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## Development of Mg<sup>2+</sup> Ion-Selective Microelectrodes for Potentiometric Scanning Electrochemical Microscopy Monitoring of Galvanic Corrosion Processes

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The fabrication of a solid-contact, micropipette-based magnesium ion-selective micro-tipped electrode (ISME) suitable for scanning electrochemical microscopy is reported and compared against a conventional micro-tipped ISME having a conventional aqueous internal reference electrode. Measurements showed that the solid-contact ISME had a lower internal resistance and a faster response time than the one with a liquid-contact. These advantages increased the spatial distribution and improved 2D images depicting concentration distributions of Mg<sup>2+</sup>. The ability of the microelectrode to image local ionic concentration has been tested over magnesium surfaces freely corroding or galvanically coupled to iron in aqueous chloride-containing solution. Scans of magnesium ion distribution, in the absence of corrosion currents, were also made over a micro-pipette source containing a concentrated magnesium chloride gel as a source of Mg<sup>2+</sup> and over a current source in the absence of Mg<sup>2+</sup>. From these measurements it was concluded that the potentiometric measurements over corroding surfaces were dominated by the changes in Mg<sup>2+</sup> distributions with small electric potential contributions due to corrosion current.

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Magnesium and its alloys have a major potential for use in many industrial sectors, particularly in automotive, aerospace and biomaterials industries, because of their high strength to weight ratio. Unfortunately, the resistance of magnesium and its alloys against corrosion in aqueous media is poor,<sup>1-4</sup> thus requiring the development of improved corrosion-resistant alloys, inhibitor and protective coatings. Currently, understanding the characteristics of metal dissolution and passivity for these materials remains a major challenge, for conflicting ideas and results have been presented.<sup>5-10</sup> Oxide films formed on magnesium are less stable than the passive films formed on industrial metals and alloys owing to the low Pilling-Bedworth-ratio of Mg(OH)<sub>2</sub>,<sup>11</sup> leading to pitting and general corrosion.<sup>12</sup> Indeed, Song and co-workers<sup>13,14</sup> suggested that corrosion of magnesium and its alloys is initiated from free-film region where the pitting corrosion is the main corrosion form. Additionally, these materials exhibit the behavior that anodic polarization results in increased hydrogen production when they are exposed to chloride-containing electrolytes similar to what is observed during pitting of aluminum.<sup>15</sup> To account for this so-called “Negative Difference Effect,”<sup>3,16,17</sup> it has been proposed that the poorly protective film developed on the surface of magnesium involves the formation of intermediate magnesium(I) species,<sup>7,18-21</sup> which directly react with water leading to local alkalization and hydrogen gas evolution.<sup>20</sup> Though evidences for such a mechanism have been presented from the use of a variety of techniques,<sup>20,22,23</sup> recent contributions claim that catalytic activation of the cathodic reaction can be induced by the anodic dissolution reaction,<sup>24-27</sup> that is, Mg dissolves with a stoichiometry close to n = 2, and these reactions are highly localized.

Chemical imaging of reactive surfaces with high spatial resolution has become available with the introduction of scanning electrochemical microscopy (SECM). In fact, this technique has become a powerful tool in the study of a wide range of corrosion processes.<sup>28-30</sup> Despite the success of SECM in corrosion science, the investigation of dissolution processes in a number of technologically-relevant metals such as magnesium, aluminum and zinc, has not been monitored with the SECM using conventional amperometric microdisks due to their very

negative redox potentials. The use of noble metal tips coated by metals that present wider stability potential ranges for water have allowed more negative potentials to be reached,<sup>31</sup> still there are applications beyond those attained in this way. An alternate approach is the use of microsized ion-selective pipette electrodes as measuring tips because they provide the selectivity in chemical imaging,<sup>32</sup> which is desirable to investigate the different stages of corrosion processes occurring in micrometric and submicrometric dimensions. As a result, scanning electrochemical microscopy will find an even wider application in materials science and corrosion technology. Unfortunately, ion-selective micropipette electrodes (ISME) are rather fragile tools, and operation lifetime of these probes is seldom longer than a few days. Mechanical contact or electrical shock easily can damage them. Furthermore, the electrical resistances of these “conventional” ion-selective micropipettes are high necessitating special electric shielding and a very slow scanning rate. This often hinders their applicability to corroding systems.

An improved ISME performance has been found with electrodes of specially prepared carbon fiber that could be placed close to the orifice of the micropipette. The internal contact potential remains constant by applying a doped, electrochemically-prepared conductive polymer coating on the carbon fiber surface based from 3,4-ethylenedioxythiophene (EDOT),<sup>33</sup> thus accounting for reversibility. The life times of these new micropipettes were found surprisingly long; many performed well many months after their preparation. Application include an ammonium and a potassium ISME.<sup>33,34</sup> More recently, we constructed a zinc(II) ion-selective microelectrode which for the first time allowed local zinc ion concentrations during the galvanic corrosion of a Fe/Zn couple to be imaged.<sup>35</sup> High spatial resolution was further developed employing a combined amperometric/potentiometric operation methodology for SECM<sup>36</sup> by using materials that exhibit a dual-function in different potential ranges as ultramicroelectrode tips.<sup>37,38</sup> This is the case with antimony as its open circuit potential responds to the pH of the environment.<sup>39</sup>

Once the capability of these micropipette measuring tips in corrosion studies was demonstrated, our investigation focused on the fabrication of an Mg<sup>2+</sup> ion-selective microelectrode. The first neutral carrier-based ion-selective electrodes for magnesium reported in the scientific literature were developed

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to monitor the hardness of water of different origins.<sup>40–42</sup> From those studies it was concluded that the best selectivity against sodium ion was achieved using amidic-based ionophores. Indeed, an amidic ionophore, octamethylenbis(N,N''-octamethylene-bis(N'-heptyl-N'-methyl-methylmalonamide) (ETH 5214), was used to build a liquid-contact magnesium ISME that was able to measure  $Mg^{2+}$  ion distributions over a Mg-based alloy in aqueous chloride-containing solution.<sup>43,44</sup> Another amidic ionophore, bis-N,N-dicyclohexyl-malonamide,<sup>45</sup> was employed for the fabrication of a  $Mg^{2+}$ -ion selective electrode tip for SECM for the first time.<sup>46</sup> In that work, a liquid-contact ion-selective micropipette electrode configuration was employed. Spatially-resolved data showing a major production of hydroxyl anions at the cathodic sites as result of oxygen reduction and local acidification in the vicinity of magnesium dissolution sites were obtained. Yet, the rather slow response times of the ion-selective microelectrode tips employed in the work severely limited the mapping capabilities of the technique and only selected one-dimensional line scans could be recorded at that time.<sup>46</sup>

In this work, the fabrication and characterization of a new, faster, robust, solid-contact, micropipette-based magnesium ion-selective electrode suitable for use as an ISME is described. The electrodes were constructed using a carbon fiber coated by a conductive polymer as internal contact. These electrodes had a higher resolution with lower resistance. Conventional micropipette  $Mg^{2+}$  selective electrodes were also fabricated for the sake of comparison. Our results on the galvanic corrosion of magnesium connected to iron in chloride solutions demonstrate that this  $Mg^{2+}$  ISME with carbon fiber internal electrodes can be employed for corrosion studies.

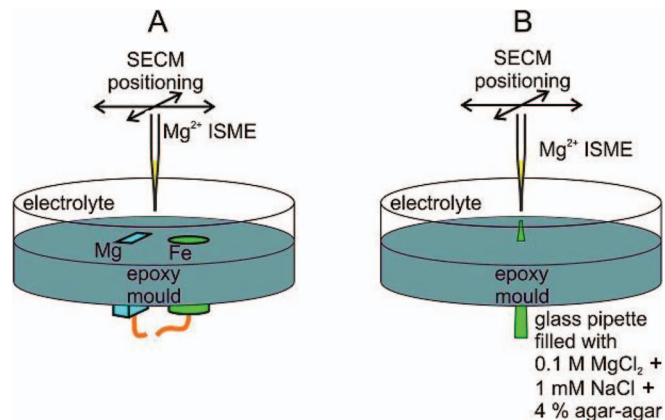
## Experimental

**Reagents and samples.**— Selectophore grade poly(vinyl chloride) (PVC), ortho-nitrophenyl octyl ether (o-NPOE), potassium tetrakis(4-chlorophenyl)-borate (PTCB), tetrahydrofuran (THF), and tris(hydroxymethyl)aminomethane (TRIS) were supplied by Fluka (Buchs, Switzerland). Carbon fiber of 33  $\mu m$  diameter was provided by Specialty Materials (Lowell, MA, USA) as a generous gift. The carbon fibers were coated with a conductive polymer. Thus, 3,4-ethylenedioxythiophene (EDOT) (ref CH04M006) monomer obtained from Starck (Golar, Germany) was electropolymerized in 1-butyl-3-methyl-imidazoliumhexafluorophosphate ( $BMIM^+ PF_6^-$ ) ionic liquid solvent from Solvent Innovation (Cologne, Germany). Analytical grade magnesium chloride hexahydrate Merck (Darmstadt, Germany). Chemicals were used as received. Aqueous solutions were prepared using ultra-pure deionized water.

A magnesium/iron galvanic couple was used as model corroding system. Iron wire 760  $\mu m$  diameter and magnesium ribbon with 200  $\mu m \times 800 \mu m$  cross section were employed. The two metals were mounted in an *Epofix* resin disk (Struers, Ballerup, Denmark). Only their cross sections were exposed on the front side of the disk-shaped resin mounting (dia. 3 cm), and they extended about 15 mm at the rear of the mount for electric connection. The front side of the mounts was polished with silicon carbide paper down to 4000 grit. The surface was degreased with acetone, abundantly rinsed with ultra-pure deionized water and allowed to dry in air. When tested, the front side of the mount faced upwards surrounded laterally by a small section of PVC plastic tubing creating a small container holding 5 mL of 1 mM NaCl test electrolyte solution, Figure 1A and a 3 M KCl Ag/AgCl reference electrode.

Detection of  $Mg^{2+}$  in a solution free of electric currents was conducted in a validation cell, Figure 1B of similar construction to 1A. The cell held a small embedded glass micropipette with a diameter of 200  $\mu m$  about 10 mm long. The micropipette was filled with 0.1 M  $MgCl_2 + 1$  mM NaCl contained in 4% agar-agar gel to establish a stable  $Mg^{2+}$  diffusion source and prevent the solution incursions when using only the  $MgCl_2$  in a liquid aqueous solution.

The effect on the performance of the ion selective microelectrodes due to electric fields with currents in the electrolyte was explored using two different arrangements with electrodes acting as point current



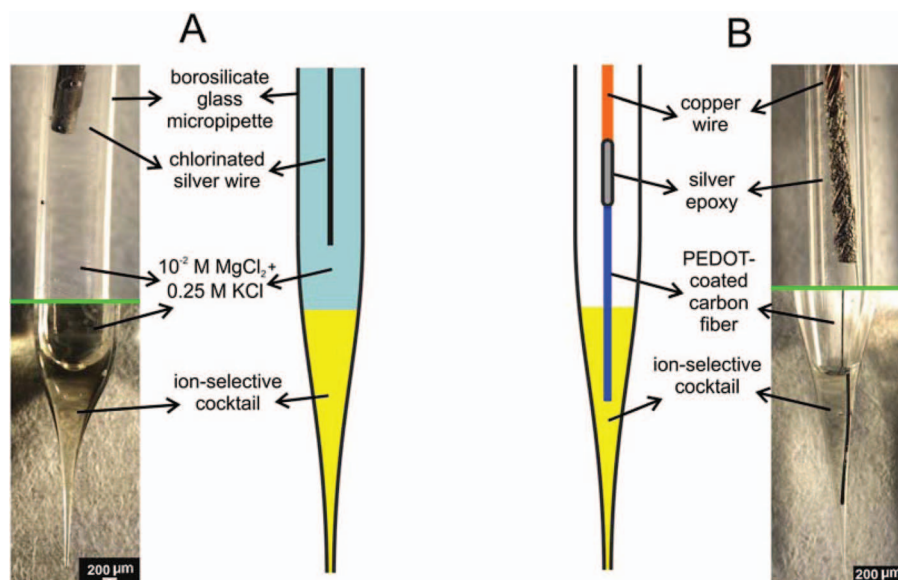
**Figure 1.** (Color online) Sketches of the electrochemical cells employed: (A) galvanic Fe-Mg system; (B) validation cell supporting a glass pipette filled with  $MgCl_2$  solution.

sources. Firstly, a noble metal disk microelectrode was considered. In this case, we employed two 100  $\mu m$  diameter Pt-Ir wires. They were embedded in *Epofix* resin with only cross sections exposed to the electrolyte. One serving as current source was placed normal to the surface to offer a 100  $\mu m$  diameter disk surface, whereas the other serving as counter electrode was placed with a certain tilt in order to offer a larger elliptical area. In the second arrangement, a glass micropipette with a tip diameter of 113  $\mu m$  was employed as the current source and dipped into the electrolyte in a small container. A platinum electrode was inserted in the pipette. Another platinum wire was present in the electrolyte and acted as a counter electrode. Batteries and resistors were used to vary the current through the pipette which was measured with an ammeter.

**Preparation of the ion-selective magnesium micropipette electrodes.**— The ionophore employed for the fabrication of the  $Mg^{2+}$  ISE was bis-N,N-dicyclohexyl-malonamide, which was synthesized following the method described in reference.<sup>45</sup> Selectivity coefficients of this ionophore toward  $Na^+$  and  $H^+$  ions are also available there.<sup>45</sup> The composition of the ion-selective cocktail is given in Table I. All the components in the ionophore cocktail were supplied by Sigma-Aldrich, except the home-made ionophore. Ion-selective microelectrodes were prepared using micropipettes pulled from borosilicate glass capillaries B100-50-10 (Sutter, Novato, CA, USA). The glass capillaries were first soaked in “piranha solution,” then thoroughly washed with twice deionized water and ethanol, and dried in oven at 105°C. Micropipettes were pulled from the capillaries by using a pipette puller (Sutter Instruments, type P-30, Novato, CA, USA). The inner wall of the pipette tips were hydrophobized by exposing them to a solution of dimethyldichlorosilane in carbon tetrachloride through capillary action, and baking them at 200°C for 30 minutes in a closed petri dish.

**Table I. Composition of the mixture employed to produce the cocktail for the  $Mg^{2+}$  ion-selective microelectrodes.**

Component	Quantities for 200 $\mu L$ of the mixture	
	Content	wt%
Tetrahydrofuran (THF)	100 $\mu L$	-
Poly(vinyl chloride) (PVC)	7.68 mg	5.06
bis-N,N-dicyclohexyl-malonamide	2.23 mg	1.47
Potassium tetrakis(4-chlorophenyl)-borate (PTCB)	2.13 mg	1.40
2-nitrophenyl octyl ether (oNPOE)	139.79 mg	92.07



**Figure 2.** (Color online) Sketches and micrographs of the micropipette electrodes fabricated for the selective detection of  $\text{Mg}^{2+}$  ions: (A) liquid-contact, and (B) solid-contact ISME's.

Figure 2 shows the sketches and micrographs of the liquid-contact and solid-contact ion-selective microelectrodes employed in this work, both using the same ion-selective cocktail but differing exclusively in the design of the electrochemical contact and the internal reference inside the micropipette electrode. The conventional micropipette  $\text{Mg}^{2+}$ -selective electrodes were prepared as described elsewhere.<sup>33</sup> The ionophore cocktail was filled into the micropipette tip under vacuum, whereas the internal solution was backfilled with the assistance of a microsyringe. The internal filling solution was 10 mM  $\text{MgCl}_2$  + 0.25 M KCl, and the internal reference electrode was a chlorinated silver wire. The internal solution and the reference electrode were confined in the micropipette with *Loctite* adhesive. A sketch and micrograph of the liquid-contact ion-selective microelectrode were shown in Figure 2A.

The solid-contact ion-selective microelectrodes were built using the same components employed for the fabrication of the conventional ISME, though in this case the internal contact was provided by a 33  $\mu\text{m}$  diameter carbon fiber cut to 35 mm length. A copper wire was previously attached to the carbon fiber using silver epoxy adhesive, to provide electric contact. The portion of the fiber to be contacting the ionophore cocktail was then coated with PEDOT conductive polymer in an electrochemical cell composed of the carbon fiber as working electrode, an Ag/AgCl wire immersed in the electrolyte as reference electrode, and a platinum wire as the auxiliary electrode. The monomer employed was 3,4-ethylenedioxythiophene dissolved in  $\text{BMIM}^+ \text{PF}_6^-$  ionic liquid.<sup>33</sup> Oxygen was purged from the EDOT-containing solution with nitrogen gas before and during the polymerization step. The resulting coated tip of the carbon fiber was immersed to a depth of 20 mm in the ionophore cocktail. The top of the micropipette electrode was sealed using *Loctite* adhesive. A micrograph of the resulting microelectrode is depicted in Figure 2B.

A voltage divider method was employed to determine the resistance of the microelectrodes using 1 mM  $\text{MgCl}_2$  + 1 mM NaCl solution. The electrochemical cell consisted of an Ag/AgCl, 3M KCl reference electrode and a freshly prepared microelectrode. Their potentials were recorded with respect to the reference electrode. The electrodes were connected to the voltage follower as shown in Figure 3A. After a steady reading was achieved, then a precision resistor  $R$  was interconnected between the inputs of the voltage follower. The experiment was performed with two different precision resistors, namely 0.5 and 1.0 G $\Omega$ .

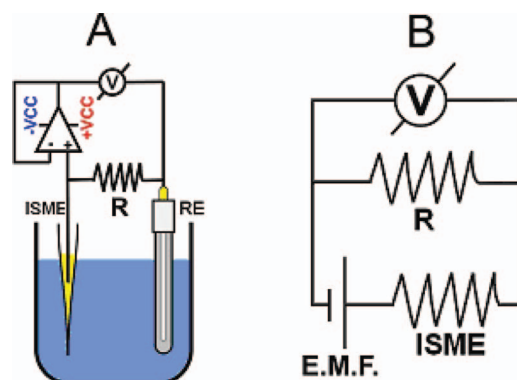
**Instrumentation.**— High-resolution SECM equipment supplied by Sensolytics (Bochum, Germany), was employed. The instrument was built around an Autolab (Metrohm, Herisau, Switzerland) electro-

chemical interface, controlled with a personal computer. Amperometric, potentiostatic and potentiometric operations were available in this configuration. For the potentiometric measurements where the  $\text{Mg}^{2+}$  sensing electrodes were employed, a voltage follower based on a  $10^{13} \Omega$  input impedance operational amplifier (TL071, Texas Instruments) was introduced in the measuring circuit,<sup>32</sup> as shown in Figure 4. The cell voltages were measured with an electrometer and collected by the PC through the electrochemical interface. The scanning system (Applicable Electronics Inc, New Haven, CT, USA) used a 3D micro-positioner driven by precision stepping motors. The distance between the scanning tip and the substrate was usually established by allowing the probe to gently touch the sample, and subsequently the probe was generally retracted to operation distance 100  $\mu\text{m}$  with the aid of the Z-positioning motor. A video camera was used to further assist positioning of the tip close to the surface. Raster scanning was employed to record the consecutive scan lines composing the XY grid.

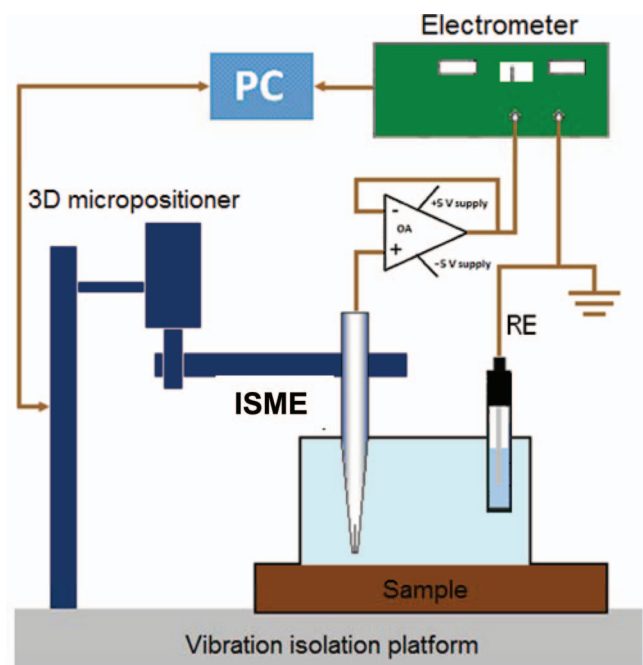
## Results and Discussion

The performances of the two types of  $\text{Mg}^{2+}$  ion-selective micropipette electrodes were compared concerning their calibration, resistance, response time, and imaging stability and reproducibility when used as potentiometric tips in SECM.

For their calibration, a series of  $\text{MgCl}_2$  solutions containing 1 mM NaCl as base electrolyte was employed. The range covered extended between  $10^0$  and  $10^{-5}$  M  $\text{Mg}^{2+}$ . As it can be seen in Figure 5, both



**Figure 3.** (Color online) (A) Sketch of the electrochemical cell used for the measurement of the internal resistance of the ISME, and (B) equivalent circuit.



**Figure 4.** (Color online) Sketch showing the main components of the instrument employed for SECM measurements, including the high input impedance operational amplifier (OA), and the ion-selective microelectrode (ISME).

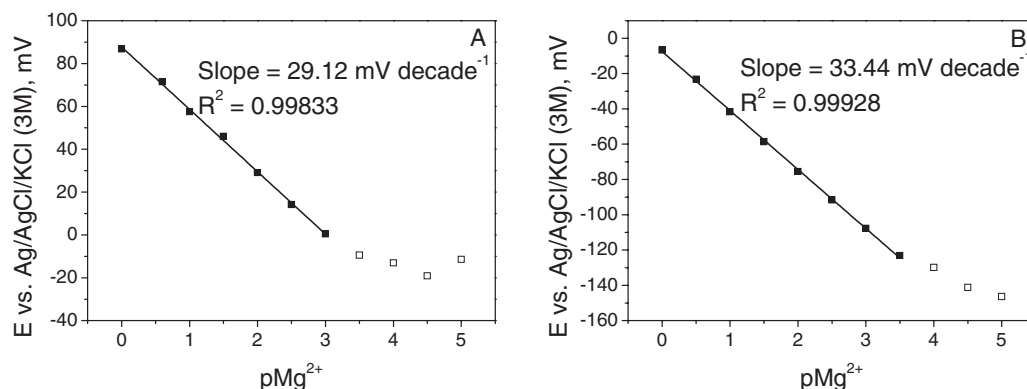
microelectrodes maintain a linear relationship at the higher concentrations. The calibration equations for the linear portions of the curves obtained for the two ISME's with the potentials expressed in mV are:

$$E_{lc-ISME} = 87.75 - 29.12 \text{ pMg}^{2+} \quad [1]$$

$$E_{sc-ISME} = -7.47 - 33.44 \text{ pMg}^{2+} \quad [2]$$

The solid-contact microelectrode, Figure 5B, attained a wider approximately linearity range to lower concentration whereas the liquid-contact electrode appeared to be insensitive to the concentration. The slopes of the linear portions ( $29.1 \text{ mV decade}^{-1}$  for the liquid-contact microelectrode, and interestingly  $33.4 \text{ mV decade}^{-1}$  for the solid-contact one) are sufficiently close to the expected Nernstian value of  $29.6 \text{ mV decade}^{-1}$  to employ these microelectrodes for quantitative measurements.

The noise present during potential measurements increases with increasing resistance of an ISME, and is therefore an indication of the



**Figure 5.** Calibration plots for the  $\text{Mg}^{2+}$  ISME in 1 mM NaCl solutions containing varying amounts of  $\text{MgCl}_2$  ( $\text{pMg} = -\log_{10} [\text{Mg}^{2+}]$ ). (A) Liquid-contact, and (B) solid-contact.

**Table II.** Resistance measurements for the two kinds of  $\text{Mg}^{2+}$  ion-selective micropipette electrodes conducted in 1 mM  $\text{MgCl}_2$  + 1 mM NaCl solution.

Parameter	ISME	
	Liquid-contact	Solid-contact
$E_{OCP}$ , mV	-49.5	-75.7
$R$ , $\text{G}\Omega$	1	1
$U_R$ , mV	-8.53	-48.41
$R_{ISME}$ , $\text{G}\Omega$	<b>4.80</b>	<b>0.56</b>

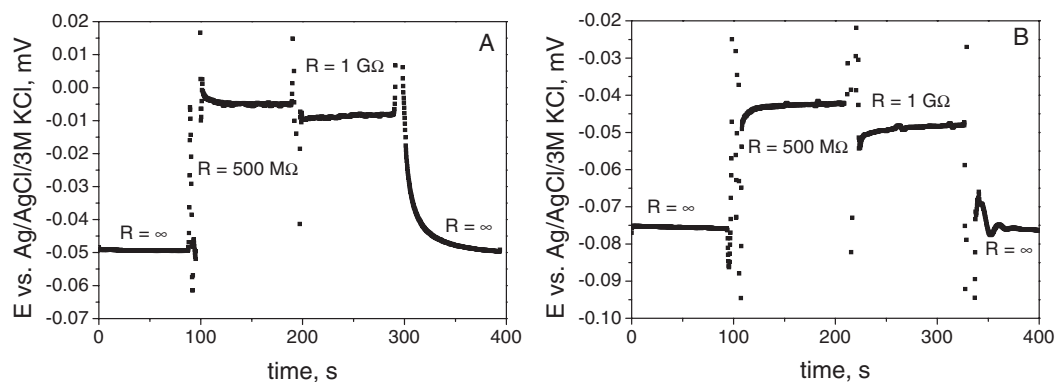
expected performance of the sensors. The equivalent circuit (EC) for the resistance measurements is depicted in Figure 3B. Resistances of the solution and the reference electrode are also part of the system, but they are very small values compared to that of the ion-selective microelectrode. Therefore, they have not been included in the EC for the sake of simplicity. In contrast, the voltage follower has an impedance of the order of  $10^{13} \Omega$ , considerably larger than the precision resistors. Hence, once again this resistance has not been included in the EC.

Figure 6 shows the current transients recorded for the liquid-contact (A) and the solid-contact (B) ISME's, respectively. After steady reading,  $U_R$  values were determined, and the resistance of the ISME was calculated using the equation describing the operation of a voltage divider:

$$R_{ISME} = R \frac{E_{OCP} - U_R}{U_R} \quad [3]$$

where  $E_{OCP}$  is the open circuit potential value established between the ISME and the external reference electrode, and  $U_R$  is the potential value measured when the resistor load  $R$  was introduced inside the electrical circuit. Table II contains the resistance values obtained for micropipette electrodes of the two types. The resistance determined for the solid-contact ISME is about a seventh of that shown by that with a liquid-contact (0.56 and  $4.80 \text{ G}\Omega$ , respectively). This observation is especially relevant when considering that the size of the micropipette openings were practically the same in both cases, thus the resistance values actually arose from differences in the interfacial resistance between the internal interfaces for each system.

Another very important factor to be considered in the applicability of the  $\text{Mg}^{2+}$  ISME is their response time, which severely limits the scan rates necessary to accurately record the concentration distribution maps of a given species. This issue is especially relevant in the case of corroding systems, where the location and size of the active sites continuously vary and are followed by changes in solution concentrations due to diffusion and convection. Ideally the scans must be recorded in a sufficiently short time to ensure that the system has not changed significantly during the measurement.



**Figure 6.** Response of ISME to shorting resistors for the voltage divider method: (A) Liquid-contact, and (B) solid-contact.

The response time of the microelectrodes was measured following the method proposed by Lamaka et al.<sup>44</sup> with a dual drop cell. The electrodes were immersed in one drop of 0.1 M  $\text{MgCl}_2$  + 1 mM NaCl and then moved to the second drop of 0.01 M  $\text{MgCl}_2$  + 1 mM NaCl after a stable potential was reached in 3 minutes. The time needed to reach 95% of the total potential change caused by the change in  $\text{Mg}^{2+}$  ion concentration was regarded as response time,  $\tau_{95}$ .

Figure 7 depicts the potential changes recorded during these experiments. A visual inspection of the transients leads to the observation that the solid-contact micropipette electrode exhibits a more reproducible and stable response than the liquid-contact one. In fact, significantly shorter transient times were needed for the solid-contact ISME when quantified as  $\tau_{95}$  values (namely, 71.1 s and 27.7 s were determined for the liquid-contact and the solid-contact microelectrodes, respectively).

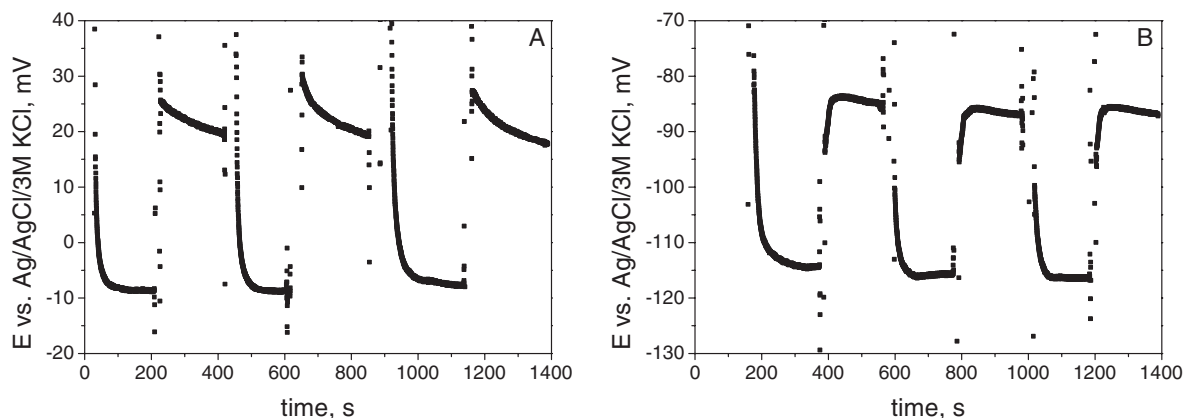
The performance of the two types of micropipette-based ion-selective electrodes for the imaging of  $\text{Mg}^{2+}$  ion concentration distributions was tested using the validation cell giving a source of  $\text{Mg}^{2+}$  ions 200  $\mu\text{m}$  diameter pipette containing  $\text{MgCl}_2$  in agar-agar. Figure 8 gives the ISME images obtained using a liquid-contact (A), and a solid-contact (B), micropipette electrode. Both 2D ISME maps were recorded at a scan rate of 12.5  $\mu\text{m s}^{-1}$ . The same pipette holding the 0.1 M  $\text{MgCl}_2$  agar solution was used in the measurements plotted in Figures 8A and 8B. The experiment was initiated using the solid-contact ISME. The 2D array scan image in Figure 8B was recorded after about 5 to 10 minutes following immersion of the  $\text{Mg}^{2+}$  containing pipette. Subsequently, the solid-contact ISME was replaced by the liquid-contact, and array scan in Figure 8A was obtained ca. 150 minutes later. As a result of the sustained diffusion from the  $\text{Mg}^{2+}$  pipette source in the validation cell the flux of  $\text{Mg}^{2+}$  would have de-

creased by about 4 to 5 times according to the Cottrell equation.<sup>47</sup> Additionally, some stirring of the aqueous solution takes place during the experiment because of unavoidable convection currents and gravitational effects due to the higher density of the  $\text{MgCl}_2$  containing solution. Also the rather high scan rate employed for enhanced resolution could produce for some convective distortion. Nevertheless, the approximate circular shapes of the higher concentrations is the same as that of the pipette. Visual inspection of the two images clearly shows significant image distortion in the X-direction with the liquid-contact ISME (cf. Figure 8A) which possibly occurred because of its slower response.

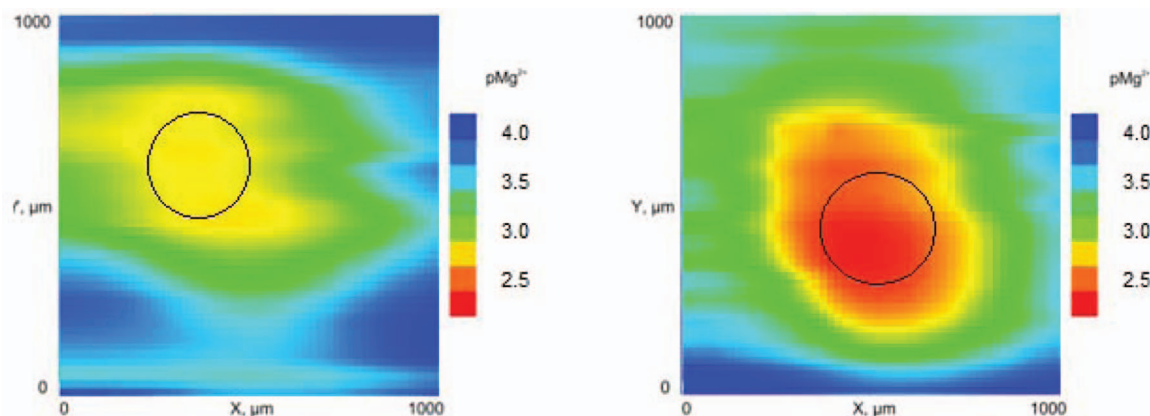
Differences in the performance of the two types of micropipette electrodes are more easily seen in the graphs depicted in Figure 9. They correspond to a sequence of scan lines taken from Figure 8 at the Y-positions indicated. It is seen that the liquid-contact microelectrode, exhibited a much broader curve indicating a poorer electrode performance in accord with a slower response.

On the other hand, we regard these experiments with the validation cell to clearly highlight the new opportunities opened by this new solid-contact micropipette-based ion-selective electrode for the monitoring of concentration distributions of species participating in corrosion with good spatial resolution using an SECM. This hypothesis was further checked by imaging the concentration distributions of  $\text{Mg}^{2+}$  ions over a corroding magnesium sample. Separate experiments were conducted on the magnesium strip galvanically coupled to iron and at open circuit when the two metals were electrically disconnected.

Freely corroding magnesium in the chloride-containing aqueous solutions leads to the release of metal ions that were detected in SECM measurements. The concentration distributions of  $\text{Mg}^{2+}$  are



**Figure 7.** Dynamic response curves obtained for response time measurements to changes in  $\text{MgCl}_2$  concentrations of  $10^{-1}$  M and  $10^{-2}$  M, in  $10^{-3}$  M NaCl. (A) liquid-contact, and (B) solid-contact  $\text{Mg}^{2+}$  ISME.



**Figure 8.** (Color online) SECM images displaying the of  $\text{Mg}^{2+}$  ion concentrations  $100 \mu\text{m}$ ; above the tip of a centered pipette source. (A) liquid-contact, and (B) solid-contact. Scan rate:  $12.5 \mu\text{m s}^{-1}$ . Drawn circles indicate the approximate location of the pipette in each case.

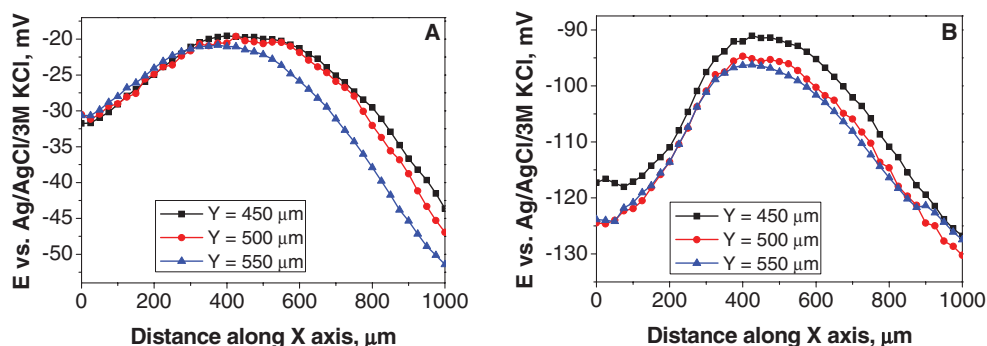
shown in Figure 10 for two separate experiments. The images of the concentrations of  $\text{Mg}^{2+}$  ions looked very different. In the case of the liquid-contact electrode, the ion concentration is rather homogeneously distributed which suggests a uniform corrosion process occurring over the entire metal strip. The morphology of the corrosive attack deduced from the inspection of Figure 10A seems to contradict the results reported in our previous work using the same type of liquid-contact ISME tip.<sup>46</sup> The observations derived from the analysis of a sequence of single scan lines supported the conclusion of a localized corrosive attack on the magnesium strip. The origin for such discrepancy must arise from the higher scan rates needed for recording a 2D map compared to the line scans in reference<sup>46</sup> which may originate blurring effects that could not be satisfactorily resolved here because of the long response times of the microelectrode. A different situation is observed when the solid-contact ISME was employed however confirms the previous result. Metal dissolution is detected from a highly localized source over the metal strip (see Figure 10B), which only covers a small fraction of the exposed metal surface. Most of the metal is thus effectively in contact with an electrolyte either free from  $\text{Mg}^{2+}$  ions or with a very low ion concentration originating from their diffusion in the electrolyte away from the actual source for the metal ions. This result is consistent with a corroding pit or crevice corrosion located at the upper end of the magnesium strip demonstrating that the time response of the solid-contact ISME is low enough to achieve the spatial resolution required for imaging the concentration distribution of  $\text{Mg}^{2+}$  ions in the system.

Similar localized features can be observed from the inspection of the images obtained for the magnesium strip galvanically coupled to iron shown in Figure 11. Despite the increased number of active anodes established on the surface of the metal with the higher con-

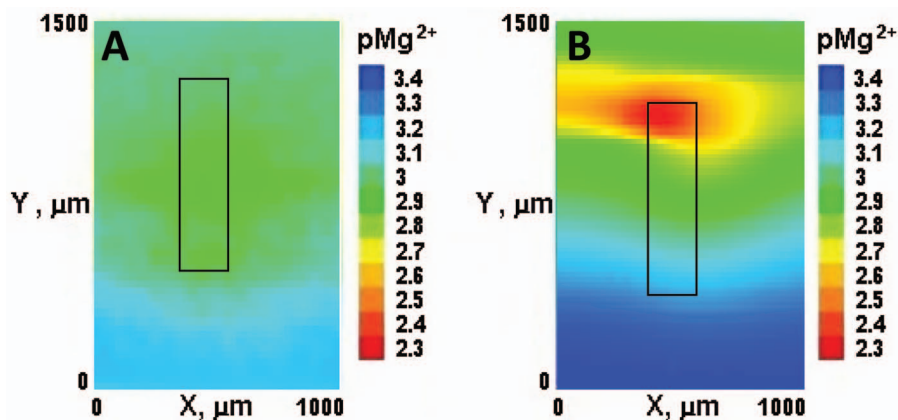
centration gradients in this system, the liquid-contact electrode also shows that the anodic activity on the metal strip occurs in a localized manner. That is, though blurring still affects the system, the high metal ion concentration allows for better spatial resolution than in the case of the free-corroding magnesium in Figure 11A. Indeed, very high dissolution rates for magnesium are observed when the metal was connected to iron, which are related to potential differences beyond those used for calibration of the ISME. At this stage, the negative pMg values in Figure 11 should only be considered as semi-quantitative estimates of high local  $\text{Mg}^{2+}$  concentrations compared to lower releases over most of the metal coupon. In typical experiments, less aggressive conditions should be employed in order to detect earlier stages of the localized attack on the metal, and the linear range of the ISME calibration will thus be applicable.

In summary, from inspection of the SECM images in Figures 10B and 11B, the magnesium sample was observed to corrode in a heterogeneous fashion regardless the electrical condition imposed to it, as it has been previously reported.<sup>46</sup> The main difference imposed by galvanic coupling this metal to iron is that metal dissolution greatly increases, as evidenced by the measurement of low pMg values for the electrically-connected condition, and the observation of more than one anodic site simultaneously operating on the surface.<sup>46</sup> However, general corrosion was also observed to occur.

In the preceding discussion it has been assumed that the potential measured by the ISME, above the corroding magnesium surface, was solely determined by the local  $\text{Mg}^{2+}$  concentration. But it has been pointed to us<sup>48</sup> that there might also be an additional contribution to the measured potential difference due to the electric field present above the corroding surface. These potential differences in the electrolyte arise ohmically as a consequence of the ionic current fluxes generated



**Figure 9.** (Color online) Line scans displaying the distribution of  $\text{Mg}^{2+}$  ion concentration close to the center of the magnesium ion pipette source. (A) liquid-contact, and (B) solid-contact ISME's. The scans were extracted from the middle of the SECM images given in Figure 8. Tip-substrate distance:  $100 \mu\text{m}$ ; scan rate:  $12.5 \mu\text{m s}^{-1}$ .



**Figure 10.** (Color online)  $\text{Mg}^{2+}$  ion concentration images above freely corroding magnesium in 10 mM NaCl. (A) liquid-contact, and (B) solid-contact. Tip-substrate distance: 100  $\mu\text{m}$ ; scan rate: 12.5  $\mu\text{m s}^{-1}$ . The location of the magnesium strip is drawn on the images.

by the local corrosion cell, an effect that has been effectively exploited to visualize localized events in a corroding metal using the scanning reference electrode technique (SRET).<sup>49</sup> Though the ISME employed in this work are not conventional micro-tip reference electrodes, they nevertheless will be subject to such effect when positioned over a corroding surface. Also SRET is influenced by the concentration of the salts of the dissolving metal as it alters the solution conductivity reducing the electric potentials.

We attempted to measure the response of the solid-contact ISME over 100  $\mu\text{m}$  diameter Pt-Ir current source embedded in an epoxy holder. However, the measurements were poor and attributable to the changes in pH and bubbles that formed on the surface due to water electrolysis during the experiment with the observation of vigorous gas evolution. The presence of bubbles and pH changes during these measurements was confirmed by video camera imaging with a pH indicator, phenolphthalein, added to the electrolyte. The indicator changes from colorless to purple at the concentrations used. The purple coloration is seen at the cathodes and a corresponding acidic formation occurs at the anode. The pH changes affect the offset potential of the ISME because the ionophore exhibits a Nernstian response toward protons activity in acidic solution.<sup>45</sup> The bubbles adhering to the electrodes also tended to adhere to the tip of the ISME and they distorted the current flow directions.

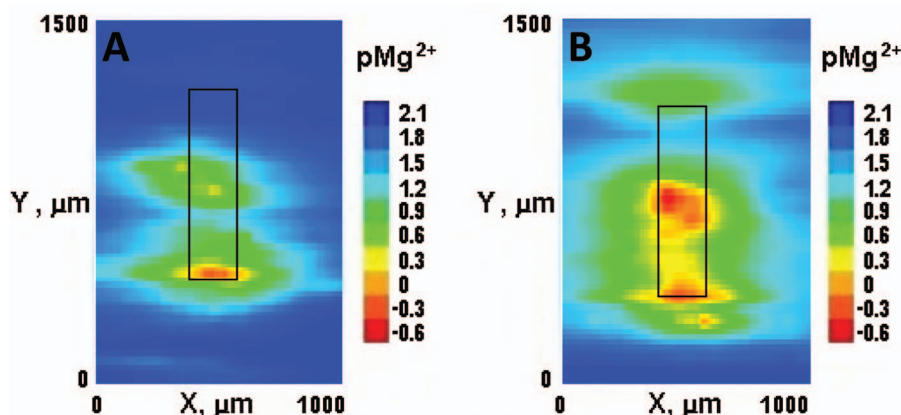
The effects due to pH changes and bubbles evolution were overcome using a glass micropipette. In this case, the solid-contact ISME was placed 100  $\mu\text{m}$  from its tip. In Figure 12A it can be seen that the background potential of the ISME remains virtually constant throughout all the measurements as indicated by the drawn dotted lines. The application of different currents ranging from  $-0.57$  to  $+2.86 \mu\text{A}$  produced potential changes in the ISME amounting 3–18 mV, respectively. Scan lines are shown in Figure 12B. The scans produced well defined potential peaks without perfect symmetry. This feature is attributed to the practical difficulties found in order to produce perfectly

symmetrical glass capillary openings parallel to the scan direction. Despite these practical limitations, the potential changes occurring at the ISME clearly reflect the magnitude and the sign of the electric field developed from the glass micropipette current source. Next, a stable potential response of the ISME was found at the end of the experiment when no current was flowing in the cell. An important observation in Figure 12A is the rapid change following application or removal of the current flow. The changes, particularly those on disconnecting the current, occurred too rapidly to be a result of interfacial effects. Delays in the response were less than about 20 s which were seen with the larger cathodic currents.

The magnitude of the potential change produced by the applied currents in Figure 12A are plotted in Figure 13. A linear relationship was established between these two parameters, thus allowing the response of the ISME to be calibrated regarding an electric field operating in the solution where the concentration of the ion being monitored does not change. The predicted variation is given by

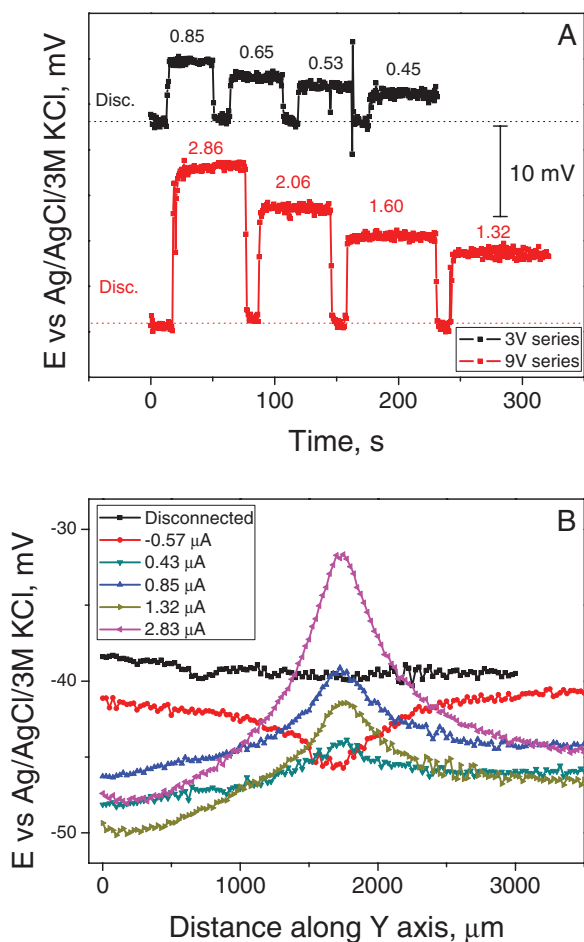
$$V = \frac{i\rho}{2\pi r} \quad [4]$$

where  $V$  is the electric potential at a point due to the flow of current  $i$  from a point source, at a distance  $r$ , in an electrolyte of resistivity  $\rho$ .<sup>50</sup> A very close fit of these results is obtained with a ratio of resistivity to probe distance ( $\rho/r$ ) of 38  $\text{k}\Omega$ . This result is plotted in Figure 13. However, it must be pointed out that for a distance of  $r = 100 \mu\text{m}$ , a resistivity of 380  $\Omega \text{ cm}$  is obtained (although the measured resistivity was 6060 and a literature value of 8084  $\Omega \text{ cm}$  was found for 1 mM NaCl).<sup>50</sup> The differences may in part be due to the source and probe having real diameters, and the distance between the two tips being approximately equal to these diameters so that ideal point to point conditions were not met or that the probe or that the distances between the tips were greater than measured. Because of

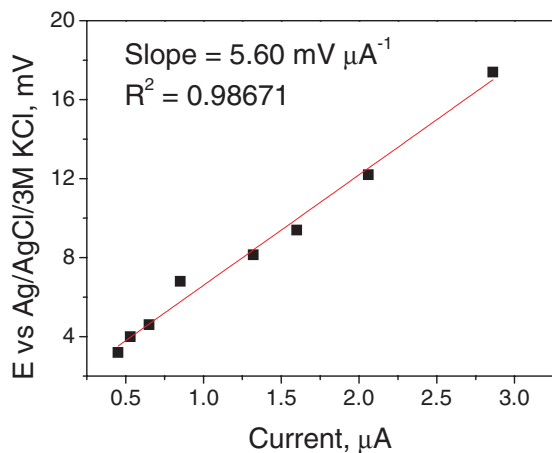


**Figure 11.** (Color online)  $\text{Mg}^{2+}$  ion concentration images above a magnesium strip galvanically shorted to iron in 10 mM NaCl solution (A) liquid-contact, and (B) solid-contact. The position of the iron strip was 5 mm to the right of the magnesium strip in the images. Tip-substrate distance: 100  $\mu\text{m}$ ; scan rate: 12.5  $\mu\text{m s}^{-1}$ .





**Figure 12.** (Color online) Potential response of a solid-contact  $\text{Mg}^{2+}$  ISME in 1 mM NaCl solution to the application of different currents from a glass micropipette current source. (A) The current was varied using batteries (namely 9 and 3 V, respectively) and resistors by following a sequence of connection/disconnection steps; the current values measured with an ammeter during each electrical connection, given in  $\mu\text{A}$ , are indicated in the figure; probe placed  $100 \mu\text{m}$  above the center of the source. (B) Line scans taken  $100 \mu\text{m}$  above the source for the indicated current values flowing through the pipette; scan rate:  $12.5 \mu\text{m s}^{-1}$ .



**Figure 13.** Calibration plot for the potential response of the solid-contact  $\text{Mg}^{2+}$  ion selective micropipette electrode with the amount of current flowing in the solution from a glass micropipette current source. The ISME was placed  $100 \mu\text{m}$  above the glass micropipette current source.

these uncertainties and that experiments conditions were repeated for the different sets of measurements we rely on the experimental results rather than on the predictions based on equation 4. We consider that with our experimental conditions currents in excess of  $3 \mu\text{A}$  must flow from the current source located  $100 \mu\text{m}$  from the probe in a 1.0 mM NaCl solution to produce a potential change of about 20 mV, which from Equation 1 and 2 would be equivalent to a change in the magnesium concentration smaller than one order of magnitude.

The external galvanic current was measured between the Mg and the Fe and found to be about  $2.5 \pm 1.0 \mu\text{A}$ . There were three active anodic areas detected with ISME in Figure 11A and about four in 11B in addition to activity over virtually its whole Mg area. The total anodic current flowing from the Mg surface producing these sites would be divided between them. The total anodic current, would in turn, be made up of the external current flowing from the iron, and also that contribution supported by the cathodic current on the Mg. Generally, it would be expected that the external current would be the major contributor because of more rapid cathodic kinetics for water reduction on the Fe. There could also be a contribution to the pitting currents from the presence of hydrogen ions produced by hydrolysis of the  $\text{Mg}^{2+}$  as discussed by Bender<sup>17</sup> and Frankel<sup>27</sup> but the sites where the hydrogen reduction takes place must be at a sufficient distance from the pits for currents in solution to be detected. It is therefore difficult to extract the total anodic current. However, in order to compare possible contributions from (ohmic) electric potential contributions to the potential changes measured using an ISME over a corroding surface, an upper value of  $2.5 \mu\text{A}$  flowing from a single site will be used. It should have a shape similar to that from the curves in 1 mM NaCl solution (Figure 12B). The maximum potential for the  $2.8 \mu\text{A}$  curve corresponds to a peak potential of less than 20 mV. However, the bulk solution in which the results in Figure 11 were obtained, was 10 mM NaCl which has a resistivity 9.7 times smaller than that of the calibration solution.<sup>51</sup> The lower resistivity would then give a peak potential of about 2 mV in the corroding solution. This potential is to be compared with the peak potential in Figure 11B which correspond a peak height above background of about 90 mV (using the calibration curve given by Equation 2, or taken from Figure 5B). Hence it is clear that the magnitudes of the ISME potential response, is dominated by the concentration changes of  $\text{Mg}^{2+}$ , and potential contributions due to corrosion currents are small in comparison. It is also important to note that the SRET potential measurements carried out over a corroding surface may also be influenced by the presence of dissolved corrosion products. This is especially true when the bulk solution is dilute, and rapid localized corrosion takes place that can reduce the resistivity and consequentially the ohmic potential.

## Conclusions

A new ISME construction to investigate corrosion processes on magnesium-based or magnesium-containing materials with high spatial resolution has been presented. It is based on a robust solid-contact with the ionophore which exhibits smaller internal resistance and a faster response times compared to one with a conventional liquid-contact having the same tip dimensions. Both types of magnesium ion measuring micropipette probes were successfully employed to perform in situ experiments on model corroding systems. The solid-contact ISME with its greater stability and lower internal impedance had a marked impact on the ability to collect these images with a high spatial resolution needed to study early stages of localized corrosion. Most of the corrosion studies were due to localized pitting and crevice corrosion but examples of general corrosion were seen. In the corrosion experiments the observed potential changes with the ISME were possibly attributed to both changes in  $\text{Mg}^{2+}$  concentrations and to corrosion currents. The Nernstian potential changes due to the  $\text{Mg}^{2+}$  concentrations were much larger than those produced by the ohmic electric potentials in solution.

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### References

- M. M. Avedesian, in *ASM Handbook, Vol. 13, Corrosion*, ASM International, 4th Edition, Metals Park, OH (1992).
- D. Eliezer, E. Aghion, and F. H. Froes, *Adv. Performance Mater.*, **5**, 201 (1998).
- G. L. Song and A. Atrens, *Adv. Eng. Mater.*, **1**, 11 (1999).
- R. C. Zeng, J. Chen, W. Dietzel, R. Zettler, J. F. Dos Santos, M. Lucia Nascimento, and K. U. Kainer, *Corros. Sci.*, **51**, 1738 (2009).
- G. Song, A. Atrens, D. St John, J. Nairn, and Y. Li, *Corros. Sci.*, **39**, 855 (1997).
- G. L. Song, A. Atrens, X. L. Wu, and B. Zhang, *Corros. Sci.*, **40**, 1769 (1998).
- R. Ambat, N. N. Aung, and W. Zhou, *Corros. Sci.*, **42**, 1433 (2000).
- S. Bender, J. Goellner, A. Heyn, and E. Boese, *Mater. Corros.*, **58**, 977 (2007).
- T. R. Thomaz, C. R. Weber, T. Pelegrini, L. F. P. Dick, and G. Knörmisch, *Corros. Sci.*, **52**, 2235 (2010).
- N. T. Kirkland, G. Williams, and N. Birbilis, *Corros. Sci.*, **65**, 5 (2012).
- W. A. Ferrando, *J. Mater. Eng.*, **11**, 299 (1989).
- A.-M. Lafront, W. Zhang, S. Jin, R. Tremblay, D. Dubé, and E. Ghali, *Electrochim. Acta*, **51**, 489 (2005).
- M. C. Zhao, M. Liu, G. L. Song, and A. Atrens, *Corros. Sci.*, **50**, 3168 (2008).
- G. L. Song and Z. Xu, *Electrochim. Acta*, **55**, 4148 (2010).
- Z. Szklarska-Smialowska, *Corros. Sci.*, **41**, 1743 (1999).
- G. Song and A. Atrens, *Adv. Eng. Mater.*, **9**, 177 (2007).
- S. Bender, J. Goellner, and A. Atrens, *Mater. Corros. – Werkstoffe Korros.*, **63**, 707 (2012).
- P. Brouillet, I. Epelboin, and M. Froment, *C. R. Acad. Sci.*, **239**, 1795 (1954).
- R. L. Petty, A. W. Davidson, and J. Kleinberg, *J. Amer. Chem. Soc.*, **76**, 363 (1954).
- A. Atrens and W. Dietzel, *Adv. Eng. Mater.*, **9**, 292 (2007).
- D. Sadcheva, *Corros. Sci.*, **60**, 18 (2012).
- G. L. Song, A. Atrens, and D. St. John, in *Magnesium Technology 2001*, pp. 255–262, TMS, New Orleans, LA (2001).
- G. Baril, G. Galicia, C. Deslouis, N. Pébère, B. Tribollet, and V. Vivier, *J. Electrochem. Soc.*, **154**, C108 (2007).
- G. Williams and H. N. McMurray, *J. Electrochem. Soc.*, **155**, C340 (2008).
- J. Świątowska, P. Volovitch, and K. Ogle, *Corros. Sci.*, **52**, 2372 (2010).
- G. Williams and R. Grace, *Electrochim. Acta*, **56**, 1894 (2011).
- G. S. Frankel, A. Samaniego, and N. Birbilis, *Corros. Sci.*, **70**, 104 (2013).
- S. E. Pust, W. Maier, and G. Wittstock, *Z. Phys. Chem. (Muenchen Ger.)*, **222**, 1463 (2008).
- L. Niu, Y. Yin, W. Guo, M. Lu, R. Qin, and S. Chen, *J. Mater. Sci.*, **44**, 4511 (2009).
- M. B. Jensen and D. E. Tallman, in *Electroanalytical Chemistry: A Series of Advances*, Vol. 24, A. J. Bard and C. G. Zoski, Editors, pp. 171–286, CRC Press, Boca Raton, FL (2012).
- R. M. Souto, Y. González-García, D. Battistel, and S. Daniele, *Chem. Eur. J.*, **18**, 230 (2012).
- R. M. Souto, J. Izquierdo, J. J. Santana, A. Kiss, L. Nagy, and G. Nagy, in *Current Microscopy Contributions to Advances in Sciences and Technology*, Vol. 2, A. Méndez-Vilas, Editor, pp. 1407–1415, Formatex Research Center, Badajoz, Spain (2012).
- G. Gyetvai, S. Sundblom, L. Nagy, A. Ivaska, and G. Nagy, *Electroanalysis*, **19**, 1116 (2007).
- G. Gyetvai, L. Nagy, A. Ivaska, I. Hernádi, and G. Nagy, *Electroanalysis*, **21**, 1970 (2007).
- J. Izquierdo, L. Nagy, Á. Varga, I. Bitter, G. Nagy, and R. M. Souto, *Electrochim. Acta*, **59**, 398 (2012).
- J. Izquierdo, L. Nagy, J. J. Santana, G. Nagy, and R. M. Souto, *Electrochim. Acta*, **58**, 707 (2011).
- B. Czoka and Z. Mekhalif, *Electrochim. Acta*, **54**, 3225 (2009).
- J. Izquierdo, L. Nagy, J. J. Santana, R. M. Souto, and G. Nagy, *Electrochim. Acta*, **56**, 8846 (2011).
- B. Horrocks, M. V. Mirkin, D. T. Pierce, A. J. Bard, G. Nagy, and K. Toth, *Anal. Chem.*, **65**, 1213 (1993).
- M. V. Rouilly, M. Badertscher, E. Pretsch, G. Suter, and W. Simon, *Anal. Chem.*, **60**, 2013 (1988).
- U. E. Spichiger, R. Eugstrer, E. Haase, G. Rumpf, P. M. Gehrig, A. Schmid, B. Rusterholz, and W. Simon, *Fresenius J. Anal. Chem.*, **341**, 727 (1991).
- Z. Hu and D. Qi, *Anal. Chim. Acta*, **248**, 177 (1991).
- S. V. Lamaka, O. V. Karavai, A. C. Bastos, M. L. Zheludkevich, and M. G. S. Ferreira, *Electrochem. Commun.*, **10**, 259 (2008).
- S. V. Lamaka, M. G. Taryba, M. L. Zheludkevich, and M. G. S. Ferreira, *Electroanalysis*, **21**, 2447 (2009).
- K. Tóth, E. Lindner, M. Horváth, J. Jeney, E. Pungor, I. Bitter, B. Ágai, and L. Töke, *Electroanalysis*, **5**, 781 (1993).
- J. Izquierdo, L. Nagy, I. Bitter, R. M. Souto, and G. Nagy, *Electrochim. Acta*, **87**, 283 (2013).
- A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, p. 143, John Wiley & Sons Inc., New York (1980).
- Comment raised by a reviewer to the manuscript. Authors are greatly indebted for the valuable contribution.
- H. S. Isaacs and B. Vyas, in *Electrochemical Corrosion Testing*, F. Mansfeld and U. Bertocci, Editors, pp. 3–33, ASTM, Baltimore, MD (1981).
- H. S. Isaacs, *J. Electrochem. Soc.*, **138**, 772 (1991).
- W. R. West, Editor, *Handbook of Physics and Chemistry*, 55th edition, p. D-132, CRC press Inc., Cleveland, OH (1974).