



A kinetic model explaining the enhanced rates of hydrogen evolution on anodically polarized magnesium in aqueous environments



S. Fajardo^{a,*}, G.S. Frankel^b

^a Department of Surface Engineering, Corrosion and Durability, National Center for Metallurgical Research (CENIM-CSIC), Madrid 28040, Spain

^b Fontana Corrosion Center, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210, USA

ARTICLE INFO

Keywords:

Hydrogen evolution
Magnesium
Kinetic model
Anodic dissolution
Negative difference effect (NDE)

ABSTRACT

A model to explain the increasing rates associated with hydrogen evolution (HE) originating at the dissolving regions of Mg under anodic polarization is presented. The actively dissolving anodes have been shown experimentally to be the primary source of anomalous evolution of hydrogen. In this model, standard electrochemical laws are used to account for this phenomenon. The fractional coverage of active Mg sites is introduced to localize the cathodic contribution of HE during anodic polarization. A kinetic equation is derived showing that the rate of HE will increase with increasing potential if the charge transfer coefficient associated with the Mg oxidation reaction is greater than the charge transfer coefficient for the HE reaction. Experimental data obtained on high purity Mg galvanodynamically polarized at potentials above and below its E_{corr} in 0.1 M NaCl solution are presented to validate the model.

1. Introduction

According to the standard electrochemical kinetics (as exemplified by the well-accepted Butler-Volmer equation), the reaction rate of any activation-controlled cathodic half-reaction in an electrochemical system is predicted to decrease exponentially as the potential for such reaction increases above its reversible potential (E_{rev}) [1]. Analogously, when a metallic electrode is immersed in an aqueous electrolyte, the rate of the cathodic reaction is expected to decrease at potentials above the corrosion potential (E_{corr}). However, this is not the case for magnesium (Mg) where the evolution of H_2 (the primary cathodic reaction at the E_{corr}) increases with increasing anodic polarization [2]. Although the occurrence of this phenomenon, commonly known as negative difference effect (NDE), has been observed for decades [3], a satisfactory mechanism to fully explain this contradictory behavior has still not been provided. In recent years different theories have been proposed to explain the anomalous HE exhibited by anodically polarized Mg. Briefly summarized, they rely on three different possible phenomena: effects of the corrosion product surface layer, the surface enrichment of impurities, and the effect of local anodic sites [2].

The dark colored corrosion product film that forms on Mg in NaCl-containing solutions has been shown to exhibit enhanced catalytic properties towards the hydrogen evolution reaction (HER) when compared with the pristine Mg surface under open circuit conditions [4–6]. Salleh et al. [7] confirmed these findings using scanning

electrochemical microscopy (SECM) on pristine and $\text{Mg}(\text{OH})_2$ covered Mg surfaces without external polarization. Most importantly, Williams et al. [8] identified using the scanning vibrating electrode technique (SVET) that the visually detected corrosion film forming during Mg dissolution exhibited net cathodic behavior even under anodic polarization. For this reason, it has been considered to be responsible for the enhanced rates of HE under anodic polarization. However, it was recently determined using SVET and gravimetric hydrogen collection that the dark corroded regions only contribute to a small fraction of the total HE rate [9].

The effect of noble metal impurities in Mg on the rates of HE (and concomitant Mg oxidation rates) at the E_{corr} has been known for a long time [10]. The solubility of most metals in Mg is very low with only a small number of elements presenting appreciable solubility (i.e., > 1 wt%) [2]. Consequently, impurity elements and intermetallic particles (IMPs) are common in Mg and its alloys. Note that metal impurity traces are found even in high purity Mg. The impurities and IMPs are comparatively more noble than Mg (because Mg is so active), exhibiting more positive electrochemical surface potentials. Therefore, they act like strong local cathodes during Mg dissolution and support high rates of HER at the Mg E_{corr} . Despite this, the notion that incongruent dissolution of Mg during anodic polarization may produce regions enriched with noble elements to support the HER at faster rates is rather new. However, recent investigations have shown that the enrichment efficiency of impurities is low [11,12]. Furthermore, extremely high

* Corresponding author.

E-mail address: fajardo@cenim.csic.es (S. Fajardo).

rates of anomalous HE were reported to occur even on anodically polarized ultra-high purity Mg (99.9999 wt% Mg), discrediting the notion that this phenomenon is driven by impurity enrichment [13].

Finally, it has been suggested that the enhanced rates of HE may be a result of an increase in the exchange current density for the HER on Mg ($i_{0,H,Mg}$) as the rate of Mg dissolution increases [14]. This model considers that $i_{0,H,Mg}$, essentially the rate constant for the HER, increases with increasing applied anodic polarization, and the HE is hypothesized to originate at the net anodic regions. Recent studies support this thesis [9,15]. In these works strong evidence was provided that the primary location of anomalous HE is the regions dominated by the anodic dissolution reaction. Even though the source of HE on Mg subjected to anodic polarization were shown to be the anodic regions, a mechanistic model to explain the reason why the actively dissolving Mg anodes exhibit this behavior has not been introduced to date.

This paper presents a kinetic model to explain the enhanced rates of HE on anodically polarized Mg surfaces originated at the dissolving anodic regions. Standard electrochemical laws are used to account for this phenomenon.

2. Materials and methods

High purity (HP) Mg, was used as test specimen and its composition is given elsewhere [13]. Test samples were mounted in epoxy resin with a copper wire attached to the back of the Mg specimen to provide the electrical connection. All experiments were carried out in quiescent 0.1 M NaCl solution. All solutions were prepared from laboratory grade reagents and with high purity water of 18.2 MΩ cm (Millipore™ system).

Cathodic and anodic galvanodynamic polarization measurements were performed in separate experiments, scanning downwards and upwards from the E_{corr} to -75 and $+75$ mA cm⁻², respectively at a scan rate of 0.1 mA cm⁻² s⁻¹. A three-electrode configuration was used with the HP Mg acting as the working electrode, a Pt mesh acting as the counter electrode and a saturated calomel electrode (SCE) acting as the reference electrode. A Gamry Instruments Reference 600 potentiostat/galvanostat controlled by the Gamry Framework software was used to perform the electrochemical experiments.

Hydrogen collection measurements were carried out using the gravimetric method proposed by Curioni [16] and further developed by Fajardo et al. [17]. Full details of the gravimetric method can be found elsewhere [17]. This method exhibits extremely high sensitivity in HE detection and allows for real-time H₂ volume collection during dynamic polarization measurements with high temporal resolution.

3. Theory

After exposure to water, the surface of Mg is covered with an MgO native oxide surface film [18]. In the presence of chloride ions and when subjected to anodic polarization, this MgO film undergoes localized breakdown. This process involves the creation of active Mg sites exposed to the electrolyte where dissolution of the metal occurs. In accordance with previous experimental observations, the present model assumes that these active regions are also the source of anomalous HE. It is further assumed that, during anodic polarization, the active Mg sites may be deactivated (i.e. blocked) due to adsorption of species such as OH⁻ or, simply, by the deposition of corrosion products on the electrode surface, in the dynamic process of continuous creation and subsequent deactivation of active Mg sites. Consequently, the concentration of active Mg sites available for both anodic dissolution and HE (n_{Mg} , mol cm⁻²) changes according to the following rate equation:

$$\frac{dn_{Mg}}{dt} = R_{Mg} - \lambda_{Mg} n_{Mg} \quad (1)$$

where R_{Mg} is the rate of production of active Mg sites (mol cm⁻² s⁻¹) and λ_{Mg} (s⁻¹) is a constant associated with the subsequent deactivation

of the active Mg sites produced. Under steady-state conditions, the number of active Mg sites available for both anodic dissolution and HE can be described by:

$$n_{Mg} = \frac{R_{Mg}}{\lambda_{Mg}} \quad (2)$$

It is further assumed that R_{Mg} is directly proportional to the current density associated with Mg dissolution (i_{Mg} , A cm⁻²):

$$R_{Mg} = \frac{i_{Mg}}{zF} \quad (3)$$

where z (eq mol⁻¹) is the number of electrons involved in the electrode reaction and F (96,487 C eq⁻¹) is the Faraday constant. Substituting Eq. (3) into Eq. (2) yields

$$n_{Mg} = \frac{i_{Mg}}{zF\lambda_{Mg}} \quad (4)$$

The ratio between the number of active Mg sites available for oxidation and the concomitant anomalous HE, and the total number of atoms present on the surface (N_T , mol cm⁻²) determines the fraction coverage of active Mg sites, defined as $\theta = n_{Mg}/N_T$. Consequently,

$$\theta = \frac{i_{Mg}}{zF\lambda_{Mg}N_T} \quad (5)$$

Activation-controlled kinetics for an anodic and a cathodic electrochemical reaction far from the reversible potential (which is the case for the Mg oxidation reaction and the HER on an anodically polarized Mg electrode) can be described by their corresponding Tafel Equations [1]:

$$i_{Mg} = i_{0,Mg} \exp\left(\frac{\alpha_{Mg}zF}{RT}(E - E_{rev,Mg})\right) \quad (6)$$

$$i_{HER} = \theta i_{0,H,Mg} \exp\left(\frac{-\alpha_{HER}zF}{RT}(E - E_{rev,H})\right) \quad (7)$$

where $i_{0,Mg}$ is the exchange current density for the Mg reaction (A cm⁻²), $i_{0,H,Mg}$ is the exchange current density for the HER on Mg (A cm⁻²), E is the anodic cell potential (V), $E_{rev,Mg}$ is the reversible potential for the Mg oxidation reaction (V), $E_{rev,H}$ is the reversible potential for the HER (V) and α_{Mg} and α_{HER} are the charge transfer coefficients for the Mg oxidation and the HE reactions, respectively. The rest of the terms have their usual meaning or have been already described. Note that the current density associated with the HER (Eq. (7)) is dependent on the fraction coverage of active Mg sites since these are considered in the present model to be the source of anomalous HE. With the aim of accounting exclusively for the anomalous HE originating at the anodic regions, thus discerning the contribution of this hydrogen source from other possible mechanisms (i.e. catalytic corrosion film and noble impurities), θ was introduced in the right part of Eq. (7). Note that in this model θ is assumed to exhibit a linear relationship with i_{Mg} , as shown in Eq. 5. In brief, greater anodic polarization leads to a higher fraction of active Mg sites available for dissolution and HE. Substituting Eq. (6) into Eq. (5) leads to the following expression for the fractional coverage of active Mg sites:

$$\theta = \frac{i_{0,Mg}}{zF\lambda_{Mg}N_T} \exp\left(\frac{\alpha_{Mg}zF}{RT}(E - E_{rev,Mg})\right) \quad (8)$$

Substituting Eq. (8) into Eq. (7) one gets the current associated with HE during anodic polarization:

Download English Version:

<https://daneshyari.com/en/article/6469487>

Download Persian Version:

<https://daneshyari.com/article/6469487>

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