A novel approach to on-line measurement of gas evolution kinetics: Application to the negative difference effect of Mg in chloride solution

S. Lebouil a, A. Duboin b, F. Monti b, P. Tabeling b, P. Volovitch a, K. Ogle a,∗

a Chimie Paris Tech, 11 rue Pierre et Marie Curie, 75005 Paris, France
b Laboratoire Microfluidique, MEMS et Nanostructures, ESPCI-PSL, 10 rue Vauquelin, 75005 Paris, France

A R T I C L E   I N F O
Article history:
Received 11 April 2013
Received in revised form 16 July 2013
Accepted 16 July 2013
Available online 31 July 2013

Keywords:
Anodic dissolution
Magnesium
Negative difference effect
Kinetics
Gas volume

A B S T R A C T
Gas evolution at the surface of a dissolving material plays an important role in the overall dissolution process. In order to measure the kinetics of the gas evolution as a function of time (time resolved volumetry, TRV), a microfluidic system was constructed combined with high speed camera and a dedicated image analysis algorithm to measure the volume of gas as a function of time. This instrumental setup was added to an existing coupling between an electrochemical cell and a time resolved atomic emission spectroscopic detection. This article presents the instrumental development and first results concerning the spontaneous dissolution of zinc in a dilute HCl solution, the spontaneous dissolution of Mg in 0.01 M NaCl at open circuit potential and under an applied anodic potential. For Zn dissolution, an excellent correlation was obtained between the quantity of hydrogen measured and the quantity of zinc dissolved, with average accuracy of 5%. For Mg however, the anomalous production of hydrogen was observed attributed to the negative difference effect. A steady Mg dissolution was observed correlating with the electrochemical current for an n = 2 dissolution mechanism with superimposed bursts of Mg dissolution and hydrogen release corresponding to the anomalous dissolution mechanism.

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1. Introduction
The measurement of gas evolution has been critical to the understanding of material dissolution dating at least to the 18th century work of Joseph Black [1]. This is particularly true for systems that undergo what might be referred to as “abnormal” or “anomalous” hydrogen evolution. For example, hydrogen evolution in the anodic domain of magnesium dissolution is a constantly debated topic. Since the pioneering work of Petty et al. and Brouillet et al. [2,3] in the 50’s, there has been a huge controversy concerning the “negative difference effect” (NDE) which involves an increase in the rate of hydrogen production with increasing applied potential in contradiction with the conventional Tafel equation. Similarly, aluminum and aluminum alloys, when polarized in the cathodic direction, show an “anomalous” release of hydrogen [4] due to the cathodic corrosion of Al. Finally, oxygen evolution may also be critical in the process of aluminum anodization as this reaction might lead to pores in the alumina film formed at the surface, especially for Cu containing Al alloys. [5,6]

A goal of our research is to measure the kinetics of elementary dissolution phenomena as a function of time ideally for transient systems of technical interest that do not exhibit a clearly defined steady state. For example we have used a combination of downstream inductively coupled plasma atomic emission spectrometry with an electrochemical flow cell (AESEC or atomic emission spectrotelectrochemistry) to measure the rates of element release during dissolution reactions. In recent work, this technique has been applied to many different phenomena including the above-mentioned anodic dissolution of Mg [7], the cathodic corrosion of Al [8] and the anodization of Al alloys [9]. For many situations, it would be of interest to have a direct measurement of gas formation simultaneous with and on a similar time resolution as the “conventional” AESEC technique.

The problem is how to perform this measurement? Despite the remarkable progress of coupling spectroscopic, gravimetric and electrochemical techniques during the last few decades, the state of the art for the measurement of evolved hydrogen still essentially relies on the gas buret, surprisingly similar to the methodology of the pneumatic chemists of the 18th century. For example, in the study of the negative difference effect for Mg the buret system has been combined with electrochemical measurements [10–13] or combined with electrochemical and weight loss measurements [14] and spectrometric analysis [15,16]. However, only indirect comparisons were possible as hydrogen and elemental dissolution data are collected for a long period of time and only the total amount may be compared. More advanced methodology has been proposed to measure bubble detachment through electrochemical noise but with no correlation with the total volume [17].
In this work, we present for the first time an on-line volumetric method of monitoring gas evolution as a function of time that may be applied downstream from an electrochemical flow cell. This time resolved volumetry (TRV) was coupled with the AESEC technique so that elemental dissolution rates and gas formation may be measured simultaneously. This paper gives a description and validation of the experimental apparatus for three systems of technical interest: (1) the spontaneous dissolution of Zn in acid solution, permitting a fine correlation of Zn dissolution and hydrogen evolution, (2) the spontaneous dissolution of Mg in 0.01 M NaCl solution showing the limits of detectability, and (3) the negative difference effect observed during anodization of Mg in 0.01 M NaCl.

2. Experimental

2.1. Overview of instrumentation

The instrumentation is illustrated in the simplified schematic of Fig. 1. The reaction is carried out in a three electrode electrochemical flow cell (1). Three measurement devices are used to follow various parameters as a function of time: (A) potential and current are continuously controlled and/or monitored by a potentiostat (M273-PAR); (B) elemental dissolution rates are monitored with an optical emission inductively coupled plasma system (3); and the quantity of hydrogen gas (C) is monitored with a microfluidic cell coupled to a rapid video camera and a dedicated image analysis software.

2.2. Atomic emission spectroelectrochemistry (AESEC)

The reaction between the metal and the electrolyte was carried out in the AESEC electrochemical flow cell previously described [18,7,9]. The idea of AESEC is that a solid specimen with a flat surface is exposed to an aggressive electrolyte in a three electrode electrochemical flow cell. Dissolved species are transported in the electrolyte toward the ICP-OES in order to quantitatively measure their concentrations as a function of time. The instantaneous dissolution rate is related to the instantaneous downstream concentration of element, \( M \), \( C_M \), by:

\[
\nu_M = fC_M
\]

where \( f \) is the flow rate. The technique provides the electrochemical data set (total current \( j_e \) and potential \( E \)) as well as the elemental dissolution rates (\( \nu_M \)) as a function of time. With the present configuration, up to 30 elements as well as \( j_e \) and \( E \) may be measured simultaneously with millisecond time resolution. To facilitate comparison of the dissolution rate data and the electrochemical data, it is often of interest to express the dissolution rate as an equivalent current density by Faraday’s law, \( J_M = nF \nu_M \), or to express the electrochemical current density, \( j_e \), as an equivalent electron transfer rate: \( \nu_e = j_e/F \).

The electrolyte flow rate was approximately 1 cm\(^3\) min\(^{-1}\) and was measured to \( \pm 0.02\ \text{cm}^3\ \text{min}^{-1} \) prior to each experiment. The electrochemical current density, \( j_e \), and potential \( E \) are recorded with an EG&G M273A potentiostat/galvanostat using a Pt plate counter electrode and a Ag/AgCl reference electrode (200 mV vs SHE). With this configuration, high frequency impedance measurements using a Pt working electrode in the 0.01 M NaCl solution revealed an uncompensated resistance of 2.25 k\(\Omega\).

The inductively coupled plasma optical emission spectrometer (ICP-OES) used in this work was an Ultima 2 C from Horiba Jobin Yvon that combined a polychromator Paschen Runge dispersive system (50 cm focal length) equipped with an array of 30 phototubes for detecting preselected elements and a monochromator (1 m focal length) for a single arbitrary element when high spectral resolution was needed. Zn and Mg concentrations were determined from the emission intensity at 213.856 nm and 279.079 nm, respectively. The Y signal, at a wavelength of 371.029 nm was chosen as an internal standard. Calibration was performed using commercial standards (Précis) and conventional ICP-OES methods.
where $T$ is the electrolyte temperature in K and $R$ is the ideal gas constant. In this work, the hydrogen gas is assimilated to an ideal gas. Correction for non ideal gas behavior using the Beattie–Bridgman model [19] gave a difference of only 0.15% in terms of the recalculated moles of hydrogen and Eq. (2) was used for all subsequent work.

2.4. Microfluidic system fabrication

The microsystems were manufactured using classical soft photolithography methods [20]: a transparent mask was used to produce a mold with a silicon wafer covered by photosensitive resin SU 8. The wafer was placed in aluminum sheet in order to build a mold and 50 mL of polydimethylsiloxane (PDMS) was poured into this mold. It was placed under vacuum in order to remove the bubbles from the polymer and then heated to accelerate the curing. After the PDMS was cured and peeled off the mask, the systems were cut; inlets and outlets were pierced using a manual puncher (Harris Uni-Core, World Precision Instruments, Inc., Florida, USA) of 0.5 mm diameter. PDMS channels and microscope glass slides were exposed to an oxygen plasma during 45 s and then sealed together. The systems were used immediately after so the PDMS remained hydrophilic. Between experiments the hydrophilic property was maintained by injecting water in the systems prior to closing. The heights of each channel were characterized using a Stylus Dektak 6 M profilometer from Veeco, typical dimensions were: length = 2 cm, height = 200 μm (SD = 20 μm), width = 1 mm. The microsystem was back illuminated using a transmitted light source from Zeiss as shown in Fig. 2D.

2.5. Hydraulic parameters

During preliminary studies it was observed that under certain conditions of current or flow, the bubbles formed were very large and extended beyond the field of vision of the video microscope. In order to solve this problem it was necessary to break the large bubbles into a series of small bubbles of relatively homogenous shape and size. This was done using a “bubble breaker” microsystem with a T-junction geometry based on the work of Garstecki et al. [21]. The role of this T-junction is to cut the large bubbles into smaller bubbles that can be easily tracked and measured by the algorithm. It has no influence on smaller isolated bubbles. A schematic of a T-junction is shown in Fig. 1B where the carrier fluid is used to cut long bubbles into smaller bubbles. In the work described here the flow rate of the carrier electrolyte was set to 0.6 cm² min⁻¹ so that the total flow rate into the nebulizer of the spectrometer was 1.6 cm² min⁻¹. A non ionic surfactant, Tween 20 (TM) at 2% w/v, was added in order to avoid the coalescence of bubbles in the channel, in this work, the carrier fluid [21].

In addition to the possibility of measuring gas production as a function of time, this set up has a number of advantages for conventional ASEE confinement experiments. Firstly, it is possible to add an internal standard to the carrier fluid for spectroscopic detection without disturbing the reactivity of materials in the electrochemical cell since the carrier fluid does not pass through the cell. Yttrium at 10 mg/L was systematically added for all the presented experiments. Further the surfactant was shown to facilitate the flow in the nebulizer and the required wetting of the spray chamber inner walls.

2.6. Volume and pressure measurements

A high speed camera (PIKE 640 × 480 pixels) from R&D Vision mounted with a 25 mm focal length objective from TAMRON was placed above the system to continuously monitor the passing electrolyte in the channel as a function of time at 800 frames per
second. A dedicated algorithm was developed by R&D Vision so as to identify each bubble in the channel and measure the volume and velocity of each bubble as it passes through the channel. The algorithm detects a bubble when darker pixels form a continuous line as seen in the photograph of Fig. 1C. The “bubble object” has to exist on 5 successive frames in order to be taken into account. This has the benefit of automatically rejecting artifacts due to bubbles close to each other and eliminates the possibility that a single bubble will be counted twice. Likewise, a particle or foreign object carried by the electrolyte cannot be assimilated to a bubble as it has no clear pixels inside the line formed by the darker pixels.

The algorithm measured directly the 2D area of the bubble in the channel. To estimate the volume of a bubble, the algorithm classified the bubbles into three categories: (a) spherical, when the 2D diameter is smaller than the height of the channel (200 μm); (b) cylindrical, when the 2D diameter is between the height and the width of the channel, and (c), elliptical, when the shape shows a larger diameter in x than in y direction. From these categories, the corresponding volume was determined using the height of the channel.

With these conditions the smallest bubble that can be detected with this system would have to cover a minimum of 10 pixels. This would correspond to a diameter of approximately 72 μm. This is the sensitivity level in terms of detection and it gives a 2 nl bubble or 0.08 nmol of hydrogen for a pressure of 1 atm. By comparison, the bubble size in this work ranged from 0.0013 mm² (1.3 nl) to 1.5 mm². The upper size limit was of course due to the cutting up of much larger bubbles that originate in the cell.

A pressure sensor Honeywell S&C-24PCFA6D-15 PSID was used at the outlet of the channel in order to measure the pressure of the flow. The pressure drop due to the capillarity and the hydraulic resistance as predicted by the Laplace equation was determined to be negligible as compared to the atmospheric pressure. This sensor was calibrated using pressurized nitrogen between 0 and 150 mbar. The stability of the calibration was checked over three days at different room temperatures. Typical pressure inside the system is between 0.94 and 1.02 atm depending on the pump rates, the viscosity of the electrolytes and the nebulizer capacity.

2.7. Hydrogen solubility

Hydrogen is soluble in water and it might lead to a certain loss of hydrogen gas during the experiments, however, the experiment was designed to minimize this effect. During hydrogen formation at the metal surface, adsorbed H atoms recombine to form hydrogen gas which will dissolve into the electrolyte phase. Prior to saturation of course, no hydrogen gas will be detectable setting a fundamental limit to the measurement of cathodic hydrogen production. Once the electrolyte is locally saturated, the bubbles will grow and coalesce in a hydrogen saturated media on the metal surface. After detachment, bubbles are carried within seconds to the microsystem were they are brought in contact with the carrier fluid, creating a physical barrier that will minimize the dissolution of gas or the exchange between the surrounding water and the inside of the bubble. These exchanges are favored in systems such as the gas buret which has a free interface between the electrolyte and the atmosphere and which is maintained over long periods of time. This is why the vapor pressure is taken into account in these experiments [10] while it does not affect the measurement described here.

2.8. Materials

Zinc dissolution experiments were performed using specimens of a commercial hot dip galvanized steel of 7 μm Zn thickness, containing approximately 0.2% Al. The sample was cleaned with ethanol and ultrasound and otherwise used as received. The Mg dissolution experiments were performed using 99.9% Mg (Good Fellow) with a nominal composition of Al 70 ppm, Cu 20 ppm, Fe 280 ppm, Mn 170 ppm, Ni < 10 ppm, Si 50 ppm, Zn < 20 ppm. The sample was ground to 4000 grit with SiC disks with ethanol.

All solutions were prepared from analytical grade materials and deionized water of 18.2 MΩ cm (prepared using a Millipore™ system.) Electrolyte at 0.5 M HCl was prepared for the Zn dissolution experiments. A borate buffer of pH 9.4 composed of 0.04 M boric acid and 0.04 M KCl with final pH adjustment using NaOH. A 0.01 M NaCl solution was prepared for Mg spontaneous dissolution and constant potential experiments. All solutions were deaerated for at least 40 minutes with ultrapure argon (99.9995% from AirLiquide) and a partial pressure was maintained during the duration of the experiment.

3. Results and discussion

3.1. Spontaneous reactivity of zinc in 0.5 M HCl

The spontaneous dissolution of zinc in deaerated 0.5 M HCl was chosen as a simple test system to verify the accuracy of the method. The overall reaction is

$$\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2(g)$$

In an HCl solution, Zn²⁺ is highly soluble and the deaeration with argon ensures that hydrogen reduction is the only significant cathodic reaction. Therefore it is reasonable to expect an excellent correlation between the quantity of hydrogen gas generated and the quantity of Zn²⁺ dissolved. This hypothesis is tested in Fig. 3.

Fig. 3A shows the elemental dissolution rate of zinc and the open circuit potential as a function of time during the experiment. The dissolution profile is divided into two periods. At t = 0, the sample is exposed to the 0.5 M HCl solution. The Zn dissolution rate increases with time until approximately 830 s when the HCl solution is replaced with a pH = 9.4 borate buffer to stop the reaction.

![Fig. 3](image-url)
Prior to t = 0, the electrolyte bypasses the electrochemical flow cell which allows for a measurement of the background intensity and the detection limit in the HCl electrolyte. The dissolution rate of Zn increases steadily with time during the HCl exposure. Likewise the open circuit potential increases slightly but steadily from \(-1000 \text{ mV} \) to \(-975 \text{ mV}\). The sharp variations in dissolution rate are probably associated with sequential blocking and exposure of the metal surface to the electrolyte by the formation and breaking away of \(\text{H}_2\) bubbles. The largest bubbles, here indicated with a \(\text{**}^\text{**}\) do correlate with a sudden decrease in the zinc dissolution rate and the appearance of small spikes in the Y signal.

At approximately \(t = 830 \text{ s}\), the borate buffer replaced the HCl electrolyte so as to stop the reaction quickly. The buffer is used to rapidly neutralize residual HCl and bring the pH to a value close to the minimum in the Zn dissolution rate [22,23]. This results in a rapid decrease of the Zn dissolution rate and an increase in the open circuit potential to \(-950 \text{ mV}\) followed by a slow rise to \(-940 \text{ mV}\).

Fig. 3 B gives \(n_{\text{H}_2}\) in \(\mu\text{mol}\) determined from Eq. (2) as described previously. The data are presented on the same time scale as the dissolution profile of Fig. 2A. Also shown for comparison is \(n_{\text{Zn}}\) in \(\mu\text{mol}\) the integral of the \(v_{\text{Zn}}\) from Fig. 3A. This experiment shows the very good correlation between these two data sets which were measured with two total independent instruments. Reproducibility tests were carried out in order to verify this tendency and similar results were obtained: the highest deviation of HE to the zinc ions dissolution was 6.5%.

The form of the \(n_{\text{H}_2}\) vs time curve shows a staircase structure. Each step corresponds to a single bubble emerging from the flow cell which is then broken down into a large number of smaller bubbles in the microchannel, giving rise to the series of points during the step occurring nearly simultaneously on the time scale of Fig. 3B. There is slight off set in time for hydrogen evolution compared to zinc dissolution which may be interpreted as the time needed for the bubbles to grow at the surface, coalesce and become large enough to detach.

### 3.2. Spontaneous reactivity of Mg in deaerated 0.01 M NaCl

Fig. 4 shows the spontaneous reaction of Mg with deaerated 0.01 M NaCl. In contrast to the reaction of Zn with HCl, this electrolyte is very weakly aggressive and the dissolution of Mg is very slow. The reaction rate passes through an early maximum of \(0.36 \text{nmol s}^{-1}\) coincident with a minimum potential of \(-1840 \text{ mV}\). The potential then rises to around \(-1650 \text{ mV}\) as the Mg dissolution rate decreases to a near steady state of \(0.08 \text{nmol s}^{-1}\) (0.03 mA cm\(^{-2}\)). Hydrogen evolution is very small and in fact only four bubbles were actually detected and then only after 1250 s. This delay may be interpreted as the time needed for the local environment at the metal/electrolyte interface to become saturated with hydrogen, the bubbles to nucleate, grow and coalesce on the surface, and then to break from the surface.

### 3.3. The negative difference effect for the dissolution of Mg

Fig. 5A shows the dissolution profile \((v_\text{Mg} = j_\text{Mg}/F\) and \(v_\text{Mg})\) for 99.9% Mg at an applied potential of 0.0 V vs (Ag/AgCl). (Note that this value of potential has no thermodynamic relevance because of the high ohmic resistance of the electrolyte. Measurement of the uncompensated ohmic resistance in the cell from high frequency impedance spectroscopy using a Pt working electrode, yielded a value of 2.25 kΩ. With \(j_\text{Mg}\) in the 1 mA range, as indicated in Fig. 5, this would suggest that essentially the entire applied potential drop is due to ohmic resistance in solution.) The potential was applied immediately on contact of the electrolyte with the Mg. Consistent with our previous experimental results [7], the dissolution rate is
very nearly identical to that predicted by Faraday’s law assuming $n = 2$ as indicated by the good agreement between $v_{\text{Mg}}$ and $v_e$. However significant pulses of Mg dissolution are observed periodically becoming more frequent as the reaction progresses. The Y signal remains nearly constant throughout this period implying that these perturbations are due to the reaction at the Mg surface rather than perturbations in the electrolyte flow or the nebulizer. This conclusion is confirmed by the frequent (but not consistent) correlation between the pulses in $v_{\text{Mg}}$ and sudden step increases in $v_e$ in the later stages of the reaction.

Fig. 5B shows $n_{\text{H}_2}$ vs time compared with the integrals of $n_e$ and $2n_{\text{Mg}}$. The negative difference effect is clearly illustrated in the later stages of the reaction by the fact that $2n_{\text{Mg}} > n_e$ and the observation of significant hydrogen gas shown in Fig. 4B. Further, hydrogen gas evolution is very slow during the early stages of this reaction but increases markedly during the later stages correlating well with the difference $\Delta = 2n_{\text{H}_2} - n_e$. A moderate HE was already observed in our previous work [7] for anodic pulses applied during 240 s. In the present work the time duration of the experiment is significantly longer (1800 s).

It is also observed that $2n_{\text{H}_2}$ is significantly larger than $\Delta$ suggesting that some of the oxidized Mg remains on the surface as insoluble hydroxides or oxides. Indeed it is well known that the oxidized magnesium forms a partially protective film composed of magnesium hydroxide due to the alkalinization of the surface because of water reduction as discussed by Williams and McMurray [24] based upon spatially resolved measurements of electrochemical activity. Our time resolved results suggest that Mg dissolution occurs in two unique mechanisms, one driven by the anodic polarization with a two electron exchange:

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \tag{4}
\]

and a second mechanism involving simultaneous hydrogen formation and soluble and insoluble Mg$^{2+}$ which increases in intensity with time. The overall reaction would appear as:

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow x\text{Mg}^{2+} + (1-x)\text{Mg(OH)}_2 + \text{H}_2(g) + 2x\text{OH}^- \tag{5}
\]

were Mg(OH)$_2$ is assumed as the insoluble form of Mg$^{2+}$ in these experiments. Both reaction (4) and (5) involve the dissolution of Mg as Mg$^{2+}$; however reaction (5) is kinetically distinct from reaction (4). From the data in Fig. 4, it is clear that the NDE mechanism (reaction (5)) producing soluble Mg$^{2+}$ occurs in short bursts while the electrochemically driven reaction (4) is uniform in time. Following previous investigations it is reasonable to suppose that the two reactions are separated in space on the sample surface as well. One possibility, following the conclusions of Baril et al. [25] is that the NDE mechanism, reaction (5), occurs on the oxide/hydroxide film free surface while reaction (4) occurs across the film.

A stoichiometric analysis of (4) and (5) gives:

\[
2n_{\text{Mg(OH)}_2} + 2n_{\text{Mg}} = n_e + 2n_{\text{H}_2} \tag{6}
\]

and from Fig. 5 we determine, $x = \Delta / 2n_{\text{H}_2} = 0.16$. At the end of the experiment, analysis of Fig. 5 yields $2n_{\text{Mg(OH)}_2} = 11.5 \mu$mol $(1.3 \times 10^{-3} \text{ g cm}^{-2})$. Assuming a uniform precipitation this would correspond to a relatively thick film of about 6 µm assuming an average density for Mg(OH)$_2$ of 2.3446 g/cm$^2$. A more complete series of experiments has been conducted and will be presented later so as to refine the mechanistic model of the negative difference effect.

4. Conclusions

In this article we have presented the development and use of a time resolved imaging technique to quantitatively measure gas evolution during the reaction of a solid material with an electrolyte. Gas bubbles are carried by the flowing electrolyte from the electrochemical flow cell to an ICP-OES spectrometer passing through a rectangular channel where they are continuously filmed at 800 frames per second. A microfluidic technology is used to split the larger bubbles into components of similar size and geometry and to control the solution composition to favor a specific size of the bubbles. A specially designed image analysis software is then used to identify each individual bubble, measure its volume, and record the time of its passage. In this way the volume of hydrogen evolving from the reaction of metals with aggressive electrolytes could be measured as a function of time. The minimum detectable volume was approximately 0.0014 mm$^3$ corresponding to about 0.08 nmol H$_2$.

The use of the system was demonstrated for three systems of technical interest: (1) the dissolution of Zn in an acid electrolyte; (2) the spontaneous dissolution of Mg in a dilute, neutral NaCl solution; (3) a measurement of the negative difference effect during the anodization of Mg.

During the dissolution of Zn in an acidic electrolyte, it was found that hydrogen evolution followed zinc dissolution closely as expected for $\text{Zn} + 2\text{H}^- \rightarrow \text{Zn}^{2+} + \text{H}_2(g)$ with only a slight offset in time between the two data sets which is explained by the time required for transfer of the electrolyte from the channel to the spectrometer. Overall an excellent quantification was obtained with no more than 6% variation between the hydrogen gas and dissolved zinc on a mole to mole basis. During the very early stages of the reaction, very small hydrogen bubbles were formed which became significantly larger as the dissolution rate increased.

The spontaneous corrosion of Mg in 0.01 M NaCl solution occurs very at a very low rate. In fact only four bubbles of hydrogen were measured and these of very small size and only late in the experiment. The amount of hydrogen produced was significantly less than the amount of Mg dissolved, no doubt due to the necessity of obtaining a critical hydrogen formation rate to ensure local electrolyte saturation with hydrogen and bubble detachment.

For Mg in 0.01 M NaCl with an imposed anodic potential, a very rapid dissolution was observed coupled with significant hydrogen production during the later stages of the reaction, consistent with the negative difference effect. In fact two mechanisms appear to be operative: an electrochemically driven reaction which is relatively stable with time showing good correlation between the Mg dissolution rate and the total current, assuming $n = 2$, and a series of intense pulses of dissolution which do not correlate with the electrochemical current. A stoichiometric analysis of total electrical charge, hydrogen production and dissolved Mg indicate that a significant quantity of oxidized Mg remains insoluble no doubt in the form of a surface film. A more complete series of experiments has been conducted and will be presented later so as to refine the mechanistic model of the negative difference effect.

Acknowledgments

The authors would like to thank Nicolas Savoie of R&D Vision, SA for the algorithm development.

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