Application of \textit{in situ} digital holography to the study of the effect of a magnetic field on the anodic dissolution of iron in trichloroacetic acid

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Abstract: The effect of a magnetic field on the anodic dissolution of iron in 1.0 mol dm\textsuperscript{-3} trichloroacetic acid solution was studied by the potentiodynamic polarization method and \textit{in situ} digital holography. It was found that the magnetohydrodynamic force increased the mass transport, which resulted in a faster anodic dissolution of iron. The effect of the magnetic field was analyzed by holograms and is discussed in terms of the magnetohydrodynamic force.

Keywords: digital holography, magnetic field, magnetohydrodynamic (MHD) force, anodic dissolution, iron.

INTRODUCTION

The effect of an externally imposed magnetic field on electrochemical processes has been extensively studied in the past years. The processes of mass transport, electrode kinetics and deposit morphology can all be influenced by a magnetic field. Reviews concerning the effect of a magnetic field on electrochemical reactions were given by Fahidy\textsuperscript{1} and Tacken and Janssen.\textsuperscript{2} White \textit{et al.} reported the ability of the magnetohydrodynamic (MHD) force to establish well defined MHD flows within nanoliter volumes of solution adjacent to the electrodes of micrometer and submicrometer diameters.\textsuperscript{3,4} The anodic dissolution of iron in sulfuric acid solution was studied and the results showed that the magnetic field had obvious effects on the processes.\textsuperscript{5–7}

Laser interferometry was used by O’Brien to study the effect of a magnetic field on electrochemical reactions.\textsuperscript{8,9} Digital holography was used recently in our lab to study the dynamic changes at the electrode/electrolyte interface during electrochemical reactions.\textsuperscript{10} The results showed that the method offered a new approach to ob-
tain information about the diffusion layer, the concentration gradient, etc. In the present work, the same technique was used to investigate the anodic dissolution of iron in trichloroacetic acid in a weak magnetic field in an attempt to understand its effect through *in situ* dynamic observations of the electrode/electrolyte interface.

**EXPERIMENTAL**

A stationary iron disk electrode (Aldrich, 99.9 %), 2 mm in diameter, was used as the working electrode. It was carefully sealed with a very thin layer of epoxy resin in a glass tube, leaving only the end of the rod exposed to the solution during the electrochemical tests. A large sheet of platinum was used as the counter electrode. The reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary placed between the working electrode and the reference electrode. All potentials reported here are with respect to SCE. The iron electrode was mechanically polished with emery papers to a mirror-like brightness and then cleaned with alcohol and triply distilled water in an ultrasonic bath before each experiment.

The electrolyte, 1.0 mol dm\(^{-3}\) CCl\(_3\)COOH solution, was prepared from reagents of analytical grade and triply distilled water. All experiments were carried out at room temperature. Voltammetric measurements were performed using a CHI602A electrochemical station.

The holographic light path, the configuration of the magnets and the setup of the electrochemical cell are illustrated in Fig. 1. For the convenience of holography recording, a pair of small permanent magnets was used. The magnetic field strength \(B\) of the applied magnets was measured by a Gaussmeter via a Hall probe. The degree of nonuniformity of the magnetic field in the experimental area was not more than 2 % at a magnetic strength of 55 mT. The magnetic field was applied parallel to the surface of the disk electrode. The electrochemical cell was centered carefully between the pole faces prior to each experiment. The working and counter electrodes were placed horizontally facing each other.

The theory and the procedure of digital holography were detailed in a previous paper.\(^{10}\)
RESULTS AND DISCUSSION

The potentiodynamic polarization curves of the iron electrode in 1.0 mol dm\(^{-3}\) CCl\(_3\)COOH solution with and without magnetic field are shown in Fig. 2. The whole curve can be roughly divided into three ranges: the active range, the prepassive range and the passive range. When the potential was below \(-0.2\) V, the effect of the magnetic field could be neglected, but in the prepassive range, the magnetic field caused an increase in the current.

![Fig. 2. Potentiodynamic polarization curves of the iron electrode in 1.0 mol dm\(^{-3}\) CCl\(_3\)COOH solution at 10 mV/s with and without an applied magnetic field.](image)

The dynamic processes were recorded \textit{in situ} by digital holography. Figures 3 and 4 show holograms of the Fe/electrolyte interface obtained at different points on the \(I-E\) curves. Figures 3a and 4a were obtained at the open circuit potential of the reference. The right, darker side of the holograms presents the electrode part and the left, brighter side presents the solution part. The fringes in the solution part were caused by the interference of the object wave and the reference wave.

Figure 5 shows the production of the holograms. When the object wave part (Fig. 5a), interfered with the reference wave (Fig. 5b) at the beam splitter cube, hologram Fig. 3a with fringes appeared. The fringes were very sensitive to the surroundings. The concentration of the solution in the vicinity of the electrode surface changed during the electrochemical reactions, which in turn affected the refractive index of the solution. The fringes were deformed accordingly. The density of the fringes in the holograms relates directly to the concentration gradient: the steeper the concentration gradient, the denser the fringes.

As the potential was swept anodically, the rate of iron dissolution increased. The concentration diffusion layer appeared at the electrode/electrolyte interface, as shown in Fig. 3b. The previous open circles of the fringes began to close at the interface. As the process continued, the fringes at the interface became denser and
denser (Figs. 3b–3d), and the circles extended leftwards to the solution part. When the current dropped to almost zero, passivation began and the fringes extracted gradually (Fig. 3e). There are some differences between Fig. 3 and Fig. 4 when a magnetic field was applied parallel to the electrode surface. The fringes in Fig. 3 are symmetrical, but they are bent to one side in Fig. 4, as indicated by the arrows.

Fig. 3. Holograms of the iron/solution interface obtained at different points on the I–E curve when the iron electrode was anodically polarized in 1.0 mol dm$^{-3}$ CCl$_3$COOH at 10 mV/s without a magnetic field. Image a) was obtained at open circuit potential.
The experimental setup of the electrode and the magnetic field is shown in Fig. 6. The magnetohydrodynamic force ($F_{\text{MHD}}$) arises from the motion of charged ions across the lines of magnetic flux. The magnetic field was in parallel to the electrode surface, hence the $F_{\text{MHD}}$ was directed along one side of the electrode and was perpendicular to the plane containing the direction of the charging ion $v$ and the magnetic field $B$, as shown in Fig. 6. The force produced an increase in mass transport.

![Holograms of the iron/solution interface obtained at different points on the $I$–$E$ curve when the iron electrode was anodically polarized in 1.0 mol dm$^{-3}$ CCl$_3$COOH at 10 mV/s with magnetic field of 55 mT parallel to the electrode surface. Image a) was obtained at open circuit potential.](image)

Fig. 4. Holograms of the iron/solution interface obtained at different points on the $I$–$E$ curve when the iron electrode was anodically polarized in 1.0 mol dm$^{-3}$ CCl$_3$COOH at 10 mV/s with magnetic field of 55 mT parallel to the electrode surface. Image a) was obtained at open circuit potential.
In the potential region of active dissolution, the rate determining step for the anodic dissolution of iron is the electron-transfer step, which is not affected by a magnetic field. However, there is a dynamic equilibrium of the formation and dissolution of porous Fe(OH)$_2$ in the prepassive range:

\[
\text{(Fe}^{2+})_a + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2, \text{film} \quad \frac{2\text{H}^+}{\text{Fe}^{2+}} \rightarrow (\text{Fe}^{2+})_b + 2\text{H}_2\text{O} \quad (1)
\]

The electrodissolution of iron in this region depends mainly on equilibrium (1). The mass transfer rate should be increased when a magnetic field parallel to the electrode surface is applied. The $F_{\text{MHD}}$ even caused the fringes to bend to one side in the holograms, as shown in Fig. 4c. The $(\text{Fe}^{2+})_b$, formed by the dissolution of the Fe(OH)$_2$ film, driven by the $F_{\text{MHD}}$, moved faster to the bulk solution, hence $v_2$ increased. The rate $v_1$ in equilibrium (1) would in turn increase to maintain the equi-
librium, which caused a faster dissolution of iron, which can be seen from the $I-E$ curves in Fig. 2.

**CONCLUSION**

1) The magnetohydrodynamic force increased the anodic dissolution of iron in 1.0 mol dm$^{-3}$ trichloroacetic acid by accelerating the mass transport.

2) Digital holography can be used to investigate the effect of a magnetic field on electrochemical processes.

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**REFERENCES**