

Anomalous Hydrogen Evolution on Magnesium

Aline D. Gabbardo and G. S. Frankel

Abstract

When Mg undergoes anodic polarization in a corrosive environment, the rate of hydrogen evolution (HE) increases with increasing applied anodic potential or current, which is opposite of the expected behavior based on standard electrochemical kinetics. This anomalous HE has been the recent focus of researchers worldwide. In this work, the behavior of sputtered Mg thin films and scratched Mg electrodes is presented. HE vanished when the potential of a pit in Mg thin films was increased into the region where a salt film formed. The peak anodic current on scratched samples was not anomalous, as it decreased slightly with increased potential. These observations indicate that the HE rate on Mg depends on the nature of the surface and that anomalous HE results from the surface being more catalytic to the HE reaction with increasing dissolution rate.

Keywords

Magnesium • Corrosion • Anomalous hydrogen evolution

Extended Abstract

A thorough understanding of Mg corrosion properties is necessary for further developments in its application for engineering structural components. However, the Mg dissolution mechanism cannot be easily explained with classical electrochemical theories and further experimental clarification is still needed. The typical kinetics for electrochemical reactions follow activated state theory as described by the Butler–Volmer equation and, for sufficiently large difference in potential from the reversible potential, the Tafel equation

describes the relation of current density (i) and overpotential [1]. Based on the Tafel equation, the anodic current density increases exponentially and the cathodic current density decreases exponentially with increasing potential. A potentiostat only measures the net current, or net current density if the electrode area is known, ($i_{\text{net}} = i_{\text{anodic}} - |i_{\text{cathodic}}|$). At high anodic potentials, i_{cathodic} is expected to be very low, and i_{net} is approximately equal to i_{anodic} . However, the behavior of Mg during anodic dissolution is different than that predicted by the theories described above [2]. The phenomenon is usually called the negative difference effect (NDE) and more recently the anomalous hydrogen evolution (anomalous HE) [2]. The cathodic reaction rate, described by the hydrogen evolution current density (i_{H_2}), is expected to decrease as the applied potential increases above the OCP, but many authors have shown that for Mg the hydrogen evolution current density increases as the anodic applied potential increases [2–5]. This situation complicates the evaluation of Mg corrosion properties through standard electrochemical tests such as polarization curves because the measured i_{net} does not equal i_{anodic} at high anodic overpotentials [3]. Understanding the mechanism of the anomalous HE phenomenon could facilitate the development of new Mg alloys and more efficient corrosion protection systems for Mg.

Some of the recent theories to explain anomalous HE assumes that the behavior is a localized phenomenon that happens on sites close to the Mg dissolving areas, whereas in others the anomalous HE phenomenon is associated with the actual active dissolving sites on the Mg surface [6–8]. The effects of impurities, corrosion product film and the role of the active surfaces have all been reviewed in detail elsewhere [4, 5].

In this work, the 2D pit growth method and the scratched electrode technique were used as new approaches to further understand the anomalous HE phenomenon [9–11]. The 2D pit growth method has been used to study pitting corrosion in Al and stainless steel [12, 13], but can also be used to evaluate the anomalous HE phenomenon on Mg [9, 10]. The pit growth in metallic thin films is two-dimensional, allowing

A. D. Gabbardo · G. S. Frankel (✉)
Fontana Corrosion Center, The Ohio State University, Columbus,
OH 43210, USA
e-mail: frankel.10@osu.edu

i_{anodic} and i_{net} to be measured by recording the surface of a single growing pit. The pit cathodic current density (i_{cathodic}) can be indirectly obtained by $i_{\text{net}} = i_{\text{anodic}} - |i_{\text{cathodic}}|$, which accounts for the hydrogen evolution rate (i_{H_2}) in the case of Mg. One advantage of this method in comparison with volumetric or gravimetric hydrogen measurements [14] is that the active corroding area, or the 2D pit wall, is tracked in space by the recorded video. It was therefore confirmed that the location of the anomalous HE phenomenon is the active Mg surface [9] and the mechanism is more related to the state of the corroding surface than to the accumulation of impurities or corrosion products. 2D pits have small active areas and thus low ohmic resistance, allowing for the application of higher potentials. When high enough potential is applied, a salt film covers the active surface and the anomalous HE vanishes [10]. The hypothesis is that direct contact of water with the active Mg surface is blocked in this case and HE decreases. The anomalous HE is then a consequence of the increased catalytic activity for the HER of the active sites created during dissolution and it will increase with increasing dissolution rate but will decrease or vanish if these sites are blocked. The scratched electrode technique was used to evaluate the corrosion kinetics of freshly generated Mg surfaces mechanically created in situ by a diamond scribe [11]. Active sites are thought to be fresh, film-free, surfaces. In fact, it was observed that the catalytic activity for the HER increased on the scratched surface when compared to a filmed surface and this increased catalytic activity persisted until repassivation (or reformation of a monolayer of Mg hydroxide). Interestingly, the peak hydrogen evolution current density on the scratched samples was not anomalous, as it decreased slightly with increased potential. The HE rate only depends on the transient state of the Mg surface created by the diamond scribe and is directly related to the catalytic activity of this surface for the HER, in line with the previous results.

References

1. Frankel GS, Landolt D (2003), "Kinetics," Ch. 1.3, Encyclopedia of Electrochemistry, Volume 4, Stratmann M, Frankel GS, eds., Wiley-VCH, Weinheim, Germany
2. Esmaily M, Svensson JE, Fajardo S, et al. (2017) Fundamentals and advances in magnesium alloy corrosion. *Progress in Materials Science* 89: 92–193. <https://doi.org/10.1016/j.pmatsci.2017.04.011>
3. Frankel GS, Samaniego A, Birbilis N (2013) Evolution of hydrogen at dissolving magnesium surfaces. *Corrosion Science* 70: 104–111. <https://doi.org/10.1016/j.corsci.2013.01.017>
4. Frankel GS, Fajardo S, Lynch BM (2015) Introductory lecture on corrosion chemistry: a focus on anodic hydrogen evolution on Al and Mg. *Faraday Discussions* 180: 11–33. doi:180: 11–33. <https://doi.org/10.1039/c5fd00066a>
5. Thomas S, Medhekar NV, Frankel GS, Birbilis N (2015) Corrosion mechanism and hydrogen evolution on Mg. *Current Opinion in Solid State & Materials Science* 19(2): 85–94. <https://doi.org/10.1016/j.cossms.2014.09.005>
6. Fajardo S, Glover CF, Williams G, Frankel GS (2016) The Source of Anodic Hydrogen Evolution on Ultra High Purity Magnesium. *Electrochimica Acta* 212: 510–521. <https://doi.org/10.1016/j.electacta.2016.07.018>
7. Michailidou E, McMurray HN, Williams G (2018) Quantifying the Role of Transition Metal Electrodeposition in the Cathodic Activation of Corroding Magnesium. *Journal of the Electrochemical Society* 165(5): C195–C205. <https://doi.org/10.1149/2.0251805jes>
8. Yang Y, Scenini F, Curioni M (2016) A study on magnesium corrosion by real-time imaging and electrochemical methods: relationship between local processes and hydrogen evolution. *Electrochimica Acta* 198: 174–184. <https://doi.org/10.1016/j.electacta.2016.03.043>
9. Gabbardo AD, Frankel GS (2019) Application of 2D Pit Growth Method to Mg Thin Films: Part I. Initiation, Growth and Repassivation. *Journal of The Electrochemical Society* 166(11): C3254–C3265. <https://doi.org/10.1149/2.0331911jes>
10. Gabbardo AD, Viswanathan G, Frankel GS (2019) Application of 2D Pit Growth Method to Mg Thin Films: Part II. Salt Film and Hydrogen Evolution. *Journal of The Electrochemical Society* 166(11): C3266–C3274. <https://doi.org/10.1149/2.0351911jes>
11. Gabbardo AD, Frankel GS (2019) Hydrogen evolution on bare Mg surfaces using the scratched electrode technique. *Corrosion Science*. <https://doi.org/10.1016/j.corsci.2019.108321>
12. Frankel GS (1990) The Growth of 2-D Pits in Thin-Film Aluminum. *Corrosion Science* 30(12): 1203–1218. [https://doi.org/10.1016/0010-938x\(90\)90199-f](https://doi.org/10.1016/0010-938x(90)90199-f)
13. Ryan MP, Laycock NJ, Isaacs HS, Newman RC (1999) Corrosion pits in thin films of stainless steel. *Journal of the Electrochemical Society* 146(1): 91–97. <https://doi.org/10.1149/1.1391569>
14. Fajardo S, Frankel GS (2015) Gravimetric Method for Hydrogen Evolution Measurements on Dissolving Magnesium. *Journal of the Electrochemical Society* 162(14): C693–C701. <https://doi.org/10.1149/2.0241514jes>