

# Electrochemical Sensing of Dissolved Hydrogen in Aqueous Solutions as a Tool to Monitor Magnesium Alloy Corrosion

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## Abstract

Magnesium and its alloys have been the focus of the development of biodegradable metallic implant materials for years. Since water is reduced to form hydrogen gas during their corrosion, the amount and rate of hydrogen evolution, and therefore the dissolved hydrogen, could be used as an indicator to monitor and compare the corrosion. Here we report on a commercially available Clark-Type amperometric microsensor and a simple potentiometric sensor for hydrogen to monitor the corrosion of a magnesium alloy in aqueous solutions. The sensors were compared using rare-earth containing Mg alloy discs (Mg with 4% Y, 2% Nd, 0.5% Ga, 0.5% Dy) immersed in phosphate buffered saline (pH 7.4) and 3.5% NaCl.

**Keywords:** Biodegradable implants, Magnesium alloy, Electrochemical hydrogen sensing, Potentiometry, Amperometry

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Magnesium (Mg) and its alloys have been at the center of the development of biodegradable metallic implant materials for years [1]. Measuring the hydrogen (H<sub>2</sub>) gas evolution during corrosion of Mg and its alloys is a commonly used method to analyze the overall corrosion rate and crosscheck corrosion rates determined with other methods. It has been suggested that measuring the H<sub>2</sub> evolution is one of the more reliable parameters to consistently determine the corrosion rate of Mg alloys [2]. The H<sub>2</sub> evolution is generally measured by placing an eudiometer or a funnel and a burette filled with corrosion solution above the Mg material. As the evolving gas displaces the liquid, the volume of gas can be determined from the scale on the glass tube. This simple method does not need any type of calibration or expensive instrumentation [3]. Although this works well for bench top corrosion studies, it does not take dissolved gas into account nor is it very suitable when working with in vitro or in vivo systems [4]. Changes in temperature and pressure will also affect the volume of gas produced according to the Ideal Gas Law, which could make analysis and comparison of H<sub>2</sub> evolution data more complicated, especially when data recorded in different parts of the world (different elevations above sea level) are compared. Additionally, the collection of gas bubbles on the surface of the material and the sidewalls of the glassware could lower the overall gas volume measured. While there are many different

methods to measure H<sub>2</sub> gas including mass spectrometry [5] and gas chromatography [6], electrochemical sensors have the advantage that they are relatively inexpensive and can easily be miniaturized to fit small in vitro systems. They could potentially even be used in vivo since the formation of gas cavities after implantation of Mg alloys has repeatedly been reported in the literature [7]. Although no major complications due to gas cavities in animal tests have been reported and some studies even found that these cavities disappear as soon as one month after implantation (depending on the material and the area of implantation) [8], H<sub>2</sub> evolution needs to be monitored to ensure biocompatibility and to better understand the corrosion behavior of Mg alloys. The accumulation of larger volumes of gas could potentially lead to necrosis of the tissue or even gas embolism when released into the blood stream [9].

Electrochemical H<sub>2</sub> sensors play an important role in environmental monitoring to ensure safety during manufacturing processes that involve H<sub>2</sub> and in the development of fuel cells, just to name a few applications [10]. They have also been used in a few biological applications such as studying obesity [11] or inhibiting reactive oxygen species [12]. To the best of our knowledge, this is the first use of electrochemical H<sub>2</sub> sensors for monitoring the corrosion rate of a Mg alloy for the purpose of developing biodegradable metal implants. While there are various

techniques to determine  $H_2$ , the focus of this work is on amperometric and potentiometric  $H_2$  sensors.

A commonly used electrode material for these sensors is Pt, which is known to catalyze the dissociation of  $H_2$  gas [13] and is widely used as a catalyst for hydrogenation reactions. The most prominent example is the standard hydrogen electrode (SHE), which was used as a reference electrode to determine the standard reduction potentials of metals.  $H_2$  gas reacts at Pt according to the following equation:



Amperometric  $H_2$  sensors [10b,14] work by measuring a current between a working and a reference electrode while applying a constant potential. The resulting current is linearly proportional to the partial pressure of  $H_2$ , and thus the concentration of dissolved  $H_2$  in solution according to Faraday's Law. The commonly used Clark-Type amperometric  $H_2$  sensor uses a membrane that covers the working and reference electrodes to enhance selectivity by blocking interferences in the sample that would oxidize at the same potential. Thus the current is no longer limited by the kinetics of the electrode reaction, but rather by the rate of  $H_2$  diffusion across the membrane [10b]. Taking into account the limitation of the  $H_2$  diffusion process by the sensor design, the current depends on the area of the diffusion barrier ( $A$ ), the electric charge of an electron ( $q$ ), the diffusion coefficient of  $H_2$  ( $D$ ), the thickness of the diffusion barrier ( $x$ ) and the partial pressure of  $H_2$  ( $p_{H_2}$ ), as indicated by Equation 2 [10a].

$$I = 2qAD_{H_2} \frac{\partial p_{H_2}}{\partial x} \quad (2)$$

Amperometric sensors are widely used and well studied, but they can quickly be affected by rapid adsorption of proteins and cells (biofouling) on the electrode surface, as the current is dependent on the active surface area of the working electrode. The silicone membrane used in a Clark-Type sensor protects the Pt electrode from fouling. However, it could also be affected by adhesion of biomolecules or degradation.

Potentiometric  $H_2$  sensors function by measuring the open circuit potential between an indicator and a reference electrode and are independent of the surface area of the sensor [10a]. According to the Nernst equation (Equation 3), the measured potential is ideally proportional to the natural logarithm of the partial pressure of  $H_2$ .

$$E = E^\circ - \frac{RT}{nF} \ln \frac{p_{H_2}}{[H^+]^2} \quad (3)$$

However, it has been reported in the literature that the oxidation of  $H_2$  on Pt is complex and shows non-Nernstian behavior in the presence of  $O_2$  [15]. The most commonly used potentiometric  $H_2$  sensors are intended for

the detection of  $H_2$  in air, using solid-state electrolytes [10a]. However, there are some applications that require detection of dissolved  $H_2$  gas. The  $H_2$  washout technique, which has been used to measure regional blood flow [16] and to detect intravascular shunts [17], is one of the few applications where dissolved  $H_2$  is measured electrochemically and that comes close to the application proposed here.

One issue with the detection of dissolved  $H_2$  is its low solubility in aqueous solutions, which further decreases with increasing salinity and temperature [18]. Another issue is the high diffusivity and the low level of  $H_2$  in the atmosphere, which creates a large concentration gradient and thus drives the escape of dissolved  $H_2$  from solutions in open containers [13].

In this study, a commercially available Clark-Type amperometric microsensor and a simple and inexpensive potentiometric method were demonstrated that allows observation of the corrosion of biodegradable metallic implant materials in aqueous solution by monitoring the evolution of  $H_2$ . The commercial Clark-Type amperometric  $H_2$  microsensor also served as a standard to evaluate the response of the potentiometric sensor.

First, the  $H_2$  sensors were tested in phosphate buffered saline (PBS) at pH 7.4, because it is a commonly used buffer (Figure 1). This also represented a solution that has been used to study the corrosion of potential Mg based implant materials in solutions buffered at physiological pH [19]. Both sensors were immersed in PBS stirred at a constant rate. After recording a baseline for about 15 min, a rare-earth containing Mg alloy disc was added to the solution (indicated by the arrow). Gas bubbles were visibly ascending from the alloy disc and both sensors responded to the evolving  $H_2$  gas immediately after addition. Calibration curves were used to convert the current or potential to concentration in  $\mu M$  and % saturation (vide infra). After 1 h, both sensors had

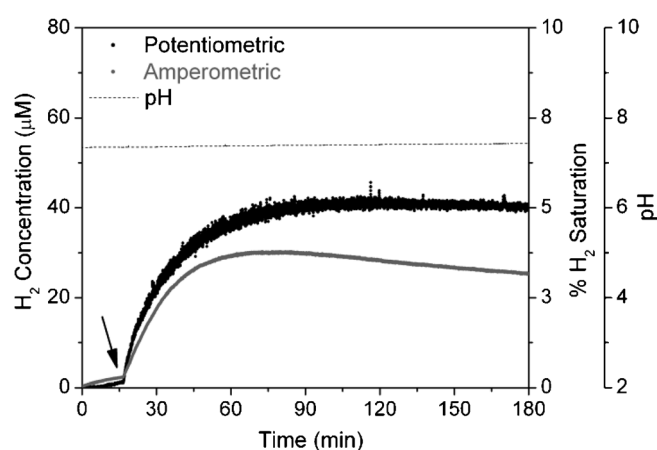


Fig. 1. Response of amperometric (grey symbols) and potentiometric (black symbols)  $H_2$  sensors and pH sensor (dashed line) during corrosion of Mg alloy containing rare-earth elements in PBS (pH 7.4) at room temperature. Arrow indicates addition of Mg alloy disc to solution.

reached stable values. The amperometric sensor indicated a  $\text{H}_2$  concentration of  $29 \mu\text{M}$  (4%  $\text{H}_2$  saturation) and the potentiometric sensor showed  $36 \mu\text{M}$  (5%  $\text{H}_2$  saturation). After 3 h the  $\text{H}_2$  concentration was  $25 \mu\text{M}$  (3%  $\text{H}_2$  saturation) and  $40 \mu\text{M}$  (5%  $\text{H}_2$  saturation) according to the amperometric and the potentiometric sensor, respectively. The pH stayed constant at 7.4 throughout the immersion in PBS indicating that the amount of  $\text{OH}^-$  generated did not exceed the PBS buffer capacity.

As a second solution, 3.5% NaCl was chosen (Figure 2) because it is a standard solution used to determine corrosion rates of metals and alloys [20]. The higher  $\text{Cl}^-$  concentration in the NaCl was expected to result in a higher corrosion rate and more  $\text{H}_2$  generation. A baseline was recorded for about 15 min, and then the Mg alloy was added to the solution (indicated by the arrow). The gas bubbles evolved faster and more vigorously than in PBS. About 1 h after addition of the Mg alloy disc, the amperometric microsensor measured  $50 \mu\text{M}$  (6%  $\text{H}_2$  saturation) and the potentiometric sensor was reading  $97 \mu\text{M}$  (12%  $\text{H}_2$  saturation). The concentration measured by the amperometric and potentiometric sensors after 3 h reached  $155 \mu\text{M}$  (20%  $\text{H}_2$  saturation) and  $151 \mu\text{M}$  (19%  $\text{H}_2$  saturation), respectively. These values show a higher  $\text{H}_2$  concentration in the 3.5% NaCl solution after 3 h than in PBS. They also indicated that the concentration measured with the potentiometric sensor was higher than that measured with the amperometric sensor. Neither sensor reached a steady signal after 3 h, therefore the concentration of dissolved  $\text{H}_2$  had not reached a steady state indicating that the rate of  $\text{H}_2$  evolution and the rate of  $\text{H}_2$  exchange with the atmosphere was the same. In addition to that, the pH increased from 7.1 to 9.6 after 1 h and reached a value of 10.2 after 3 h. The effect of pH change on the potentiometric  $\text{H}_2$  sensor response was determined in a separate experiment (data not shown) and showed that the sensor responds to an increase above pH 9. Therefore, we attempted to adjust for the influence of the pH change, which resulted in a calculated  $\text{H}_2$  concentration of far below that measured by the amperometric microsensor. This indicated a deviation from the Nernstian behavior. Although the potentiometric sensor shows a similar trend, which is the higher dissolution of the Mg alloy in 3.5% NaCl, the results are higher than those from the amperometric  $\text{H}_2$  microsensor. Therefore, it is recommended that the potentiometric sensor should be used in buffered solutions only, as any increase in pH above pH 9 would also affect the sensor response and a pH correction is difficult to calculate due to the deviation from the Nernst equation. Both sensor signals showed some noise that can be attributed to other people working close to the experimental setup. To prevent this type of noise, measurements should be carried out in a Faraday cage.

These results confirmed the expected slower corrosion rate of the Mg alloy in PBS. When comparing both signals, it was apparent that both sensors were responding to the continuous increase in dissolved  $\text{H}_2$  in the solution.

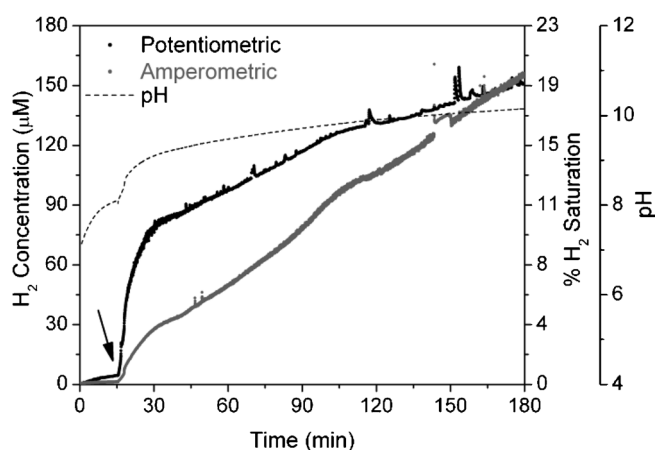


Fig. 2. Response of amperometric (grey symbols) and potentiometric (black symbols)  $\text{H}_2$  sensors and pH sensor (dashed line) during corrosion of Mg alloy containing rare-earth elements in 3.5% NaCl solution. Arrow indicates addition of Mg alloy disc to solution.

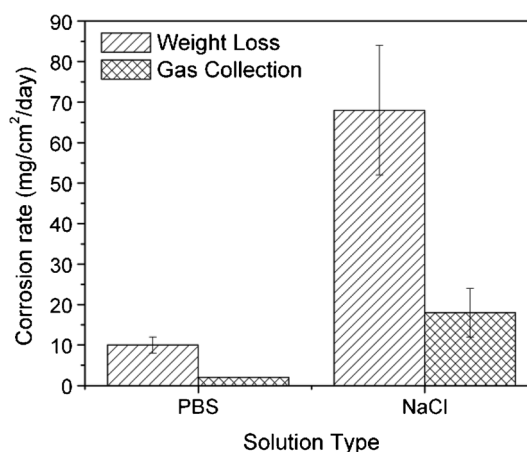


Fig. 3. Corrosion rates from weight loss ( $n=4$ ) and gas collection ( $n=2$ ) measurements during corrosion of the Mg alloy in PBS (pH 7.4) and 3.5% NaCl.

The amperometric sensor indicated that the corrosion was 6-times higher in NaCl than in PBS, while the potentiometric sensor showed a corrosion that was 4-times higher. This difference could be due to the influence of the pH change.

After the immersion test, the corrosion products were removed with chromic acid and the weight difference before the immersion test and after the corrosion product removal was used to calculate the corrosion rate ( $R$ ) according to Equation 4 [21]:

$$R = \frac{1.00 \times 10^4 W}{At} \quad (4)$$

where the weight loss ( $W$ ) in mg is divided by the exposed surface area ( $A$ ) in  $\text{cm}^2$  and the time ( $t$ ) of exposure in days.

To compare the sensor readings and the corrosion rate from the weight loss measurements, gas collection experiments were carried out as well. For these, a funnel and a burette filled with corrosion solution were put above the Mg alloy during the immersion test. The evolving gas displaced the liquid and the gas volume collected ( $V_{\text{H}_2}$ ) in the burette was converted to corrosion rate ( $R$ ) using Equation 5 [22]:

$$R = 2.279 V_{\text{H}_2} \quad (5)$$

The corrosion rates calculated from both methods (Figure 3) showed a similar trend, which was a lower corrosion rate in PBS than in 3.5% NaCl. This is consistent with the results from the  $\text{H}_2$  sensors. Although the corrosion rates calculated from weight loss were significantly higher than those calculated from gas collection, the corrosion rate determined from weight loss was 9-times higher in NaCl than in PBS, while the corrosion rate determined by gas collection was 7-times higher in NaCl. The difference in corrosion rate calculated with these two methods could be attributed to either excess material lost during the chromic acid treatment or gas bubbles collected on the surface of the Mg alloy and inside of the funnel.

After the sensors were shown to exhibit the capability to monitor  $\text{H}_2$  evolution in both media, we evaluated the calibration curves for both sensors. Calibration curves were recorded in PBS and 3.5% NaCl. The concentration of dissolved  $\text{H}_2$  was calculated using the Bunsen solubility coefficient  $\beta$ , which was reported to be 0.01759 mL  $\text{H}_2$  in 1 mL solution at 24 °C and 1 atm [18]. The Bunsen solubility coefficient  $\beta$  was converted to the Ostwald solubility coefficient  $\lambda$  using Equation 6 [23], where  $t$  is the temperature in degree Celsius:

$$\lambda = \beta (1 + 0.0367 t) \quad (6)$$

The dissolved volume given by the Ostwald solubility coefficient was then used to calculate the dissolved equilibrium  $\text{H}_2$  concentration with the Ideal Gas Law.

The calibration curves for the two sensors were different since the potential for the potentiometric sensor is logarithmically proportional to the partial pressure of  $\text{H}_2$ , while there is a linear relationship between the current and the  $\text{H}_2$  partial pressure for the amperometric microsensor. The amperometric microsensor (Figure 4a) showed the expected linear response and gave a slope of  $2.2 \pm 0.1 \text{ pA}/\mu\text{M}$  in PBS and  $1.8 \pm 0.1 \text{ pA}/\mu\text{M}$  in 3.5% NaCl with a regression coefficient of 0.996 and 0.991, respectively. However, over the course of this study the sensor showed some loss of sensitivity as the slope dropped to below  $1 \text{ pA}/\mu\text{M}$ .

The calibration curve for the potentiometric sensor (Figure 4b) did not show an overall linear correlation, but resembled a trend that is similar to the behavior described by Siebert and Bouchet, who proposed three different regions representing the local  $\text{H}_2$  concentrations

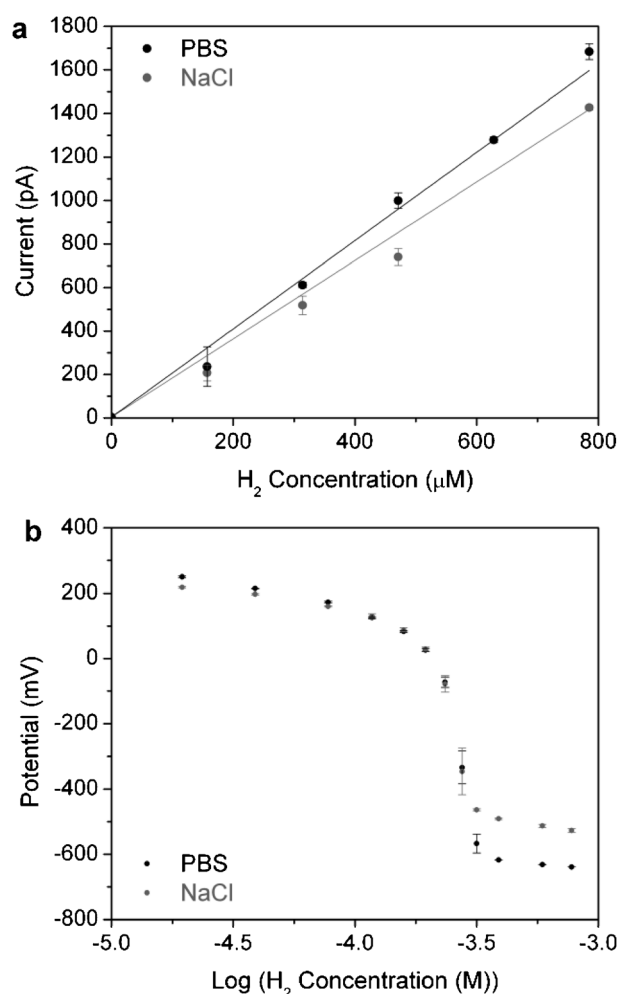


Fig. 4. Calibration of (a) the amperometric and (b) the potentiometric  $\text{H}_2$  sensors recorded in PBS (black symbols) and 3.5% NaCl (grey symbols).

for  $\text{H}_2$  detection in air [15a, 24]. This may be pertinent to the application described in this study as well. This again suggested a deviation from simple Nernstian behavior of a single redox couple and indicated that the response was due to a mixed potential, where  $\text{O}_2$  reduction and  $\text{H}_2$  oxidation reactions occurred simultaneously. The presence of water and/or other species adsorbed to the Pt may also influence the potential. We tried fitting the three regions individually depending on the concentration range of  $\text{H}_2$  as well as finding a non-linear least squares fit for the entire curve. However, neither one yielded any results that were comparable with those of the amperometric sensor. As an approximation the data points were fitted with a linear regression curve through the area of the calibration curve where the potential changes abruptly. While this is not an ideal fit, this method gives the best agreement with the amperometric sensor in estimating the dissolved  $\text{H}_2$  concentration or the %  $\text{H}_2$  saturation of the solution. This type of fitting was used to calculate the  $\text{H}_2$  concentration and the %  $\text{H}_2$  saturation during the immersion tests and the results are comparable to those

from the amperometric microsensor. Additionally, calibration curves were recorded before and after the immersion tests and we observed that the potential for low concentrations of  $H_2$  drops to lower values after longer exposure to  $H_2$ , which could indicate a change in species on the Pt electrode surface. The calibration curves recorded after immersion gave better correlation with the amperometric sensor in our study and for that reason calibration curves recorded after the immersion test should be used.

In this study, a simple and inexpensive potentiometric technique was used to measure  $H_2$  evolution in aqueous solutions, to monitor corrosion of rare-earth containing Mg alloy discs, and the results were compared to those obtained with a commercial amperometric  $H_2$  microsensor in Figures 1 and 2. The amperometric sensor performed very well for this application. Its main disadvantage was the steady loss of sensitivity over the duration of the project, which is a characteristic noted in the manufacturer's instructions. It was demonstrated that potentiometric sensing of  $H_2$  in aqueous solutions is possible and that this technique shows a response that is in reasonable agreement with the results from the commercial amperometric  $H_2$  microsensor. The measurements can be done on a standard potentiometer like a pH meter and do not require more expensive instrumentation that allows recording of pA currents. Furthermore, there is no difficult or costly preparation of the sensor involved nor does it have a membrane that could potentially be prone to degradation or biofouling when used in biological samples or cell culture systems. A simple Pt disc electrode would suffice as the indicator electrode and is not expected to be as readily affected by biofouling during the first 24 h [25]. This would also allow for easy miniaturization of the sensor to fit different cell culture systems. Although the Pt disc electrode could also respond to other electroactive species in solution, this issue might be overcome by keeping the concentration of other electroactive species, especially the pH, constant. However, this would need to be investigated for applications involving samples containing electroactive species. Also, any change in sensitivity of the Pt to  $H_2$  during long-term measurements would need to be further investigated. The main disadvantage of this sensor is the deviation from the Nernst equation and the complex calibration plot. Despite the above-mentioned limitations, this method allows the estimation of the %  $H_2$  saturation in solution as indicated by the comparison of both sensors during the immersion tests in this study. The sensor would be adequate for applications where a high level of accuracy is not required, but its low cost, simplicity and ease of miniaturization are paramount (e.g., in vitro monitoring). However, if a more accurate measurement is needed, the amperometric sensor should be used. In summary, agreement of results between corrosion rates in Figure 3 and measurements of dissolved  $H_2$  by both sensors also suggest that measurement of dissolved  $H_2$  can be used for comparing corrosion rates of Mg alloys.

### Experimental

Potentiometric  $H_2$  measurements were performed using a 1.6 mm diameter Pt disc electrode and a Ag/AgCl (3 M KCl) reference electrode (both from BASi, Lafayette, IN, USA). The Pt electrode was polished with 0.05  $\mu\text{m}$  Micro-Polish II deagglomerated alumina suspension (Buehler, Lake Bluff, IL, USA) before use. Amperometric  $H_2$  measurements were done using a  $H_2$  microsensor with a 50- $\mu\text{m}$  tip diameter (Unisense, Aarhus, Denmark) that was polarized at +800 mV for at least 1 h immediately before use. After a stable current in the low picoampere range was established, the amperometric microsensor was ready to be used. The potentiometric and amperometric measurements were recorded simultaneously with a four-channel multimeter (Unisense, Aarhus, Denmark), with the internal pre-amplifier range set to 1 mV/pA for the amperometric channel. Both sensors were calibrated by adding known amounts of  $H_2$  saturated corrosion solution to a known volume of corrosion solution (according to manufacturer recommendations [26]). The Bunsen solubility coefficient was used to calculate the concentration of the dissolved  $H_2$  [18], which was then divided by the dissolved equilibrium  $H_2$  concentration to calculate the %  $H_2$  saturation. The pH was monitored during each of the corrosion tests with an Accumet pH combination electrode (Fisher, Pittsburgh, PA) that was calibrated with standard pH buffers at pH 4, 7 and 10 (Fisher Scientific, Pittsburgh, PA).

Rare-earth containing Mg alloy discs (Mg with 4% Y, 2% Nd, 0.5% Ga, 0.5% Dy; 8.0 mm diameter  $\times$  1.5 mm thickness; permanent mold cast; machined and polished) provided by Norbert Hort (Helmholtz Center Geesthacht, Germany) were used. The corrosion of the Mg alloy discs was monitored in 250 mL PBS (pH 7.4) containing 137 mM NaCl, 2.7 mM KCl, 10 mM  $\text{Na}_2\text{HPO}_4$  and 2 mM  $\text{KH}_2\text{PO}_4$  (all from Fisher Scientific, Pittsburgh, PA) in deionized  $\text{H}_2\text{O}$  [27] and in 250 mL 3.5% NaCl (Fisher Scientific, Pittsburgh, PA) in deionized  $\text{H}_2\text{O}$ . The measurements were carried out in stirred solutions at 24 °C and normal atmosphere. After the immersion test, the corrosion products were removed by treating the Mg alloys discs with chromate solution containing 200 g/L  $\text{CrO}_3$ , 10 g/L  $\text{AgNO}_3$  and 20 g/L  $\text{Ba}(\text{NO}_3)_2$  in deionized  $\text{H}_2\text{O}$  for 5 min at room temperature according to ASTM standard G1-03 (2011) [28]. The weights of the Mg alloy samples were determined with an AE200 analytical balance (Mettler-Toledo, Columbus, OH) before the immersion test and after removal of the corrosion products. Gas collection was done in stirred solution with a funnel and 25-mL burette filled with corrosion solution placed over the alloy disc at 24 °C.

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