



# The Source of Anodic Hydrogen Evolution on Ultra High Purity Magnesium



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## ARTICLE INFO

### Article history:

Received 20 June 2016

Received in revised form 1 July 2016

Accepted 4 July 2016

Available online 5 July 2016

### Keywords:

hydrogen evolution

magnesium

scanning vibrating electrode technique

anodic dissolution

NDE

## ABSTRACT

The enhanced catalytic activity of hydrogen evolution reaction on anodically polarized Mg surfaces, commonly referred to as the Negative Difference Effect, has been the topic of intense investigation in recent years. However, the cause of anodic H<sub>2</sub> remains unclear. To determine the primary source of H<sub>2</sub> evolution on dissolving Mg polarized at anodic potentials, an in-situ scanning vibrating electrode technique (SVET) analysis during galvanostatic polarization, coupled with gravimetric H<sub>2</sub> volume collection and potentiodynamic polarization experiments, were carried out on ultra-high purity Mg (99.9999% Mg). The combination of these methods provided solid evidence that the evolution of hydrogen on dissolving ultra-pure Mg is primarily associated with the regions dominated by the anodic reaction. Although local cathodes corresponding with the dark corrosion film formed during anodic dissolution were revealed by in-situ SVET, they appeared to play a minor role in the process.

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## 1. Introduction

The hydrogen evolution reaction (HER) occurs spontaneously on the surface of magnesium and its alloys under open circuit conditions in the presence of an aqueous electrolyte. The low open circuit potentials (OCP) exhibited by these materials, which are well below the reversible potential for HER ( $E_{\text{rev,H}}$ ), create a large cathodic overpotential for HER and the reduction of H<sup>+</sup> ions (in acidic solution) or water (in neutral and alkaline solutions) is the primary cathodic reaction [1]. However, in contradiction to standard electrochemical kinetics for activation-controlled reactions, the dissolution of Mg and its alloys during anodic polarization is accompanied by persistent hydrogen evolution (HE) on the surface that increases with the amount of anodic polarization [1–3]. This high rate of HE on dissolving Mg has been termed the Negative Difference Effect but is referred to here as anodic HE. Despite intense investigations of this phenomenon [2,4–21], the cause of this anodic HE remains unclear. Current interpretations to explain the enhancement in cathodic activation during dissolution and the source of anodic HE include three possible mechanisms based on the effect of corrosion film

formation, the enrichment of impurities more noble than Mg and the effect of local anodic sites.

When pure Mg (with Fe impurity concentration below about 170 ppm) is polarized anodically from its OCP, a filiform-like attack is exhibited and a dark corrosion product forms on the electrode surface [4,6,22]. This corrosion film has been shown to consist of a crystalline bi-layered structure formed by an inner MgO film covered by an outer layer of MgO/Mg(OH)<sub>2</sub> [15]. Williams et al. [17] investigated anodic HE on pure Mg using the scanning vibrating electrode technique (SVET) and reported that the intense local anodic regions exhibited upon anodic polarization propagated along the electrode surface and left behind local net cathodes. Furthermore, these local cathodes corresponded on the electrode surface with the locations of the deposited dark corrosion product formed during polarization. Salleh et al. [13] performed scanning electrochemical microscopy (SECM) and cathodic polarization measurements on a Mg(OH)<sub>2</sub> coated Mg electrode and found larger HE rates than those on the uncoated surface. These findings provide experimental evidence for the concept that, during Mg anodic polarization, the HER is enhanced on the dark corrosion film, which is therefore the location of the anodic HE.

The effect of noble metal impurities on Mg corrosion and HE has been known for a long time [23], but the notion that they may be the source of anodic HE has been the subject of recent investigations. It is hypothesized that impurities more noble than

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Mg accumulate on its surface during dissolution and act as preferential cathodic sites for the HER. Based on findings of very small iron particles on the surface of corroded high purity Mg [15], Lysne et al. [10] proposed a model for the Fe enrichment efficiency on Mg specimens with different concentrations of Fe after anodic dissolution. They found Fe enrichment efficiency to be very poor and unable to explain the large amount of H<sub>2</sub> produced at potentials above the OCP. These findings were supported by Cain et al. [7] who studied Fe enrichment efficiency on previously corroded pure Mg specimens by Rutherford Backscattering Spectrometry (RBS). Despite detecting Fe enrichment of about one order of magnitude, the total concentration of Fe remained far below 1 at.%. Höche et al. [19] proposed a mechanism where Fe impurities in a pure Mg specimen (even at concentrations below 100 ppm) may leave the surface due to preferential dissolution of Mg and redeposit on the electrode surface after self-corrosion at their OCP. This mechanism, similar to that occurring on AA2024 with Cu-rich intermetallic particles [24], would create re-deposited Fe films that could drive the cathodic current and become the primary source of anodic H<sub>2</sub>. However, increased areas of such Fe-rich patches on the dissolving Mg surface are not consistent with the observation of a HE rate that is constant with time for a given fixed anodic current density. It is also not clear if noble metal re-deposition can account for the remarkably high rates of HE exhibited by ultra-high purity dissolving Mg (~0.1 ppm Fe) [4]. Furthermore, Fe deposition could be considerably affected by the intense convection in the electrolyte due to the copious evolution of H<sub>2</sub> during anodic dissolution, particularly at large polarizations. Anodic HE was recently measured on electrodes of both high purity (99.98% Mg) and ultra-high purity Mg (99.9999% Mg) [4]. Even the ultra-high purity Mg material with a total impurity content of ~1 ppm exhibited extremely high HE rates, confirming that this phenomenon cannot be fully explained in terms of impurity enrichment.

Finally, the role of dissolving anodic sites on HE at anodic potentials has also been investigated. Frankel et al. [8] proposed 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. In this model,  $i_{0,H,Mg}$  is considered a dynamic parameter instead of constant. This notion has also been applied to explain anodic HE in Al pits and on dissolving Al in concentrated acid solutions [2]. Although the underlying mechanism for this behavior is not yet clear, changes in the surface nature of dissolving Mg regions may influence its chemical reactivity, increasing the HER kinetics. This hypothesis has been supported in a recent study [4] where the contribution of the dark corrosion product on Mg and/or the enrichment of noble elements to the total amount of hydrogen collected during anodic polarization was estimated. For that purpose, it was assumed that the corrosion film and the accumulated impurities formed during dissolution are robust in that they are relatively unchanged during subsequent cathodic polarization. Extrapolation of the behavior in the cathodic region to the potentials reached during anodic polarization proved that the HE rate associated with the accumulated products (i.e. corrosion product and impurities enriched at the surface) was small during anodic polarization. The enhanced catalytic activity for the HER on dissolving Mg was found to be primarily associated with the regions dominated by the anodic dissolution reaction.

The aim of the present paper is to make advancements in elucidating the source of anodic HE and contribute to the general understanding of persistent evolution of hydrogen on anodically polarized Mg. For that purpose, the effects of anodic dissolution on ultra-high purity Mg specimens were investigated by SVET, H<sub>2</sub> collection and electrochemical measurements. The influence of

anodic regions and corrosion film on the catalytic activity for the HER is discussed.

## 2. Experimental

Ultra-high purity (UHP) Mg was used as test specimen. UHP Mg was obtained from United Mineral and Chemical Corporation (NJ, USA). This material, with a nominal purity of 99.9999%, was used in a previous work and its chemical composition is given elsewhere [4]. It is worth noting that the concentration of Fe was 0.1 ppm. Samples with a Cu wire attached to the back were cold mounted in epoxy resin and ground under ethanol to 1200 grit using silicon carbide papers. The samples used for SVET measurements were then masked with 90 μm thick extruded PTFE 5490 tape (3 M Ltd), such that only about 5 × 5 mm square area was exposed to electrolyte. A 2 M NaCl solution at pH ~6 was used as electrolyte. All solutions were prepared from laboratory grade reagents and with high purity water of 18.2 MΩ cm (Millipore™ system).

SVET measurements were carried out using a probe comprising a 125 μm diameter platinum wire sealed in a glass sheath so that the active portion of the probe tip consisted of a 125 μm diameter Pt micro-disc electrode. The probe vibration frequency was 140 Hz and the peak-to-peak vibration amplitude was 30 μm. Full details of the SVET instrument design, mode of operation and calibration procedure to give values of current flux density along the axis of probe vibration ( $j_z$ ) are given elsewhere [25]. A total net charge of 6 C cm<sup>-2</sup> was passed galvanostatically at different anodic current densities in the range of 1 to 4 mA cm<sup>-2</sup> by means of an in-house micro-galvanostat. SVET scans were performed at a constant height by holding the probe vertically 100 μm above the metal surface. Numerical area integration of  $j_z$  distributions per scan was carried out to calculate the time-dependent total measured cathodic current ( $I_c$ ), according to a protocol described in detail elsewhere [17,25]. After normalization by the nominal surface area of the electrode, this allows the evolution of the time-dependent area-averaged cathodic current density ( $i_c$ ) during the time of galvanostatic current density application to be determined.

Hydrogen collection measurements were conducted using the gravimetric method originally developed by Curioni [26] and described previously [27]. The gravimetric method is based on the buoyant force exerted by the H<sub>2</sub> produced by dissolving Mg when the gas is accumulated in a submerged container. The gravimetric method exhibits higher sensitivity in HE detection than the volumetric method and allows for hydrogen volume collection during polarization measurements with high temporal resolution. Anodic HE was investigated during galvanostatic polarization measurements by the application of the same anodic current densities used in the SVET experiments (i.e. from 1 to 4 mA cm<sup>-2</sup>).

To study the effect of the amount of corrosion product on the catalytic activity of the UHP Mg surface after anodic treatment, galvanostatic polarization experiments were carried out in 0.1 M NaCl solution passing different charges at a constant applied anodic current density of 10 mA cm<sup>-2</sup>.

The OCP of the samples was monitored for 15 minutes prior to the application of the polarization signals to allow the system to reach both a stable potential and, in the case of the gravimetric experiments, also a steady weight.

Cathodic potentiodynamic polarization curves were measured immediately after the anodic galvanostatic treatments. For these experiments the electrolyte was replaced by fresh solution (i.e. 0.1 M or 2 M NaCl) and the cathodic polarization measurement was performed scanning downwards to 700 mV below the OCP at 1 mV/s.

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