Electrochimica Acta 132 (2014) 277–283

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Evidence for enhanced catalytic activity of magnesium arising from anodic dissolution

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ARTICLE INFO

Article history:
Received 1 February 2014
Received in revised form 19 March 2014
Accepted 19 March 2014
Available online 2 April 2014

Keywords:
Magnesium
Corrosion
Polarization
Catalytic
Cathodic reaction.

ABSTRACT

The increasing rate of hydrogen evolving from magnesium (Mg) surfaces under anodic polarization is nowadays well documented and often termed the so-called “negative difference effect” (NDE). Recently, this behavior has been explained by a theory involving an increase in the cathodic exchange current density that arises from the anodic dissolution itself rather than a commonly-mentioned theory involving the formation of univalent Mg and its subsequent chemical reaction with water to produce hydrogen gas. In this work, a series of electrochemical tests were performed to provide evidence in support of the enhanced catalytic surface theory explaining the NDE. Potentiostatic, galvanostatic, and potentiodynamic polarization experiments using high purity Mg electrodes indicated substantial increases in the ability to support the rate of the cathodic reaction following discrete periods of anodic dissolution.

1. Introduction

Given that the corrosion of Mg and its alloys remains a practical barrier to wider industrial uptake, the fundamental understanding of Mg corrosion is of great interest. It is well understood that corrosion of Mg is rapid compared to all other structural metals, with the typical corrosion potentials of Mg alloys « -1 V_{SHE} in aqueous environments so that water reduction is the primary cathodic reaction. There is also no kinetic limitation of corrosion due to the inability of Mg to adequately passivate at neutral or acidic pH [2].

The behavior of anodically dissolving Mg has been studied since the late 19th century [3]. There has been extensive documentation of so-called parasitic hydrogen evolution [4] and the “negative difference effect” (NDE), which involves an increase in the rate of hydrogen evolution (HE) (which is nominally the product of the cathodic reaction, being water reduction, $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$) with increasing applied anodic potential [1,5].

A study by Petty in 1954 [6] suggested that Mg could be dissolved as unipositive (monovalent) magnesium, Mg^+, spawning a popular theory that hydrogen evolution (HE) on dissolving Mg surfaces arises from a secondary (chemical) reaction between Mg^+ and water to form excess hydrogen gas [7–11]. While the notion of unipositive Mg was debated subsequently to the work of Petty and perhaps definitively laid to rest [12–15], the unipositive Mg theory again became popularized in the past two decades, largely promoted in the reports of Atrens and co-workers [7–11,16]. In spite of the purported existence of unipositive Mg being quoted in the Mg corrosion literature [17–21], there has been significant recent works showing reproducible and independent evidence that Mg dissolution does not occur via the Mg^+ mechanism [1,5,22–31]. These recent works have employed a combination of methodologies including electrochemical experiments coupled with hydrogen collection [1,5,25], real-time video imaging [24], real time videography [25], electrochemical methods coupled with atomic emission spectroscopy [26] mass spectroscopy [27], scanning electrochemical microspcopy (SECM) [28] as well as the scanning vibrating electrode technique (SVET) [29–31]. All these studies have independently called into question the notion of unipositive Mg, and in turn any concepts related to the use of the unipositive Mg theory or its elaboration.

The recent work of Williams et al. [31] has demonstrated that persistent ‘cathodic’ sites exist on the surface of anodically polarized and dissolving Mg. This indicates that the production of hydrogen gas remains the product of a persistent local cathodic reaction, which was also independently validated by other groups very recently using different methods [5,25]. This concept was hypothesized in a study by Frankel et al. [1] who suggested a mechanism to account for HE on anodically polarized Mg described in terms of enhanced catalytic (i.e. cathodic) activity of the dissolving Mg surface. For example, if the influence of increasing anodic

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http://dx.doi.org/10.1016/j.electacta.2014.03.133

potential is compensated by an increase in catalytic activity, as embodied by the HE exchange current density, then the HE reaction will persist or even increase as the Mg potential is increased. Williams et al. revealed via the SVET method that regions of the Mg surface that have undergone dissolution are subsequently ‘cathodically activated’ and over time take the role of a cathode during the dissolution of Mg [31]. This indicates two important aspects, in that enhanced catalytic activity can occur, and that it is associated with prior dissolution.

To provide simple evidence for the enhanced catalytic activity of magnesium arising from anodic dissolution, without the need for specialized equipment, a number of straightforward electrochemical tests have been performed in this work. These tests represent a body of empirical support for the enhanced catalytic hypothesis to account for the NDE, which is considered timely given that researchers continue to promote the Mg^+ theory [16]. In addition, there remains significant interest in making better use of Mg as an anode in battery systems [32], but this requires a better understanding of Mg anode dissolution and the issues associated with self-discharge of Mg anodes, which has been noted to reduce charge capacity.

The work in this study is divided into three unique experiments, presented and discussed separately. The first experiment consists of the application of increasingly anodic galvanostatic steps to dissolve Mg. Between these increasingly anodic steps, the rate of the cathodic reaction at a fixed potential is measured for a short period immediately following anodic dissolution. The second experiment is that of simply measuring the cathodic reaction kinetics via potentiodynamic polarization of Mg prior to, and following, anodic dissolution. The third experiment involves measuring the current evolving from potentiostatically anodically polarized Mg, and monitoring the possibility of net current ‘polarity reversal’ as a result of sufficiently enhanced cathodic activity, such that the true partial current for the HE reaction (HER) exceeds the true dissolution rate.

2. Experimental

High purity Mg was supplied by Alfa-Aesar with the composition given in Table 1. Electrochemical testing was performed on surfaces ground to a 2400 grit finish under ethanol in all cases. For electrochemical testing, a VMP potentiostat (Bio-Logic ®) under the control of EC-lab software was used in conjunction with a flat cell comprising a Pt-mesh counter and saturated calomel electrode. All testing was carried out in air-exposed 0.1 M NaCl (pH 6). The conditions of each test, and the details of the related polarizing signals, are provided along with the corresponding reported results for clarity.

3. Results and Discussion

3.1. Experiment 1: Galvanostatic-Potentiostatic response of Mg

The typical potentiodynamic polarization response of pure Mg in 0.1 M NaCl is presented in Fig. 1. This experiment was performed in a quiescent electrolyte in a single upward scan at a rate of 1 mV/s following 10 min at open circuit. The figure shows an E_{corr} of ∼-1.6 V_{SCE} and low Tafel slope with no evidence of passivity. Repeat tests revealed that the E_{corr} varied over a range of approximately 50 mV, which is considered a reasonable scatter.

Table 1
Composition of high purity Mg. All compositions reported in wt. %. Compositions provided by QUANT (Quality Analysis and Testing Corporation), USA.

Element	Al	Fe	Cu	Zn	Mn	Ni	Zr	Mg
wt. %	0.02	0.008	0.003	0.03	<0.01	<0.001	<0.01	Bal.

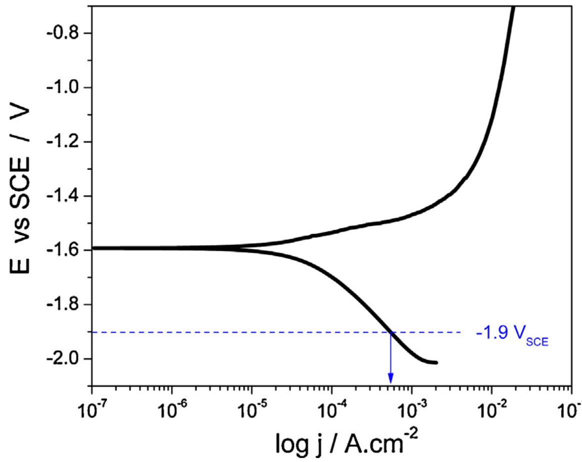

Fig. 1. Typical potentiodynamic polarization curve for high purity Mg in 0.1 M NaCl at 25 °C.The potential value of -1.9 V_{SCE} was selected as the value of potential to subsequently compare the cathodic current density following anodic dissolution as described in text.

To assess the variation in the cathodic current sustained on Mg in response to anodic dissolution, a custom electrochemical signal was scripted using EC-lab (BioLogic®). The signal involved the application of a fixed anodic galvanostatic treatment (to ensure anodic dissolution) for 2 min followed immediately by potentiostatic polarization at a cathodic potential. A potential value of -1.9 V_{SCE} was considered to be sufficiently displaced from E_{corr} on the linear portion of the curve on the E-log i plot such that polarization at this potential would allow determination of a dominant net cathodic reaction rate proximate to the true rate. This galvanostatic/potentiostatic treatment was repeated with increasing anodic current density (from 20 to 2500 $\mu A/cm^2$), always returning to the same cathodic potential (-1.9 V_{SCE}) for assessment and sequential comparison of cathodic current.

A typical set of raw data (applied and measured currents) is seen in Fig. 2. The annotations at the top of the figure indicate the controlled variable and its duration, with the measured variable therefore being obvious. Fig. 2 indicates that the measured cathodic current at -1.9 V_{SCE} increased (i.e. increasingly cathodic) with increasing prior anodic current and associated anodic charge. In other words, prior anodic dissolution efficiently enhanced the rate of the cathodic reaction.

In Fig. 3, data in Fig. 2 have been superimposed on the original polarization curve shown in Fig. 1. The potentials recorded as a result of the anodic galvanostatic signals (represented as filled circles) correspond closely to the anodic portion of the potentiodynamic polarization curve. However, the currents measured in response to the potentiostatic signal at -1.9 V_{SCE} (represented as diamonds) reveal an increasing trend dependent on the magnitude of the prior anodic dissolution current. These observations are in line with the theory proposing enhanced catalytic activity caused by anodic dissolution [1].

To further assess the notion of enhanced catalytic activity in response to greater anodic dissolution rates, the galvanostatic/potentiostatic approach was also used with higher current densities that were of similar magnitude to those applied in previous work [1], as shown in Fig. 4. The data in Fig. 4 reveal a similar trend to that seen in Fig. 2, with increasing cathodic current densities in response to an increased prior anodic current density. These data are summarized along with the previous data into an abridged plot shown in Fig. 5, which shows the cathodic current density for high purity Mg measured at the fixed potential of -1.9 V_{SCE}