Postprint: Investigation of Corrosion Behavior of Pure Magnesium Using Generation/Collection and Feedback Modes of Scanning Electrochemical Microscopy

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Date: 2023-03-19T00:00:00+00:00

Abstract

Applying the generation/collection and feedback modes of scanning electrochemical microscopy, the microscale (point, line, area) hydrogen evolution behavior and the evolution of active sites during the corrosion process of pure Mg in NaCl and Na2SO4 solutions were investigated. The experimental results demonstrate that both cathodic and anodic polarization promote hydrogen evolution in both NaCl and Na2SO4 solutions, consistent with the negative difference effect observed in the corrosion process of pure Mg using traditional gas collection methods; however, the hydrogen evolution rate exhibits enhanced fluctuations at the microscale, displays instability, and is dependent on the degree of polarization. The hydrogen evolution rate increases with increasing NaCl concentration but decreases with increasing Na2SO4 concentration. Increased NaCl concentration, decreased pH, and anodic polarization facilitate the generation of active sites on the Mg surface.

Full Text

Preamble

Acta Metallurgica Sinica, Vol. 51, No. 5, May 2015, pp. 631-640

Corrosion Behavior of Pure Mg Based on Generation/Collection and Feedback Modes of Scanning Electrochemical Microscopy

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Supported by National Natural Science Foundation of China (Nos. 51171172 and 51131005) and Fundamental Research Funds for the Central Universities (No. 2015QNA3011)

Manuscript received: 2014-10-31, in revised form: 2015-02-06

Abstract

Traditional methods such as electrochemical impedance spectroscopy, polarization curves, and hydrogen collection have been the primary techniques for studying corrosion of Mg and its alloys. However, these methods only provide averaged information across the entire electrode surface. In this work, we employed the generation/collection and feedback modes of scanning electrochemical microscopy (SECM) to investigate hydrogen evolution and active sites at localized regions (point, line, and surface) on pure Mg during corrosion in NaCl and Na_2SO_4 solutions. The results demonstrate that both cathodic and anodic polarization promote hydrogen evolution in both NaCl and Na_2SO_4 solutions, consistent with the negative difference effect observed via classical hydrogen collection. However, SECM reveals that localized hydrogen evolution is non-uniform and unstable. The hydrogen evolution rate increases with increasing NaCl concentration but decreases with increasing Na_2SO_4 concentration. Higher NaCl concentration, anodic polarization, and lower pH values accelerate the formation of active sites on the pure Mg surface.

Keywords: SECM, pure Mg, hydrogen evolution, active site

Introduction

Magnesium is an extremely reactive metal with a standard equilibrium potential of -2.34 V for oxidation to Mg^{2+}, giving it a strong tendency to lose electrons. In natural environments, a passive film forms on Mg surfaces, primarily composed of $MgO/Mg(OH)_2$. However, this film is thin and non-dense, easily breaking down in solutions containing corrosive ions (such as Cl^-) or under anodic polarization, exposing the Mg substrate to continued corrosion.

The anodic reaction of Mg corrosion is $Mg \rightarrow Mg^{2+} + 2e^-$, while the cathodic reaction is primarily hydrogen evolution: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. Oxygen reduction ($O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$) may also occur. Due to Mg' s much more negative standard electrode potential compared to the hydrogen evolution reaction, hydrogen evolution proceeds rapidly. Although dissolved oxygen is present in solution, its reduction is diffusion-controlled and has limited influence on the overall cathodic behavior of Mg corrosion. Baril and Pébère studied Mg polarization behavior in 0.1 mol/L Na_2SO_4 using a rotating disk electrode and found that Mg' s cathodic polarization curves were independent of rotation speed, indicating that hydrogen evolution is the dominant cathodic reaction. Therefore, oxygen reduction can generally be neglected in Mg alloy corrosion studies.

A distinctive feature of Mg corrosion is the negative difference effect (NDE): during anodic polarization, the hydrogen evolution rate on Mg and its alloys increases with potential, contrary to conventional electrode kinetics. Various mechanisms have been proposed to explain NDE, including the Mg^+ mechanism, second-phase particle detachment, MgH_2 formation, passive film breakdown, external circuit electron consumption, and increased hydrogen exchange current density. However, each mechanism has limitations and cannot fully explain all experimental observations. For instance, the Mg^+ and external circuit electron consumption mechanisms lack direct experimental evidence; the second-phase particle mechanism cannot explain NDE in pure Mg; MgH_2 formation is actually a reduction reaction; the passive film mechanism struggles to explain NDE in acidic solutions; and the increased exchange current density mechanism addresses macroscopic phenomena but not microscopic mechanisms.

Classical inverted funnel displacement methods are commonly used to quantify hydrogen evolution during Mg corrosion, but suffer from several drawbacks: (1) they only provide average hydrogen production over time rather than real-time rates; (2) measurement errors are large or impossible when hydrogen production is low; (3) collection systems are prone to hydrogen leakage; and (4) temperature variations alter dissolved O_2 and N_2 concentrations, causing measurement errors as the solution releases or absorbs these gases.

To investigate localized hydrogen evolution behavior during Mg alloy corrosion, this work employs SECM generation/collection mode to quantitatively characterize hydrogen evolution and feedback mode to observe the generation and evolution of microscale active sites, clarifying the effects of polarization potential and anions on Mg corrosion.

1. Experimental Methods

High-purity Mg (99.98 wt% Mg) containing Al, Si, and Mn as main impurities was used. Pure Mg electrodes were cut to 10 mm × 10 mm × 2 mm, polished sequentially with 400, 600, and 800 grit SiC paper, then mirror-polished with 1 m Al_2O_3 paste, degreased with acetone, and dried. The SECM probe was a Pt ultramicroelectrode with 10 m diameter; the glass-to-Pt radius ratio was approximately 10. Probes were polished with 0.3 m Al_2O_3 paste and cleaned with deionized water and ultrasonication to remove surface adsorbates.

SECM measurements were performed using a CHI 920C system with a bipotentiostat (software version: CHI 13.11). A four-electrode configuration was employed: Pt probe and pure Mg as working electrodes, a 2 cm Pt wire as counter electrode, and Ag/AgCl (3 mol/L KCl, +0.194 V vs. SHE) as reference electrode. All potentials are reported relative to this reference unless otherwise specified.

The pure Mg specimen was mounted at the bottom of the SECM cell using Plexiglas, an O-ring, and screws, exposing 0.28 cm^2 to the solution. The probe-substrate distance was determined from approach curves in 0.001 mol/L ferrocenemethanol (FcMeOH) + 0.1 mol/L KNO_3 solution. When the probe current reached 70% of the limiting diffusion current, the distance was set to 10 m. After approach, the solution was replaced with the test solution (NaCl or Na_2SO_4). Following 10 min immersion, the probe potential was set to 0 V to collect the oxidation current of H_2. At this potential, H_2 oxidation is diffusion-controlled, so the probe current depends only on H_2 concentration, which reflects the hydrogen evolution rate on pure Mg. Faster hydrogen evolution yields higher H_2 concentration and larger probe current.

A typical H_2 collection result is shown in [Figure 1: see original paper] (Itip represents tip current for H_2 oxidation). During the first 200 s, the tip current decreases rapidly due to mismatched rates of H_2 generation and consumption and spatial distribution effects. After 200 s, the current stabilizes, indicating dynamic equilibrium. Data from 240–300 s were averaged to obtain the tip current value. Each condition was repeated three times, and results were averaged with error bars reported. For line scans: probe potential 0 V, scan distance 2000 m. For surface mapping: scan area 200 m × 200 m, scan speed 20 m/s.

The feedback mode was used to study active site evolution on pure Mg. During probe approach, the solution was 0.001 mol/L FcMeOH + 0.1 mol/L NaCl (0.5 mol/L NaCl when investigating Cl^- concentration effects). After approach, surface mapping was performed at immersion times of 3, 12, and 24 h (scan area 400 m × 400 m, speed 40 m/s) without changing the solution. The probe potential was 0.5 V, where FcMeOH oxidation is diffusion-controlled. When the probe passes over active sites, bare Mg reduces $FcMeOH^+$ back to FcMeOH, creating positive feedback. The tip current reflects passive film integrity and active site generation, evolution, and hydrogen evolution behavior. Schematics of both modes are shown in [Figure 2: see original paper].

2. Results

2.1 Generation/Collection Mode Studies of Hydrogen Evolution on Mg

Point collection experiments were conducted in 0.1 mol/L NaCl and 0.1 mol/L Na_2SO_4 solutions. Pure Mg was held at open circuit and polarized to -0.2, -0.1, 0.1, and 0.3 V relative to open circuit to examine polarization effects, with results shown in [Figure 3: see original paper]. In both solutions, hydrogen evolution was minimal at open circuit, while both anodic and cathodic polarization enhanced hydrogen evolution, demonstrating NDE in both Cl^--containing and Cl^--free solutions. The hydrogen evolution current was higher in Na_2SO_4 than in NaCl, indicating that low Cl^- concentration does not provide stronger catalytic effects for hydrogen evolution in short-term tests. The results confirm the feasibility of using SECM to study Mg corrosion, though large polarization causes significant data fluctuations due to spatial H_2 distribution variations and non-uniform surface hydrogen evolution.

Line scan results in 0.1 mol/L Na_2SO_4 at open circuit and -0.2 V and 0.1 V polarization are shown in [Figure 4a: see original paper], with corresponding surface maps in [FIGURE:4b-f]. Hydrogen distribution was non-uniform under all conditions, with increasing non-uniformity at larger polarization. Both anodic and cathodic polarization increased hydrogen evolution compared to open circuit, with numerous current peaks of varying magnitude. Similar results were obtained in NaCl solutions.

The effect of anion type and concentration on hydrogen evolution is shown in [Figure 5: see original paper]. The hydrogen evolution rate increased with NaCl concentration but decreased with Na_2SO_4 concentration. At low concentrations (0.1 and 0.3 mol/L), rates were higher in Na_2SO_4 than NaCl, while at high concentrations (0.5 and 1.0 mol/L), the opposite was observed. Line scan results at open circuit in various concentrations ([Figure 6: see original paper]) confirm these trends and the non-uniform hydrogen distribution.

2.2 Feedback Mode Studies of Active Sites on Pure Mg

[Figure 7: see original paper] shows the evolution of active sites on pure Mg during 24 h immersion in 0.1 and 0.5 mol/L NaCl solutions. The z-axis represents normalized tip current (tip current during mapping divided by steady-state current at infinite distance). In 0.1 mol/L NaCl ([FIGURE:7a-c]), no normalized currents >1 were observed, indicating no active sites. However, some regions showed normalized currents >0.7 (the expected ratio at 10 m distance), suggesting localized passive film rupture with non-fixed positions over time. Regions with normalized currents significantly <0.7 were also observed, likely due to H adsorption on Mg surfaces causing hydrogen embrittlement and blocking FcMeOH diffusion.

In 0.5 mol/L NaCl ([FIGURE:7d-f]), active sites (normalized current >1) appeared after 12 h but disappeared by 24 h, suggesting metastable pitting that repassivated during continued immersion. The overall tip current was higher in 0.5 mol/L NaCl, indicating greater passive film damage and more active sites at higher Cl^- concentration.

The effect of polarization on active site formation was investigated in 0.1 mol/L NaCl at +0.1 V and -0.2 V ([Figure 8: see original paper]). At +0.1 V, numerous active sites appeared at 12 and 24 h, though they were transient. At -0.2 V, no active sites formed within 24 h, demonstrating that anodic polarization promotes active site generation while cathodic polarization favors passive film stability.

Solution pH effects are shown in [Figure 9: see original paper]. In pH=2 NaCl solution, active sites formed at 3 and 12 h but disappeared by 24 h. At pH=11, no active sites were observed throughout 24 h. Acidic conditions favor active site formation, while alkaline conditions promote passive film growth.

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3. Discussion

3.1 Effects of Polarization Potential and Anions on Hydrogen Evolution

The results indicate that greater polarization increases hydrogen evolution and its spatial non-uniformity. At open circuit, hydrogen evolution occurs slowly. Cathodic polarization reduces activation energy, enabling faster hydrogen evolution over larger surface areas. Anodic polarization breaks down the passive film, creating black regions (primarily MgO, $Mg(OH)_2$, and impurity inclusions) with increased surface area that facilitate hydrogen evolution. Larger anodic polarization causes more severe film breakdown and greater hydrogen evolution.

Increasing Cl^- concentration accelerates hydrogen evolution, consistent with classical collection methods. Cl^- penetrates the passive film due to its small radius, reducing film density and reacting with $MgO/Mg(OH)_2$ to form soluble $MgCl_2$. Higher Cl^- concentrations cause more damage, creating additional active sites.

In contrast, increasing ${SO_4}^{2-}$ concentration decreases hydrogen evolution. Song et al. found that adding Na_2SO_4 to 1 mol/L NaOH gradually shifts the corrosion potential positive, indicating reduced corrosion tendency. The primary reason is that ${SO_4}^{2-}$ is not fully ionized (equilibrium constant = 0.01), reducing H^+ concentration and hindering hydrogen evolution. The ${HSO_4}^-/{SO_4}^{2-}$ equilibrium binds H^+, with this effect becoming more pronounced at higher concentrations.

At 0.5 and 1.0 mol/L, hydrogen evolution is faster in NaCl than Na_2SO_4 because Cl^- more easily penetrates and dissolves the passive film. At 0.1 and 0.3 mol/L, the opposite occurs likely because the 10 min immersion was insufficient for Cl^- to significantly damage the passive film. Previous studies have shown that in short immersion times (<1 h), ${SO_4}^{2-}$ can be more aggressive than Cl^-, and that Cl^- has a longer incubation period for passive film breakdown.

3.2 Evolution of Active Sites on Pure Mg and Influencing Factors

The transient nature of active sites observed in feedback mode indicates that Mg corrosion proceeds primarily through non-steady localized corrosion, with active sites repeatedly forming and repassivating. In 0.5 mol/L NaCl, active sites that formed at 12 h disappeared by 24 h, likely due to metastable pitting where local pH increases near active regions promote repassivation. Regions with normalized currents <0.7 may result from H adsorption on Mg surfaces, causing hydrogen embrittlement and blocking mediator diffusion.

Comparing results at different Cl^- concentrations shows that higher Cl^- concentrations enhance passive film damage and active site formation. Anodic polarization at +0.1 V produced numerous active sites, while cathodic polarization at -0.2 V prevented active site formation within 24 h. Anodic polarization increases the electric field across the passive film, enhancing adsorption of aggressive anions like Cl^- and facilitating film breakdown. Cathodic polarization generates OH^-, which promotes passive film formation and stability.

pH effects demonstrate that acidic conditions (pH=2) favor active site formation, while alkaline conditions (pH=11) promote passive film growth, consistent with literature showing that Mg corrosion potential shifts negative with decreasing pH and that corrosion is suppressed at $pH > 10.5$.

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4. Conclusions

1. Using SECM generation/collection mode, we quantitatively investigated hydrogen evolution on pure Mg under various polarization conditions and in different concentrations of NaCl and Na_2SO_4 solutions. Greater polarization increases hydrogen evolution rate and spatial non-uniformity. The hydrogen evolution rate increases with NaCl concentration but decreases with Na_2SO_4 concentration. At low concentrations, hydrogen evolution is faster in Na_2SO_4 than NaCl, while the opposite is true at high concentrations.
2. Using SECM feedback mode, we studied active site formation and evolution on pure Mg under different Cl^- concentrations, polarization levels, and pH values. Mg corrosion proceeds through non-steady localized corrosion with alternating generation and repassivation of active sites. Increased NaCl concentration, anodic polarization, and decreased pH damage the passive film and promote active site formation.

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