

Summer Fellowships

Each year ECS gives up to five Summer Fellowships to assist students in continuing their graduate work during the summer months in a field of interest to the Society. Congratulations to the five Summer Fellowship recipients for 2013. The Society thanks the Summer Fellowship Committee for their work in reviewing the applications and selecting five excellent recipients. Applications for the 2014 Summer Fellowships are due January 15, 2014 (see http://www.electrochem.org/awards/student/student_awards.htm#n).

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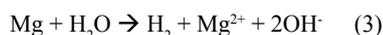
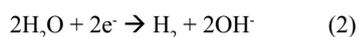
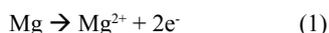
THE 2013 EDWARD G. WESTON SUMMER RESEARCH FELLOWSHIP – SUMMARY REPORT

Assessment of Magnesium Alloy Corrosion Using Potentiometric Mode of Scanning Electrochemical Microscopy

by Philippe Dauphin Ducharme

Magnesium remains a very reactive material. Different alloying, elemental composition, and casting methods can be employed to enhance corrosion properties.¹ In spite of its poor corrosion behavior, magnesium's mechanical and lightweight properties draw the attention of the automotive industry toward its addition in car components to improve fuel efficiency. The complexity of the corrosion mechanism in magnesium alloys and the size of the anodic/cathodic sites responsible for microgalvanic corrosion requires high-resolution *in situ* and *ex situ* characterization to get a proper understanding of the alloys' corrosion behavior.²

Scanning electrochemical microscopy (SECM) can achieve high-resolution *in situ* imaging while recording both surface reactivity and topography. When magnesium alloys are immersed, different electrochemical fluxes in solution can be recorded with SECM. The Mg alloy corrosion reaction proceeds following Eq. 3.



Equation 1 describes the main anodic reaction, where the Mg alloy dissolves and generates Mg^{2+} ions. Through the detection of this ionic flux at a specific position over the Mg alloy surface, it would be possible to obtain local corrosion rate information.

The potentiometric mode of SECM, initially developed in the laboratory of Allen Bard,³ enables the measurement of ionic fluxes using an ion-selective electrode. A

micron-sized quartz capillary, pulled using a P-2000 CO_2 laser (Sutter Instrument), is tip filled with a polymeric cocktail containing an ionophore selective towards Mg^{2+} (ETH 7025),⁴ as observed in Fig. 1c. The capillary is then back filled with a constant activity MgCl_2 solution where an $\text{Ag}|\text{AgCl}$ wire can then be inserted (Fig. 1a). The reference electrode enables the measurement of the junction potential difference at the tip. A calibration curve is created using standards solutions of different Mg^{2+} activities ranging from 10^{-7} to 10^{-1} . A linear behavior is measured between 10^{-5} and 10^{-1}

(Fig. 2a). The potentiometric sensor is then placed over a graphite cast AM50 Mg alloy (of interest for industrial applications), which has been polished following an established procedure,⁵ at a tip-to-substrate distance of $1 \mu\text{m}$ using shear force.⁶ Upon immersion in a $50 \mu\text{L}$ drop of 1.6 wt. % NaCl solution, the potential is recorded while the potentiometric sensor is scanned across the surface. Figure 2b illustrates a $6 \times 8 \mu\text{m}$ area scanned to locate corrosion initiation sites. Using the calibration curve, the potentials are transformed into activity units (Fig. 2a). The measured activities lie

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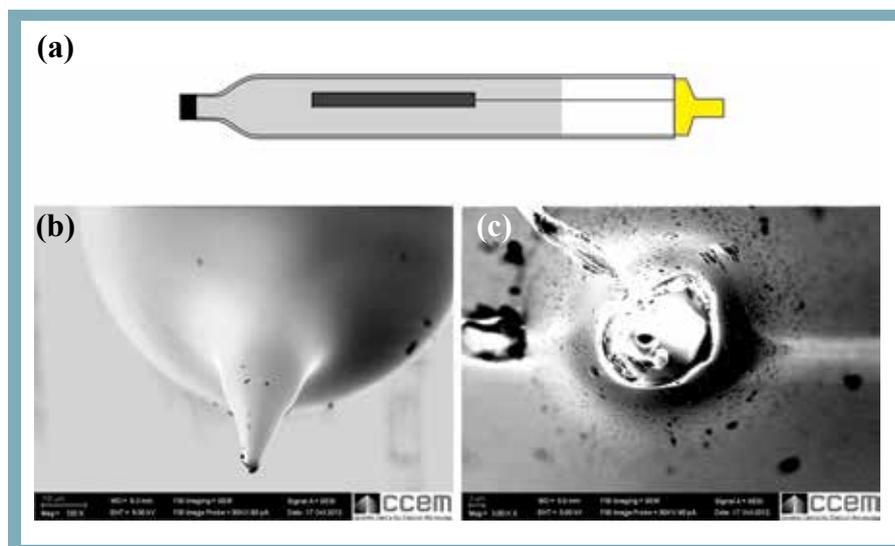


FIG. 1. (a) Schematic representation of the sensor where the black region represents the ion-selective membrane, the light grey, the constant activity MgCl_2 solution and the darker grey the $\text{Ag}|\text{AgCl}$ reference wire; (b) and (c) are respectively SEM micrographs of the potentiometric sensor from bottom up and the tip.

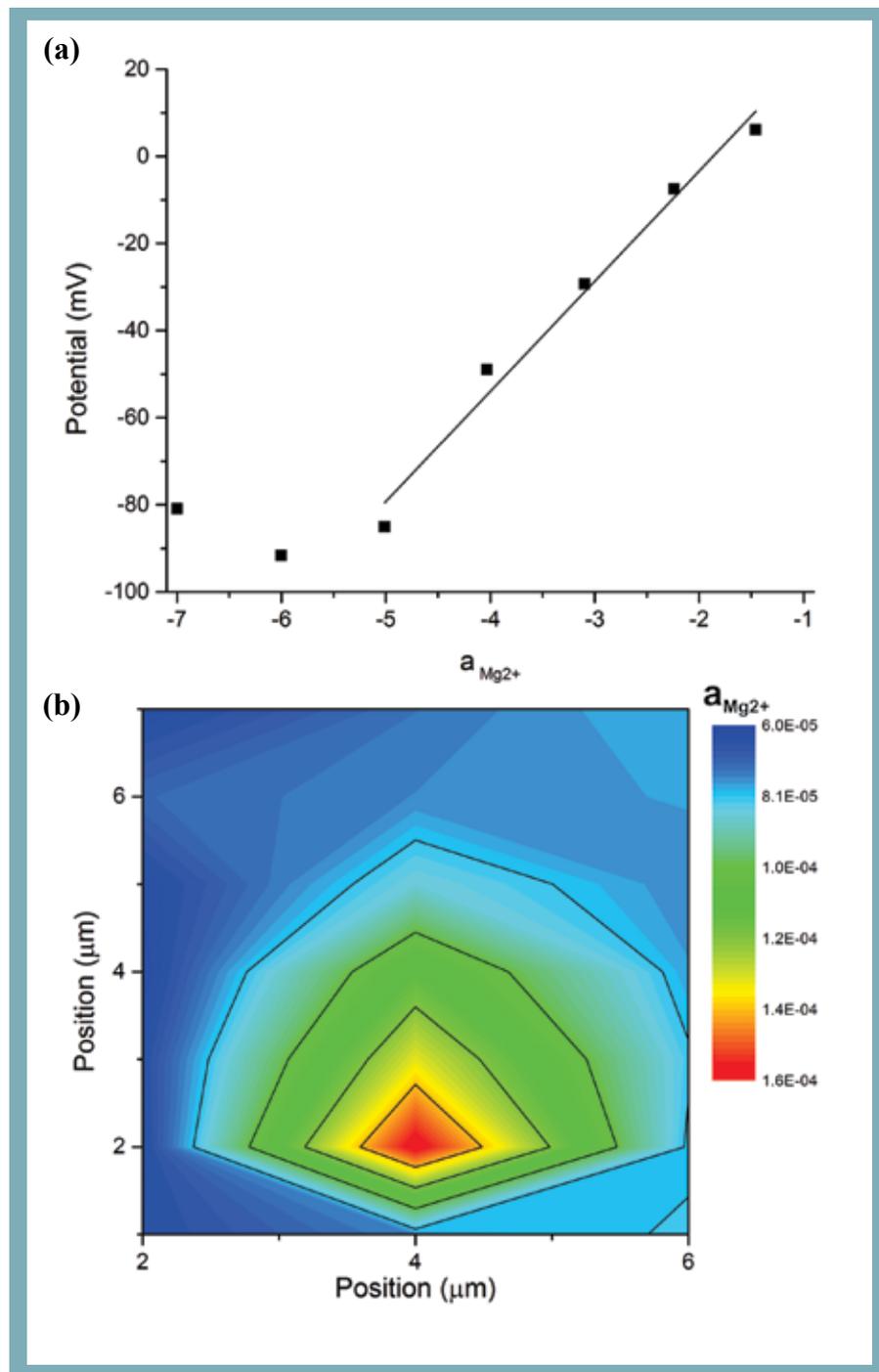


FIG. 2. (a) Calibration curve of the potentiometric sensor. The linear regression equation between $a_{Mg^{2+}} = 10^{-5}$ to 10^{-1} is $y = 25.3x + 47.2$ with a $R^2 = 0.9825$; (b) Mg^{2+} activity map recorded in SECM on top of a graphite cast AM50 Mg alloy surface when positioned at $1 \mu\text{m}$ from the surface recorded at $1 \mu\text{m/s}$. A Ag|AgCl and Pt wires are used as a reference and counter electrodes.

in the linear domain of the calibration curve and are therefore analytically valid. The areas of larger Mg^{2+} activity are currently believed to correlate with the α -Mg rich phase, which is considered an anodic site in the microgalvanic process.

Future experiments will consist in correlating the initiation sites observed in SECM with their morphology and elemental composition measured by scanning electron microscopy (SEM). The measurement of Mg^{2+} ion fluxes also enables the ability to numerically simulate alloy corrosion to predict their outcome.

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About the Author

PHILIPPE DAUPHIN DUCHARME is a third year graduate student in the Chemistry Department at McGill University, Canada. He is currently a PhD candidate under the supervision of Janine Mauzeroll. Ducharme's thesis concentrates on monitoring Mg alloys corrosion using Scanning Electrochemical Microscopy while concomitantly developing a numerical method to predict Mg corrosion for their industrial applications. He may be reached at philippe.dauphinducharme@mail.mcgill.ca.

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