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Polarization measurements from a rotating disc electrode for characterization of magnesium corrosion

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ABSTRACT

Degradation of pure Mg is characterized by potentiodynamic polarization using a rotating disc electrode (RDE) where the Mg sample is placed. The rotation makes a fluid flow which removes dissolved Mg^{2+} from the Mg surface surrounding reducing the corrosion layer precipitation. This reduces the influence of corrosion products which accelerate the cathodic activity during anodic polarization. The results are in agreement with the enhanced catalytic surface theory. The use of the RDE gives highly reproducible results at higher rotation speeds than 1500 rpm and the scan rate does not have any influence on consecutive polarisations when higher than 5 mV/s.

1. Introduction

Magnesium alloys are promising materials for use in biomedicine and in light-weight structures. They can be used for biodegradable temporal implants due to their similar density and mechanical properties compared to cortical bone, due to their potential non-toxicity and biodegradability [1–5]. As the principal justification for choosing magnesium in biomedicine is biodegradability the characterization of that degradation is of particular interest.

However, Mg as a metal, has rather unpredictable corrosion properties. The alloying additions and impurities in the Mg alloys, every processing step and the testing method can lead to different corrosion properties. Immersion experiments give an overview of the corrosion properties of the Mg alloy in long term behavior, and electrochemical methods can be applied in order to get a fast comparison between different Mg alloys. Nevertheless, many results applying electrochemistry and immersion experiments aiming at biomedical applications can be found in literature, showing that these two methods do not lead to the same corrosion rate for the same material [6]. Thus, a better understanding of these measurements is needed.

It is known that Mg exhibits abnormal anodic polarization behavior because of the so called negative difference effect (NDE) [7–9]. For most metals, a potential polarity reversal from cathodic to anodic causes an acceleration of the anodic reaction and simultaneously a decrease of the cathodic hydrogen generation rate. However, for Mg, the hydrogen evolution rate actually increases when the applied potential becomes more anodic [10–12]. Thomas et al. summarized the theories which explain Mg degradation mechanisms and can also address the NDE [13]. Many authors use the monovalent Mg ion theory to explain the low corrosion rates determined by electrochemical techniques in comparison with immersion techniques [14–17]. However Samaniego et al. [18] recently demonstrated that the evidence for the Mg^{+} existence claimed by Petty et al., 60 years ago is not entirely valid [19]. This has led to many rejecting the Mg^{+} theory to explain the NDE in favor of the enhanced catalytic surface (ECS) theory [11,20–24]. ECS describes the creation of dark corrosion products on the surface of the corroding metal during anodic polarization which act as cathodes coupled with the surrounding anode, i.e., the uncovered Mg surface.

The rotating disc electrode (RDE), where the Mg working electrode is a disc in rotation, can reduce the corrosion product deposition on the sample surface. In this case, the fluid flow removes the dissolved Mg^{2+} ions from the surrounding of the Mg surface and this, in principle, reduces the formation of a corrosion layer which influences the polarization measurement. Moreover this is a better approach for characterization with potentiodynamic polarization (PDP) methods because with this hydrodynamic

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method the steady state is attained rather quickly [25–27]. Thus, the measurements can be made with high reproducibility. Bender et al. developed a polarization method which applies a RDE and after preliminary investigations, 2000 rpm was considered the most effective rotation speed [28]. However, there is no experimental proof of why 2000 rpm is an optimal value.

In summary, the purpose of this work is to determine the influence of testing parameters such as the rotation speed and the scan rate on the polarization measurements with RDE for magnesium degradation characterization in a medium which is used in biodegradable implant research. By minimizing the chances for the formation of a corrosion layer the intrinsic corrosion response of a particular magnesium alloy can be assessed. This information is of interest in the modelling of the degradation of a biometal in a particular medium in vitro but also under more realistic conditions in vivo. We will show also that very recently advanced concepts of the enhanced catalytic surface (ECS) theory can be usefully applied in the interpretation of our results.

2. Experimental methods

2.1. Materials and methods

Pure Mg samples were cast by permanent mould gravity casting at 680 °C in neutral atmosphere (Ar + SF_6), extruded at 300 °C from 110 mm diameter to 12 mm at a speed of 0.7 mm/s. Finally, samples were machined into discs (10 × 1.5 mm). This processing route was chosen to obtain a fine and homogeneous grain size (22.6 ± 5.2 μm). The measured density of the pure Mg was 1.74 g/cm^3 and the Vicker's hardness 43.8 ± 3.2 kg/mm^2 HV 0.3 kg. Table 1 shows the chemical composition of the pure Mg used in this work, determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Varian 720 ES).

2.2. Electrochemical experiments

PDP experiments were carried out with the rotating disc electrode as shown in Fig. 1 (EG&G model 616). The sample preparation and surface finishing was done firstly by grinding with 1000 and then 4000 grit SiC paper, and finally by polishing with a 3 μm diamond suspension. The samples were placed in a sealed PTFE clamp and connected electrically to the potentiostat (EG&G model 273). This clamp left the surface of the sample in a recess (see detail in Fig. 1) which will enable an air bubble to remain on the surface, when the RDE is immersed, interrupting the electrical contact and disturbing the signal during the first 10–20 s. The electrochemical cell consisted of a classical three-electrode cell with a rotating working electrode, Pt mesh as counter electrode and Ag/AgCl saturated with KCl as reference electrode, with a potential of +197 mV against standard hydrogen electrode. The working electrode had an exposed surface of 50 mm^2. When static conditions and a broad scan range of ±1.5 V vs OCP were applied the PTFE clamp was not used. In this case, samples were embedded in resin connected with a wire in order to position the sample upwards and let the H_2 bubbles get to the atmosphere. Otherwise the large H_2 accumulation in the clamped samples recess would disturb the measurement by reducing the sample-electrolyte contact area.

The solution mainly used, in this research was phosphate buffered saline (PBS 4417, Sigma–Aldrich), but also Hank's balanced salt solution (HBSS 14175, Life technologies) was used for comparison. PBS and HBSS are commonly used solutions in research on bioabsorbable Mg implant degradation [29–37]. The composition of these two electrolytes is summarized in Table 2. The main component of PBS is NaCl but it also includes sodium phosphate, dibasic anhydrous sodium phosphate, and potassium chloride. HBSS, in contrast to PBS, also includes sodium bicarbonate and D-glucose. The volume of electrolyte applied was 400 mL. The temperature for all experiments was controlled with a double walled beaker connected to a water bath (VWR model 1136-1D) at 37 ± 0.5 °C. The measured conductivity and pH of PBS at this temperature was 20.5 mS/cm and 7.47, respectively. During polarizations with different parameters the pH was stable within the range from 7.4 to 7.5. The measured conductivity of HBSS at 37 °C was 13.7 mS/cm, in the same range as PBS.

Table 1
Chemical composition (wt.ppm) of pure Mg.

Material	Fe	Mn	Si	Ni	Co	Cu	Al	Mg
Pure Mg	46	334	130	<10	<1	14	45	Balance

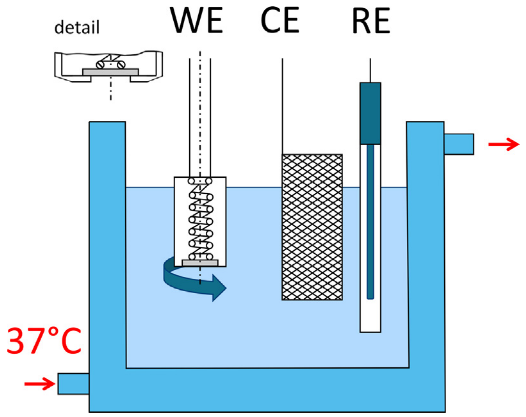

Fig. 1. Experimental setup with the rotating disc electrode as working electrode (WE), platinum mesh as counter electrode (CE) and Ag/AgCl saturated KCl as reference electrode (RE). The clamp detail shows the recess which is initially filled with air and disturbs the first seconds of an open circuit potential (OCP) measurement.

Table 2
Ionic composition of PBS and HBSS used for Mg biodegradation testing in mmol/L.

	Na^+	K^+	Cl^-	$HCO_3{}^-$	$H_2PO_4{}^-$	$HPO_4{}^{2-}$	D-Glucose
PBS	154.1	4.1	140.6	–	1.5	8.1	–
HBSS	142.8	5.8	143.3	4.2	0.44	0.34	5.6

In order to calculate the corrosion current density the Tafel extrapolation was applied, as recommended by Kirkland et al. [38]. This Tafel fit was performed over the voltage range: ±500 mV and ±300 mV around the corrosion potential to determine the anodic and the cathodic slopes. This analysis is carried out using the software of CorrView-3.3c (by Scribner Associates, Inc., USA).

Consecutive PDP experiments have been performed to get an overview of the rotation speed effect on the experiment. In this way the rotation speed at which the sample remains nominally unchanged can be determined.

Firstly, a sample with a freshly polished surface is clamped and immersed while it already is in rotation. The OCP measurement was started immediately after immersion. The OCP was measured for 120 s before all polarization tests in order to check the stability of the potential and to make sure that air bubbles do not perturb the measurement. The PDP started immediately after OCP and consecutive PDP have a time interval of 5 s approximately. The scanned potential range at 2000 rpm was ±500 mV around the OCP with a scan rate of 1 mV/s; and ±250 mV around the OCP with 2, 5, 10, 15 and 20 mV/s. The experiment termination was done by raising the sample while still rotating, and drying it as quickly as possible.