

A Study on the Local Electrochemical Processes Inside Cavities

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Abstract. In this paper, a set of experiments scanning real potential variations inside cavities under current control were employed to characterize local electrochemical information. The limiting diffusion current and the critical currents sustaining the supersaturation of dissolved gas and completed oxide film-formation were selected as the reference currents. It is demonstrated that for gas-evolving electrode, only the bubble sealing the cavity remarkably increases the total potential variation within cavities. Combined with the theoretical analysis and measurement results, kinetic parameters range inside cavities can be indirectly derived.

Introduction

Cathodic polarization of a metal surface with a cavity or pit, as often happens under conditions of cathodic protection, electroplating and electrocoagulation technology [1,2]. The presence of cavities strongly accentuates the spatial non-uniformity of the potential and current distributions on the metal surface and within the depth of the cavity. Related modeling and simulation were based on theoretical idealizations of the actual physic-chemical conditions, so that the quantitative and predictive values of the local electrochemical information inside cavities were not emphasized [3,4].

Fundamentally, the electrochemical information distribution inside cavities can be measured by scanning methods. However, the small area techniques that allow polarizing the microscopic surface areas do not apply to the scanning experiments [5,6]. In this work, we present a novel set of experiments scanning potential distributions inside cavities using a micro-reference electrode in typical three-electrode cell. Titanium is being studied since the experiences in its mechanisms of cathodic polarizations can help to design experiments. Our study has shown that the proposed approach is valuable for indirect derivation of the local electrode information but also for the direct evaluation of gas evolution and completed oxide film-formation effects on the electrochemical process evolutions within cavities in the practical conditions.

Experiments

Commercial titanium Grade 2 rods of $\phi 7\text{mm} \times 12\text{mm}$ were used as the specimens. The investigated cavity with a diameter 2mm and a depth 10mm was drilled in the middle surface of cylindrical specimens. The solutions of 1% and 5% aqueous NaCl were prepared from analytical reagent grade chemicals and distilled water.

The typical three-electrode cell was used. A Unisense micro-reference electrode REF-10 (silver/silver-chloride) with the outside tip diameter 8-12 μ m was fixed in the holder of MM33 micromanipulator mounted on a heavy laboratory stand. A platinum counter-electrode was processed into L-shape with a round cavity in the middle to allow the microcapillary pass through.

All scanning measurements were performed in constant current mode using a CHI660D potentiostat. The typical current densities and solution concentrations were chosen according to the results of potentiodynamic curves carrying out on the flat surface of specimens. Each potential-time monitoring experiment was repeated at least three times, with a fresh specimen being used for each test.

Results and Discussion

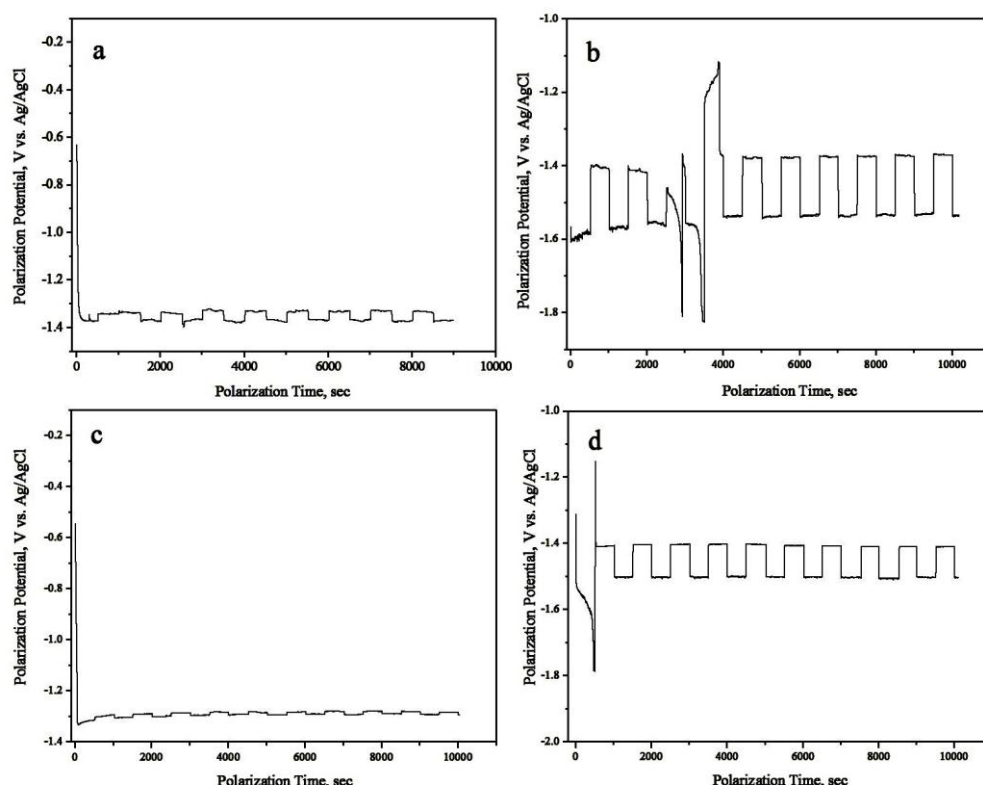


Fig. 1 Cathodic potential variations inside the 10mm-depth cavity in titanium electrode measured in 1% (a, b) and 5% (c, d) NaCl at current densities of 10^{-4} (a, c) and 10^{-3} (b, d) A/cm^2 .

Fig. 1 shows the variation amplitudes of the cathodic polarization potential within the 10mm-depth cavity of pure titanium specimens in 1% and 5% NaCl at current densities of 10^{-4} and 10^{-3} A/cm^2 . It is found that the curves show the regular “square wave” feature. In 1% NaCl the variation amplitudes are about 50 and 200mV at 10^{-4} and 10^{-3} A/cm^2 respectively. The absolute potential at cavity opening is expectedly higher than that at cavity bottom. Anomalous potential variations at 10^{-3} A/cm^2 in the time range 2500 to 6000 seconds reach about 800mV as a result of hydrogen accumulation inside the cavity. During this time range the bubble coalescence, growth and detachment can be observed at the cavity opening. After the bubble departure, the potential quickly continue the previous value. It is important to note that for most of the cathodic polarization time bubbles with much smaller diameters d_b than the cavity diameter d_c , continuously escape from the cavity. However, only when the bubbles coalesce to one

larger bubble attaching and sealing the cavity opening, the total potential variation remarkably increases. In present experiment conditions, the net effect of the bubble evolution is the expected overpotential increase. The ohmic effects associated with electrode-surface screening by attached large bubbles are predominant. The large amount of small size bubbles have little effect on the total potential variation.

In 5% NaCl the big potential variation about 700mV caused by hydrogen accumulation appears at the first 500 seconds of 10^{-3} A/cm². For the rest of monitoring time, the potential variation amplitudes are about 10 mV and 100 mV for 10^{-4} and 10^{-3} A/cm² respectively, lower than the values measured in 1% NaCl. The total overpotential variation $\Delta\eta_{(h)}$ between the cavity opening and the depth h into the cavity can be expressed as Eq. (1):

$$\Delta\eta_{(h)} = \Delta\eta_{\Omega l(h)} + \Delta\eta_{a(h)} + \Delta\eta_{c(h)} \quad (1)$$

where the subscripts “ Ω ”, “a” and “c” stand for “solution ohmic”, “activation” and “concentration”, respectively. With primary and secondary current distribution both considered, the activation overpotential variation $\Delta\eta_{a(h)}$ of hydrogen evolution can be given by the following equation:

$$\Delta\eta_{a(h)} = b \log \frac{R_{(h)} + R_{p(h)}}{R_{(o)} + R_{p(o)}} \quad (2)$$

where b is Tafel constant of hydrogen evolution reaction, $R_{(o)}$ and $R_{(h)}$ are the resistances of the solution in the electrolytic cell and within the cavity, and $R_{p(o)}$ and $R_{p(h)}$ are the polarization resistances at the cavity opening and the depth h into the cavity. The cathode polarization curves show the limiting diffusion current I_d for oxygen is about 10^{-5} A/cm² in the present experiments. Therefore, at 10^{-4} and 10^{-3} A/cm² that are greater than ten times I_d for oxygen, the presence of dissolved oxygen has little effect on hydrogen overpotential [7, 8]. Thus, the $\Delta\eta_{(h)}$ can be expressed by Eq. (3).

$$\Delta\eta_{(h)} = \Delta\eta_{\Omega l(h)} + b \log \frac{R_{(h)} + R_{p(h)}}{R_{(o)} + R_{p(o)}} \quad (3)$$

According to the resistivity diagram of NaCl solutions, the solution ohmic resistance R_o and R_h are calculated as 12 Ω and 10350 Ω for 1% g/l solution, and as 3 Ω and 2866 Ω for 5% g/l solution, respectively. Besides, the Tafel constant b is calculated as 0.134 by the following equation

$$b = \frac{\phi_2 - \phi_1}{\log i_2 - \log i_1} \quad (4)$$

Based on these data, if only primary current distribution is considered, the $\Delta\eta_{a(h)}$ can be calculated as 400mV, which is much higher than the experiment values without the presence of the larger bubble. Therefore, in the current range from 10^{-4} A/cm² to 10^{-3} A/cm², the secondary current distributions play a significant role. Consequently, with the primary and secondary current distribution both considered, the average current density j_{ave} and the $R_{p(o)}$ values range can be indirectly derived. At 10^{-4} A/cm², the j_{ave} is less than 7.7×10^{-6} A \cdot cm⁻² and 3.1×10^{-5} A \cdot cm⁻² for 1% g/l and 5% g/l NaCl solution, respectively; the $R_{p(o)}$ is higher than 4385 Ω and 335 Ω for 1% g/l and 5% g/l NaCl solution, respectively. Thus, the internal surface within the cavity has lower current densities by one or two orders of magnitude than the cavity opening surface. Obviously, the more testing depths applied in the experiment design, the more accurate values can be calculated.

Summary

In summary, this paper shows a novel approach of scanning real potential variations for the visualization of local polarization processes inside cavities in titanium electrode. The experimental results validate those anomalous potential distributions associated with gas evolution and completed oxide film formation that remained unverified up to now. Combined with the theoretical analysis, these measurements allow indirect derivation of local electrode information by means of increasing the testing points of different depths within the cavity.

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