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RESEARCH ARTICLE

Investigation of Mg/Al alloy sacrificial anode corrosion with Scanning Electrochemical Microscopy

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Abstract

Corrosion of Mg/Al alloy was investigated with the scanning electrochemical microscope (SECM) using a Mg^{2+} ion selective microelectrode (ISME) as measuring tip. Mg/Al alloys have practical application as sacrificial anodes to prevent the corrosion of various metals susceptible to corrosion. A typical application of such sacrificial anodes is in water boilers. A model (Mg/Al)/Fe target was fabricated using boiler sacrificial anode and high purity iron wires. Corrosion current was measured between the electrically connected galvanic pair, and Mg^{2+} ion flow rate was calculated with Faraday's law of electrolysis. However, Mg^{2+} flow rate could not be calculated with this method while the twometals were left electrically-disconnected. For this reason, fixed height lateral scans and retreating scans were performed above the Mg^{2+} sample with Mg^{2+} ion-selective electrodes employed as SECM tips. Mg^{2+} flow rate was estimated using the concentration profiles obtained with SECM. Relatively high-speed scans were possible with robust, solid contact Mg^{2+} micropipette electrodes, owing to their low resistance compared to conventional micropipettes of the same size.

Keywords

Scanning Electrochemical Microscope · SECM · ion-selective microelectrode · ISME · galvanic corrosion · potentiometric tip · solid contact

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Introduction

As it is well known, by electrically connecting two metals with different redox character, a galvanic pair is formed. The more reactive metal has a lower redox potential than the other one. The galvanic connection can provide cathodic protection against corrosion of the less reactive metal. When the two are coupled, electrochemical oxidation takes place at the more reactive metal surface, while at the less reactive one, reduction proceeds – most often of oxygen. The more reactive metal gets dissolved, preventing the corrosion of the other. Because of this property, such protective metals are called sacrificial anodes or active anodes. The protection persists until the entire sacrificial anode is dissolved, then the less reactive metal starts to develop anodic sites as well, and starts to corrode. Because magnesium is among the most often used sacrificial anodes, and iron has a widespread use, it was worth to investigate the galvanic corrosion of this galvanic pair. Scanning Electrochemical Microscopy (SECM) is a relatively new, powerful technique, recently started to be applied in corrosion science [1, 2]. Because corrosion processes of metals involve the formation of metal ions, SECM technique with ion-selective microelectrode (ISME) measuring tips provides a method in corrosion sciences. Corrosion of a (Mg/Al)/Fe model galvanic pair target was studied. The Mg/Al sample was made from an actual sacrificial anode used in water boilers.

Experimental

Fabrication of Mg^{2+} ISME electrodes

Fabrication of solid contact electrodes has been described elsewhere [3, 4], thus only a short description will be given here. Borosilicate micropipettes were pulled using micropipette puller (Sutter Instruments Co., Novato, USA, Model: P-30). Micropipettes were cleaned with pyranha solution (50%/50% volume mixture of hydrogen-peroxide and sulfuric acid), rinsed with distilled water, then silanized with dimethyldichlorosilane solution (Fluka, Silanization Solution 1) in a Petri dish. 100 µl of the silanization solution was added, and the lid of the dish was immediately closed, the pipettes were baked at 150 °C for 20 minutes. After silanization, the micropipettes were front-

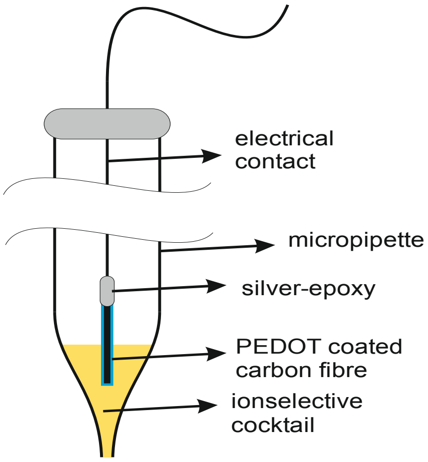

Fig. 1. Schematic design of the Mg^{2+} ISME used as measuring tip in the experiments.

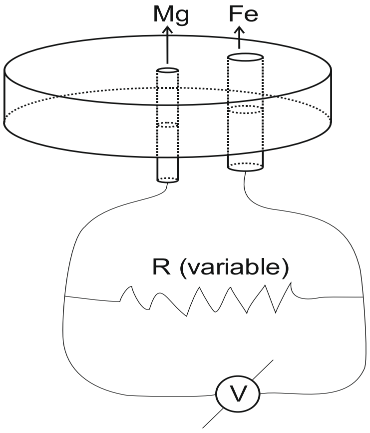

Fig. 2. Mg/Al-Fe model target in epoxy sleeve. Figure also shows the variable resistor used for estimation of the corrosion current flow between the two metals.

filled with ion-selective cocktail with vacuum applied on the back of the pipette. The cocktail was prepared using bis-N,N'-dicyclohexyl-malonamide as Mg^{2+} ionophore, potassium tetrakis(4-chlorophenyl)borate (KTCPB), 2-nitrophenyl octhyl ether (NPOE) and polyvinyl chloride (PVC) in tetrahydrofurane (THF). The composition of the mixture was: 57.7 wt.% NPOE, 3.6% wt.% Mg^{2+} ionophore, 3.4 wt.% PVC, 1.3 wt.% KTCPB, and 34.0 wt.% THF. The resulting membrane was let to dry for 24 hours before the immersion of the carbon fiber as internal solid contact. 33 µm diameter carbon fibers (obtained as a generous gift from Specialty Materials, Lowell, Massachusetts, USA) were coated with Poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer. PEDOT coating was prepared in EDOT polymerizing solution, the solvent was 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) ionic liquid. A copper wire was glued to the rear end of the carbon fiber with silver-epoxy to provide electrical contact. Electrodes were calibrated in a $MgCl_2$ dilution series ranging from 10^{-6} M to 10^{-2} M. After calibration, the electrodes were stored dry until measurement, and were conditioned in 10^{-2} $MgCl_2$ solution for 2 hours before measurements. Fig. 1. shows the schematic design of the Mg^{2+} ISME electrode.

(Mg/Al)/Fe target

(Mg/Al)/Fe galvanic couple target was prepared from 70/30 Mg/Al alloy (boiler sacrificial anode), and high purity Fe wires. The diameter was 0.67 mm for both metal samples. They were mounted in an epoxy resin sleeve, exposing only the disc shaped surfaces. Electrical contact was provided at the rear end of the mould. Frontal surface of the mould was first polished with sandpaper, then with 1.0, 0.3, and 0.03 µm alumina powder.

Potentiometric SECM

Fixed height lateral scans and retracting scans were performed above the Mg sample, using Mg^{2+} ISME electrode as measuring tip, and Ag/AgCl/3.5 M KCl reference with a home-made SECM [5]. Height of lateral scans was 100 µm, resolution was 5 µm, lateral distance was 5 mm with the Mg/Al sample in the centre. Retracting curves were recorded at $t = 10$, 20, 30, 40, 50, 60 minutes after introduction of the corrosive media, resolution was 5 µm. Since ion-selective electrodes of this size have high resistance compared to the low input resistance of potentiometers, to avoid loading the potentiometric sensor, a home-made high impedance voltage follower circuit was used as current buffer based on the TL082 operational amplifier (Texas Instruments, Dallas, USA). The potential was measured with a MeTeX potentiometer (MeTeX M-3630D) connected to a PC, the signal was recorded with the software provided by MeTeX. Scans were performed with the two metals either electrically connected or disconnected. Corrosive medium was distilled water saturated with air.

Corrosion current

Corrosion current cannot be measured directly, since the measurement itself would alter the current flow. However, it is possible to calculate it by measuring the voltage drop on the two sides of a variable resistor, which connects the Mg and Fe samples together. Plotting the voltage over the resistance (E/R) with respect to resistance, the „y" interception will be $1/i$ at $R = 0$, after taking the reciprocal, corrosion current is obtained. Using Faraday's law of electrolysis, Mg^{2+} ion flow rate from the Mg/Al sample was determined.

Results

Mg^{2+} ISME electrodes

Mg^{2+} ion selective microelectrodes were calibrated in $MgCl_2$ solutions with concentrations from 10^{-6} M to 10^{-2} M. Reference was Ag/AgCl/3.5 M KCl. Sensitivity was 26 mV/decade of $[Mg^{2+}]$ (Fig. 3.).

SECM scans

Mg^{2+} ion concentration profiles above the Mg sample were recorded by SECM scans. Vertical Mg^{2+} ion concentration distribution was determined at different instants in time of the cor-

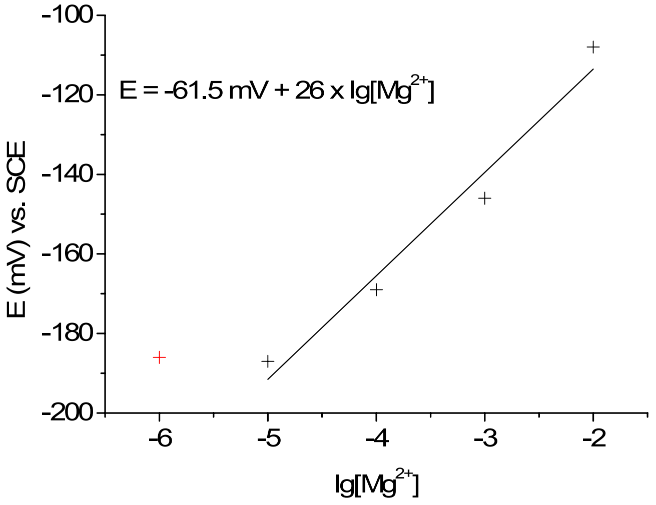

Fig. 3. Calibration plot of the Mg^{2+} ISME. Slope is 26 mV/decade of $[Mg^{2+}]$.

rosion process, with, and without coupling the Mg/Al and Fe samples. About ten times more Mg^{2+} is being formed with coupling. Mg^{2+} concentration was increasing with time above the sample while coupled, on the other hand, it was decreasing after 10 minutes when disconnected (Fig. 4). Based on the method of Scott and White [6], using the Mg^{2+} concentration profiles, Mg^{2+} flow rate from the Mg 00vpiece was possible to estimate:

$$\Omega = 4DC_s a$$

where Ω is the amount of Mg^{2+} released from the disc shaped Mg/Al surface in every second, D is the diffusion coefficient of Mg^{2+}, C_s is the surface concentration of Mg^{2+} (at the height $z = 0\,\mu$m), a is the radius of the Mg/Al sample. As the only unknown variable in the equation above, Ω could be calculated. Substituting the value of $D = 7.06 \times 10^{-8}\ dm^2s^{-1}$ [7], $C_s = 3.29 \times 10^{-2}$ M, $a = 0.0038$ dm, the result is $\Omega = 3.53 \times 10^{-11}$ mol/s.

Corrosion current

Corrosion current between the Mg/Al sample and four Fe samples with different diameters was determined. As expected, current gets higher with increasing diameter. Corrosion current was 8.87 μA, 15.83 μA, 16.72 μA, 24.4 μA with Fe sample diameters of 0.59 mm, 0.76 mm, 1.2 mm, 2.3 mm, respectively (Fig. 6.). Using Faraday's law of electrolysis, this means, that 8.20×10^{-11} mol Mg^{2+} is being dissolved in every second from the Mg/Al sample ($\Omega_{0.76mm} = 8.20 \times 10^{-11}$ mol/s). This result is in fairly good agreement with the result calculated from the SECM retracting curves ($\Omega = 3.53 \times 10^{-11}$ mol/s). Ion flow rates from Mg/Al samples coupled with Fe samples of different diameters are proportional with the surface area of the sample; $\Omega_{0.59mm} = 4.60 \times 10^{-11}$ mol/s, $\Omega_{1.2mm} = 4.66 \times 10^{-11}$ mol/s, $\Omega_{2.3mm} = 1.26 \times 10^{-10}$ mol/s.

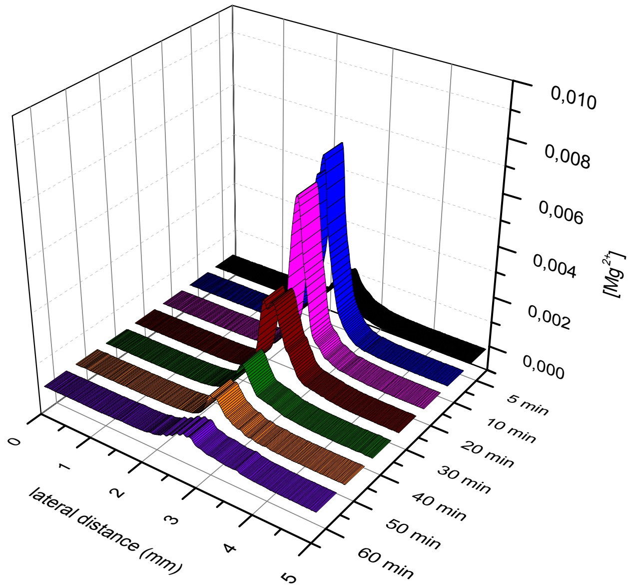

Fig. 5. Concentration-distance lateral scans at $z = 100\,\mu$m height for different instants in time over the corroding Mg/Al sample measured with the Mg^{2+} ISME tip.

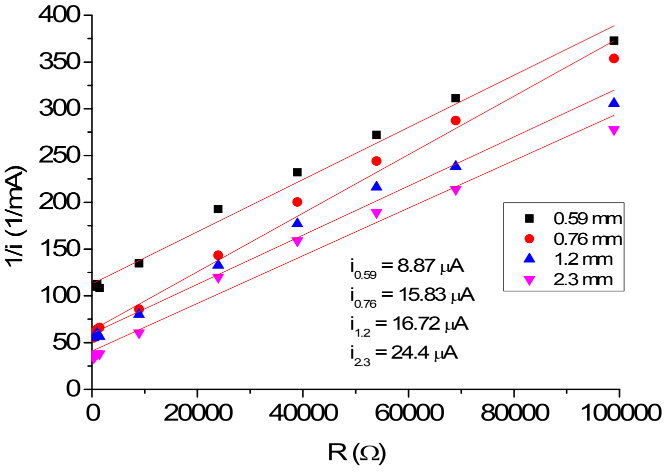

Fig. 6. $1/i$ plots used for the determination of corrosion current between the Mg/Al and various Fe samples of different diameters.

Conclusion

Most of the SECM studies in the literature have been carried out with amperometric microtips. The applicability of new potentiometric tips has been tested in this work. SECM is a powerful tool in the field of corrosion science. Mg^{2+} ion-selective electrodes combined with SECM can be used to determine Mg^{2+} ion concentration distribution in a corroding system, with, and without coupling. Useful information, such as lateral and vertical concentration distribution, can be collected concerning the corrosion of metals. The gathered information can be used to calculate other parameters such as ion flow rates. This new method can be used to study the corrosion of any metal, substituting the tip with the appropriate ion-selective microelectrode. It is expected that the efficiency of corrosion protecting coatings can be tested using SECM with potentiometric tips.

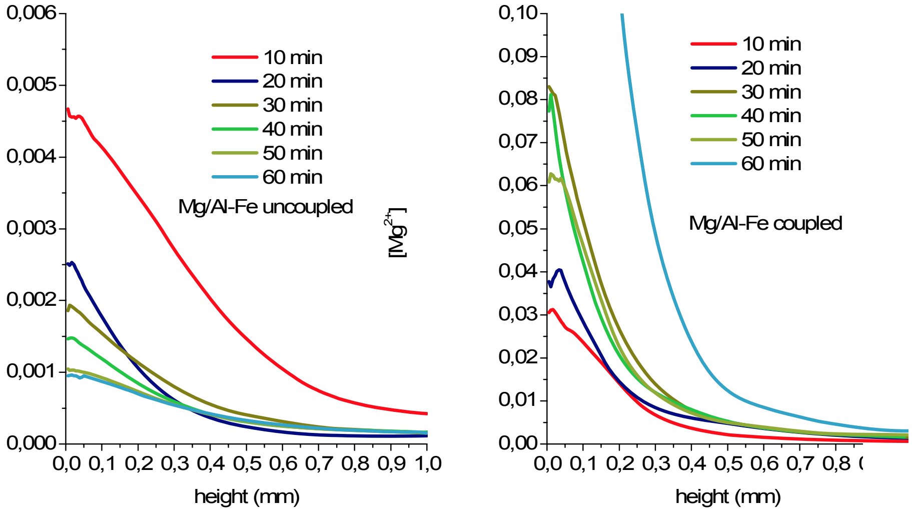

Fig. 4. Retracting scans above the center of the Mg/Al sample. Scans were carried out while the Mg/Al and Fe samples were disconnected (left), and also when they were electically coupled (right).

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