

Acidification of the Electrolyte in the Carbon Steel/ Aluminum Alloys Galvanic Couple: Modeling and Experimental Study

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ABSTRACT

An electrochemical model was developed to predict the transient distribution of species generated during corrosion of carbon steel (CS) /aluminum alloy (AA) galvanic couples under thin NaCl electrolyte films at room temperature (24 °C). Using specific geometrical configurations, strong acidification of the electrolyte, localized above the AA surface and close to the carbon steel electrode, was predicted. However, a small zone evolved (also above the AA surface) between the strong acidified area and the AA/CS joint, where the pH was neutral due to the OH⁻ production on the CS surface. Moderate acidification of the electrolyte was predicted above the rest of the AA surface. Both diluted and concentrated electrolytes were taken into account. Surprisingly, the less concentrated the electrolyte, the more significant the drop of pH on top of the AA electrode.

Transient experimental measurements were achieved with the help of an innovative setup, and findings corroborated the theoretical predictions. These results provide enough evidence to properly discuss whether such an acidification process is due to the production of intermediate aluminum compounds or by the fast consumption of hydroxyl ions (OH⁻) produced by the cathodic reaction on the steel surface.

Keywords: galvanic couples, modeling, aluminum alloys, aluminum hydrolysis, acid corrosion.

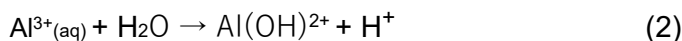
INTRODUCTION

With a vast demand for solutions for decreasing the emission of pollutants, the transport industry is developing new ideas in many fields: catalyst converters, new energies, better quality of fuels, lighter materials, etc. With regards to lighter vehicles, the automotive industry has been looking for the best steel components such as frames and chassis to be replaced by light alloys. This task is not straightforward as light alloys have inferior mechanical properties to steel, and the substitution of any part of a vehicle should be carried out avoiding designs that violate any mechanical standard.

On the other hand, it is well known that producing structures by combining different metallic components leads to a galvanic corrosion phenomenon, which takes place when two metallic samples (with different corrosion potential) are put together in contact with a common electrolyte. The more active material undergoes more aggressive corrosion than if it was just in contact with the electrolyte (but without the second metallic material). On the other hand, coatings (the artificial barrier to avoid contact between the metallic couple and the electrolyte) are just a non-permanent solution since they always end up failing.

The most common light alloys used in the automotive industry are AA. Even though Mg alloys are much lighter, their high corrosion rates are still a critical drawback to overcome. Hence, a typical dissimilar metallic couple used in automotive prototypes is the CS/AA system, which has been widely studied.^{1,2} Nevertheless, a dangerous property of this system, and rarely cited in the literature, is the generation of H^+ during the corrosion of AA.

The hydrolysis of Al^{3+} ions leads to the release of hydronium ions following Reactions 1 and 2.



Alvarez-Pampliega et al.³ provided electrolyte pH values as a function of the concentration of Al^{3+} ions in the electrolyte, but nothing is reported about the influence of the electrolyte conductivity, or geometric factors, on the pH of the electrolyte surrounding an aluminum electrode surface.

The $Al(OH)^{2+}$ ion in Reaction 2 has not been fully accepted since several complex compounds of Al have also been reported.⁴ Nevertheless, the local acidification for the liberation of protons (or hydronium ions) looks to be unanimously accepted. From the point of view of localized corrosion, acidification inside AA pits has been broadly reported.⁵ In the simulation field, on the other hand, there is plenty of information regarding the AA corrosion.^{6,7} However, there is a lack of information about the drastic acidification of the AA surface.

Ruiz-Garcia et al.² wrote one of the first works numerically predicting such an acidification phenomenon. There, the authors developed a simplified model to avoid working in 2D if the electrolyte is thin enough. The authors even reported differences in current and potential distributions when thin and thick films are on the galvanic couple CS/AA. Nevertheless, this work lacks the comparison of pH distributions in thick and thin films. Recently, Snihirova et al.⁸ have predicted acidification in the AA2024/Ti6Al4V galvanic couple. Such acidification was found on the AA, but just in a tiny and local area next to the metallic joint. On the other hand, it is well known that corrosion mechanisms that take place under atmospheric conditions are entirely different than those taking place under full immersion conditions. However, most of the works dealing with the acidification process on the AA surface carry the investigation out under full immersion conditions. This acidification of the electrolyte surrounding the AA surface could become catastrophic when pH values are smaller than three. The present work provides theoretical and experimental evidence that such values can be achieved under specific geometrical, chemical, and electrochemical conditions.

EXPERIMENTAL PROCEDURE

Dealing with the thicknesses of electrolytes of a few micrometers is not straightforward. Therefore, instead of working with liquid electrolytes, which present several issues, including surface tension, evaporation, leaks, etc., solid electrolytes were used to cover the galvanic couple system. The experimental validation performed is both original and overwhelming to prove the acidification on the AA surface. Two concentrations of NaCl were tested: 0.6 and 0.06 M.

The electrolytes were made by dissolving agar-agar powder (technical grade) and pH indicator solutions (thymol blue and methyl red) in 0.6 M and 0.06 M NaCl solutions. The solution was heated until the full dissolution of agar powder, then cast in a proper container and cooled down at room temperature. The gel had excellent mechanical properties to be handled appropriately as a portable electrolyte. It was possible to put it on top of the metallic couple (AA and CS) without complications.

Figure 1 schematizes the general setup, consisting of two metallic coupons (AA and CS), each of 5 cm in length and 1.25 cm in width, electrically connected using crocodile clips, and a solid electrolyte deposited on top of them (like a self-adhesive decal). The proper electrical connection between the electrodes was always double-checked using a multimeter.⁽¹⁾

⁽¹⁾ Fluke 189.

Before the electrolyte was deposited on top of the metallic couple, both metallic surfaces were sanded to 2000 grit sandpaper and cleaned up with ethanol.

The electrolyte's original color was yellow, which switched into the red once the pH slows down below 3.5 using thymol blue as an indicator solution (4.2 for methyl red). Both 3.5 and 4.2 pH values were determined by an original assay, used as a titration method, applied on a blank solid electrolyte (yellow color and pH=6.89): in each step of the assay 0.1 ml of a 0.01 M HCl solution were added into a neutral 0.6 M (or 0.06 M) NaCl solution and, after stirring the solution with a magnetic bar, its pH was determined using a pH-meter.⁽²⁾ Then, a drop of this solution was applied on the blank's surface while a picture was being taken. The images obtained were analyzed using a proper software video,⁽³⁾ to accurately determine the pH value with which the blank's original yellow color turns into red.

The positioning of the sensor (electrolyte) can be clearly distinguished in Figure 1. The color transition is a consequence of the electrochemical Reaction 2, which produces ions H^+ on the AA electrode's surface. This species' generation promotes a transient acid front (arrows in black), tracked using a reflex camera (60 frames per second) with a unique lens.⁽⁴⁾ It should be noted that data collection was carried out every 800 frames. The videos obtained were also analyzed with the video software to clearly distinguish the red (or pink) front's evolution.

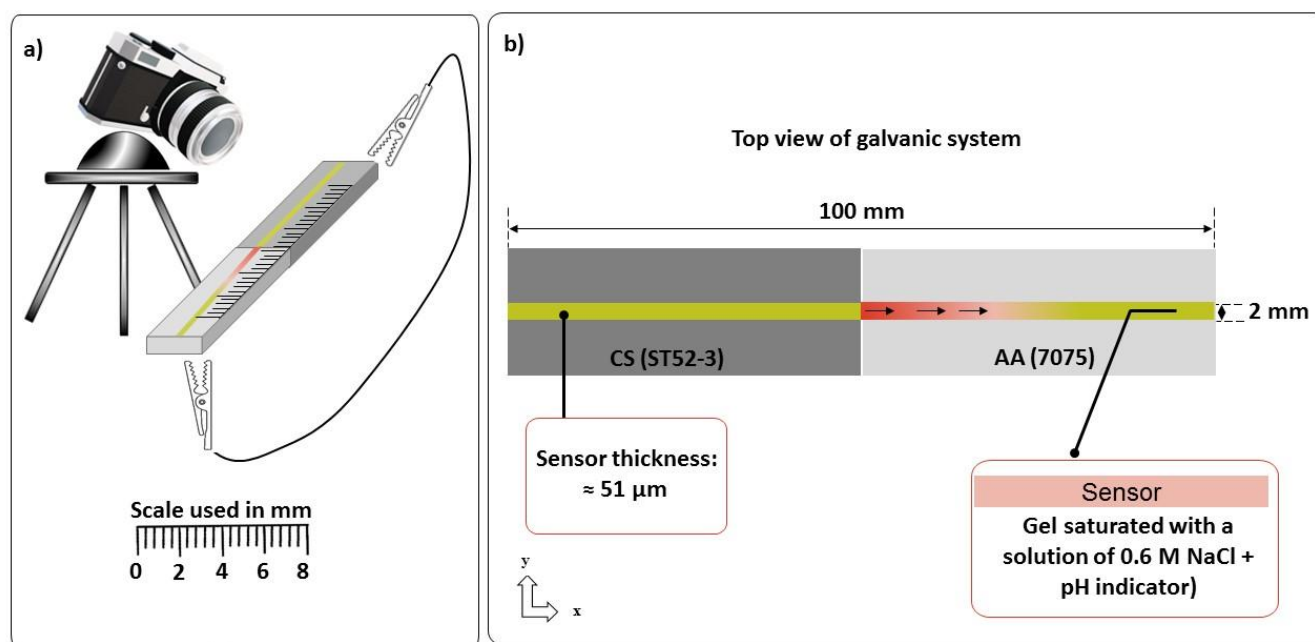


Figure 1: Schematic picture of the experimental setup used to track pH fronts. b) zoom with dimensions of the galvanic corrosion system. The metallic couple is covered with a micrometric sensor (gelled electrolyte + thymol blue); the black arrows show transient evolution of the H^+ species.

Modeling

The theory behind the numerical approximation for thin electrolyte films was taken from previous work by Ruiz-Garcia et al.², where a spatial dimension reduction was achieved according to Figure 2, which schematically describes how a 2D system could be simplified into a 1D case. The bottom boundary

⁽²⁾ Thermofisher Orion Star A329.

⁽³⁾ Tracker 5.0 video analysis software

⁽⁴⁾ Nikon F-S DX Micro-NIKKOR 40 mm f / 2.8 G.