On-line volumetric analysis of cathodic gas formation using a microfludic system

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Introduction

Gas formation reactions are ubiquitous in corrosion and surface treatment phenomena. The textbook example would be the dissolution of a metal in a strong acid in which the anodic dissolution of the metal is balanced by the cathodic reduction of H^+ ion into hydrogen gas leading to the standard mixed potential theory of corrosion. Another classic example would be the anodization of aluminum at high potential in which oxide formation competes with oxygen formation. More complex mechanisms would include the so-called "negative difference effect" observed for Mg dissolution in which the cathodic reduction of hydrogen increases with increasing anodic potential [1] or the "cathodic corrosion" of aluminum in which the aluminum dissolution rate increases with an increasing cathodic reaction [2]. These mechanisms do not follow the standard mixed potential hypothesis and it is a challenging task to characterize their elementary rates from dynamic electrochemical measurements alone.

As a means of characterizing the dissolution mechanisms of complex materials, we have developed the *atomic emission spectroelectrochemical* (AESEC) method that allows us to measure the elemental rates of dissolution from complex alloys [3, 4]. Through a number of recent publications we have demonstrated that AESEC may yield considerable insight into the nature of the anodic reaction with a consequent insight into the corrosion and passivation mechanisms. Many corrosion mechanisms however also require an independent measurement of the cathodic reaction. In this work, we have extended modified the basic AESEC apparatus to include an on-line measurement of the volume of gas produced simultaneously with the dissolution of the metal components.

Experimental

Atomic emission spectroelectrochemistry (AESEC) is a coupling between an electrochemical flow cell and an inductively coupled plasma optical emission spectrometer (fig. 1). An electrolyte passes continuously over the surface of the working electrode. Dissolved species released by the reaction between material and electrolyte are carried by the electrolyte to the spray chamber of the ICP-OES to be quantitatively analyzed. When the electrolyte contacts the surface there can also be gas generation leading to the formation of bubbles, sometimes visible to the naked eye. The bubbles may also break away from the surface and be carried downstream towards the ICP-OES.

The novelty of the present work was to add a system between the flow cell and the ICP-OES to visualize and record the gas bubbles in the capillary system as they move between the electrochemical flow cell and the ICP-OES. A simplified block diagram is given in Fig. 1. The electrolyte with gas bubbles is channeled into a microfluidic system composed of PDMS (polydimethylsiloxane) microsystem using standard lithographic techniques of preparation. The rectangular channel was 2 cm x 1 mm x 0.180 mm thick. The video images were recorded at 830 images per second. Following the acquisition, a special software is used to (i) recognize individual bubbles, (ii) measure their velocity, and (iii) estimate their 2 dimensional surface area. The later is used to estimate the total volume. Since the 2D diameter of the bubble is >> diameter of the channel. In this way, the volume of gas as a function of time may

be generated with a time resolution on the order of the time required for the formation and detachment of a bubble.

One major complicating factor is that gas bubbles may coalesce and create long chains of gas, leading to bubbles that are wider than the optical field. There we use a T-junction to break the large bubbles into a series of smaller bubbles as has been done with predroplets and bubbles with a continuous flow [5]. The challenge was to adapt this technical solution to a non continuous flow of bubbles with varying size. Figure 1 shows the final version of the T-junction microsystem the principle of bubbles breaking up. The algorithm to approximate the volume and velocity of individual bubbles was developed by R&D Vision.



Figure 1: Simplified schematic diagram of the atomic emission spectroelectrochemistry coupled with a microfluidic system and high speed camera acquisition set up for on-line volumetric analysis of gas.

The conversion of volume into moles of hydrogen also requires a measurement of the pressure which is not atmospheric due to the capillary pressure in the tubes and the effect of the pump and aspiration system for the ICP-OES. Therefore, pressure is measured at the outlet of the microsystem using a pressure sensor.

Results and Discussion

Using the above apparatus, it is possible to measure the volume of individual bubbles as a function of time. **Fig. 2** shows an example of this measurement for the reduction of hydrogen on Pt at an applied cathodic current of -100 mA in which the faradaic current all leads to the formation of hydrogen gas. Each individual point represents a single gas bubble.



Unfortunately, an independent pressure measurement was not available at the time of this experiment. However analysis of the data would suggest that the pressure within the rectangular channel was approximately 2x the atmospheric pressure in the room. Although an absolute volume x pressure measurement is desirable, data such as Fig. 2 may be used to calibrate the system.

The example of Fig. 2 represents a very large cathodic current. However, the sensitivity of the technique is very large as it is possible to detect single bubbles on a μ m scale.

In this presentation, the technique will be applied to understand the reactivity of Mg and Al-Mg-Cu containing intermetallics.

References

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