oxidation of magnesium proceeds faster than hydrogen evolution.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

The electrochemical behaviour of magnesium surfaces is important for many applications since it determines the corrosion resistance of magnesium components, the efficiency of primary magnesium batteries [1–3] and of sacrificial anodes [4–7] for cathodic protection and the lifetime of resorbable implants in the human body [8–10]. In an aqueous environment, however, the electrochemical behaviour of magnesium is relatively complex. This is due to the fact that magnesium has an equilibrium potential for oxidation that is considerably lower than the potential for proton reduction resulting in hydrogen evolution over a wide pH range. Further, the mixed oxide-hydroxide film covering the magnesium surface is only partially protective in neutral or acidic pH, so the corrosion resistance of magnesium is relatively poor [11].

Regarding the response of corroding magnesium surfaces to

electrochemical measurements, three peculiarities are important and specifically: i) the rate of hydrogen evolution ('superfluous hydrogen evolution' or 'negative difference effect') increases with increasing anodic polarization, for example during a potentiodynamic polarization experiment [11–21], ii) the cathodic activity of the magnesium surface ('cathodic activation') increases as a result of corrosion either at the free corrosion potential or following anodic polarization [22–26] and iii) an inductive behaviour generally is generally observed when performing electrochemical impedance spectroscopy measurements at the free corrosion potential [10,20,27–29].

Regarding the first effect, i.e. the superfluous hydrogen evolution, several interpretations have been proposed in the past, mainly related either to the formation of univalent magnesium [13,30,31], or to the detachment of metallic chunks of magnesium followed by their oxidation away from the electrode [32]. Such theories have been largely dismissed, since recent works indicate that the increased rate of hydrogen evolution with increasing polarization is associated with the rupture of the partially protective film at the corrosion front that results in direct exposure of metallic

\* Corresponding author.

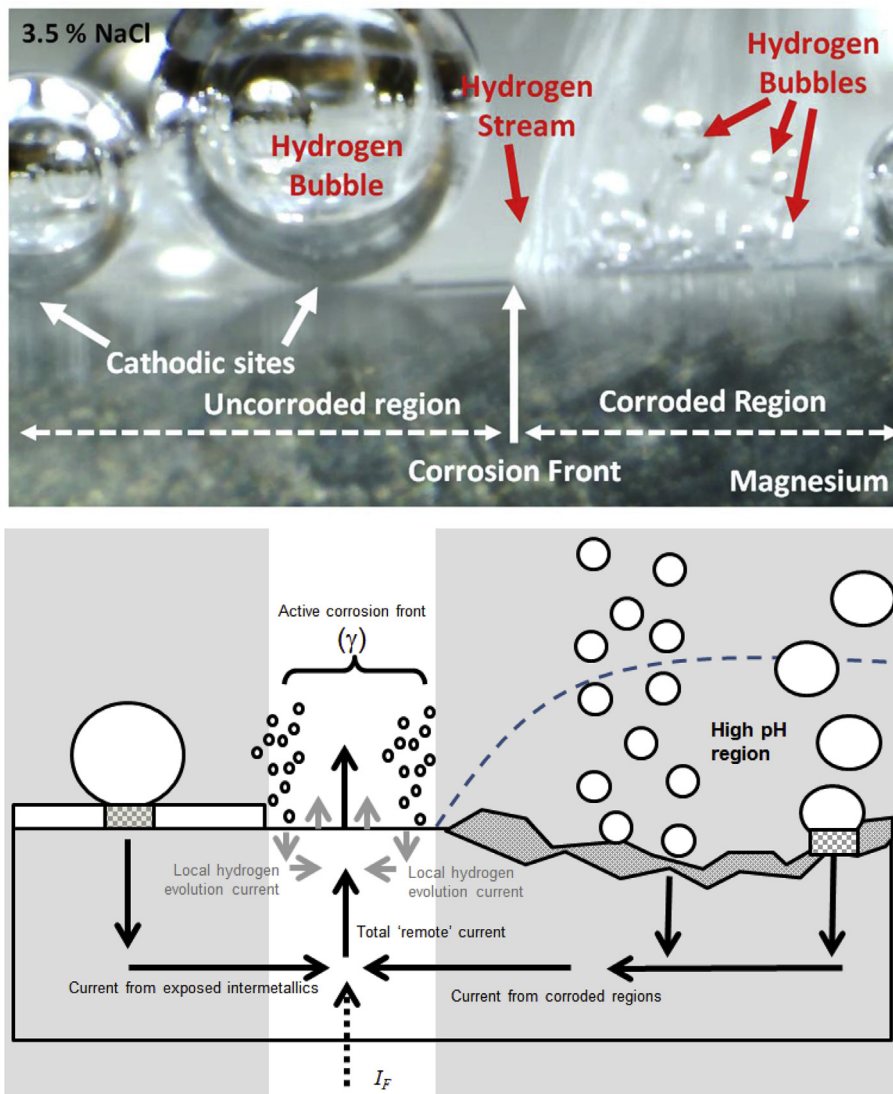
E-mail address: [michele.curioni@manchester.ac.uk](mailto:michele.curioni@manchester.ac.uk) (M. Curioni).

magnesium to the solution. Due to the available large potential difference, additional hydrogen evolution takes place at the corrosion front [18–21,33–36]. The phenomenon is illustrated in Fig. 1, where a cross sectional view of a corroding magnesium electrode is presented, together with a schematic of the associated processes. The current that maintains active the corrosion front (at the centre of the image) is provided by hydrogen evolution on cathodically active regions. These regions consist of intermetallic particles located on the uncorroded part of the electrode, ahead of the corrosion front (left part of the image), or on the cathodically active regions located behind the corrosion front (right part of the images). At the corrosion front, the film is ruptured due to the simultaneous presence of an anodic current and of depassivating conditions, for example comparatively low pH and/or presence of chloride ions. As the film ruptures, the metal is directly exposed to the electrolyte (or covered by a chloride-rich film that offers virtually no protection to the underlying surface) and additional hydrogen is evolved. In this region, streams of very small bubbles are generated instead of comparatively large bubbles generated on the cathodic sites, because the dissolving surface is intrinsically unstable and doesn't allow the forming bubbles to anchor.

situation also produces an increase in the magnesium oxidation rate, since at the corrosion front an additional current associated to hydrogen evolution is produced and, consequently, an additional magnesium oxidation current is generated [18]. A very similar mechanism has been suggested to occur on aluminium, also displaying superfluous hydrogen evolution during anodic polarization in chloride-containing environments due to local rupture of the protective oxide film [36–38].

Fajardo and Frankel [34] have recently developed a kinetic model which accounts for these processes on magnesium. In particular, they have shown for exponential kinetics that, if the reaction coefficient associated with magnesium oxidation is larger than the one associated with hydrogen evolution on the active corrosion front, then the hydrogen evolution rate is expected to increase with increasing potential, due to the increasing area fraction associated with the corrosion front. In this work we follow broadly the general framework of Fajardo and Frankel, although some significant variations are introduced in order to account simultaneously of all the multiple overlapping processes.

In addition to the 'superfluous hydrogen evolution' an inductive response is generally observed when performing electrochemical



**Fig. 1.** a) Side-view of a magnesium surface during free corrosion in 3.5% NaCl, from Ref. [18]. b) Schematic representation of the processes and associated electrical currents on the magnesium surface represented in Figure 1a, redrawn from Ref. [19].

Download English Version:

<https://daneshyari.com/en/article/6603087>

Download Persian Version:

<https://daneshyari.com/article/6603087>

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