Automatic monitoring refractive index variations of transient solution during electrochemical reactions

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ABSTRACT

We propose and experimentally demonstrate the automatic measurement of 2D refractive index (RI) changes in aqueous solution at electrode/electrolyte interface based on a Mach-Zehnder interferometer. During the electrochemical reactions, local variations of the electrolyte's RI, which correlate with the concentration of dissolved species, change the phase of the object beam when the beam pass through the electrolyte. With the application of an adaptive band-pass filter, the RI changes can be obtained automatically from interferograms, which enable direct visualization of the concentration change of the soluble species. As a proof of principle demonstration, the system is employed to detect the soluble species during the potentiodynamic sweep of the copper electrode in 0.5 mol dm^{-3} NaBr solution at 10 mV s^{-1}. The RI changes at the Cu/NaBr solution interface provide direct evidence of the reaction mechanisms of copper corrosion in NaBr solution.

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1. Introduction

The measurement of the refractive index (RI) of liquids is an important work in engineering and science. Many techniques for sensing of RI changes have been developed [1–10], such as the refractometry [1–3], reflectometry [4], interferometry [5–8] and other novel sensors [9,10]. The interferometric technique is one of the most widely used techniques for the RI field study because it is not only a whole-field technique but also a convenient and noninvasive tool for studying the dynamic changes of RI that can shed light on dynamic processes.

The sensing of the RI fields has been of great importance in chemical and biological applications since a number of substances can be detected through measurements of the RI [11–18]. In recent years, applied electrochemists and corrosion scientists have paid more and more attention to develop and utilize optical interferometric technique to study mass transfer processes, which is based sensing of RI changes in aqueous solution [12–18]. It can give more insights in the study of fluids dynamics, not only because it is important to measure the refractive indices and concentrations precisely, but also it is often essential to obtain those data as a function of time and space in a dynamic problem. Eckert and Yang

developed a Mach-Zehnder interferometer to measure the concentration field [13] and study the substantial MHD convection effects of an inhomogeneous magnetic field on copper electrolysis [14]. Tada applied Mach-Zehnder interferometry and shadowgraphy to investigate the concentration field of Zn^{2+} during galvanic corrosion of a Zn/Steel couple successfully [15]. In situ observations have been carried out in our laboratory using digital holographic interferometry to study the dynamic processes of electrochemical reactions [16,17]. The optical interferometric technique offers a simple means to study subtle changes at the electrode/electrolyte interface. The dynamic changes in transparent liquid solutions at the interface during electrochemical reactions are useful information to study the electrochemical and corrosion processes. Recently, for fast, quantitative and simultaneous measurements of the dynamic concentration changes in solution, digital image processing method has been used to analyze the interferogram sequences obtained by the interferometer and a band-pass filter were employed to abstract phase information from the interferograms [18]. However, when the RI changes in the solution experiences both increase and decrease in one processing procedure, the filter with fixed window parameter might fail in signal extraction during the image/video processing. The window parameter of the filter should be adjusted manually during the experimental measurement, which had limited its applications in the study of electrochemical and corrosion processes.

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In this work, we focus on the development of an automatic RI variations measurement system of electrolyte at metal/solution interface. An adaptive band-pass filter is utilized during the measurements. This system is employed to monitor the RI change at the electrode/electrolyte interface caused by the change of the soluble species during the potentiodynamic sweep of the copper electrode in NaBr solution. The distributions of the RI changes are presented to observe the mass transfer processes visually. It provides the direct information and high sensitivity for the analysis of soluble species during the dynamic processes, which has been proved to be effective to study mechanisms of copper corrosion in bromide solution. The design and characterization of the system with the adaptive band-pass filter is described in detail.

2. Materials and methods

2.1. Experimental setup

The optical system based on a Mach–Zehnder interferometer is the same as [18]. As illustrated in Fig. 1, a light beam with the wavelength of 632.8 nm was generated by a He–Ne laser. It was split into two beams: one acted as object beam and the other as reference beam. The object beam passed through the electrolyte near by the working electrode in an electrochemical cell, which finally combined with the reference beam after a beam splitter cube. The interference between the object beam and the reference beam created the interferograms. A CMOS image sensor was placed in front of the beam splitter cube to record the interferograms.

The electrochemical cell was a quartz glass cuvette with an inner volume of 100 ml, as shown in Fig. 2. The working electrode was a copper rod with a diameter of 2 mm (Alfa Aesar, 99.99%) sealed in a glass tube, with one end of tube sanded flat to expose the surface of copper. The three electrode system was used in each test. A large sheet of platinum (0.8 cm × 2.8 cm) and a saturated calomel electrode (SCE) with a Luggin capillary served as counter electrode and reference electrode, respectively. The electrode location and the coordinate system are illustrated in Fig. 2. The electrolyte was 0.5 mol dm^{-3} NaBr solution which prepared from reagents of analytical grade and triply distilled water. The potentiodynamic measurement of the current density (scan rate 10 mV s^{-1}) was performed by means of CHI660B electrochemical station at room temperature (20 ± 0.5 °C).
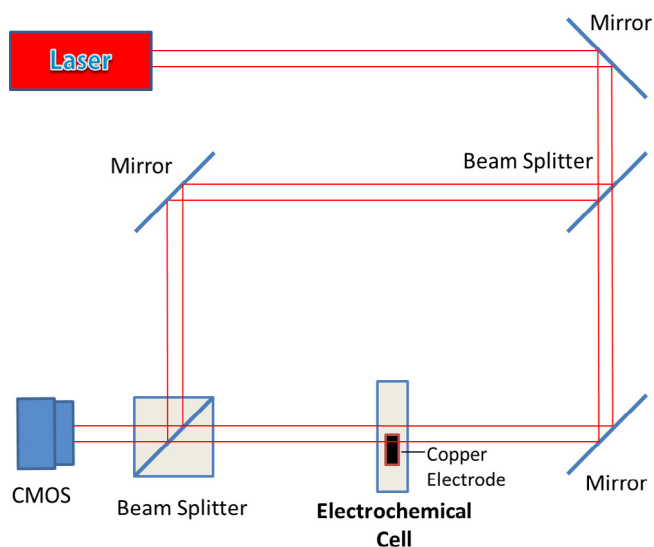

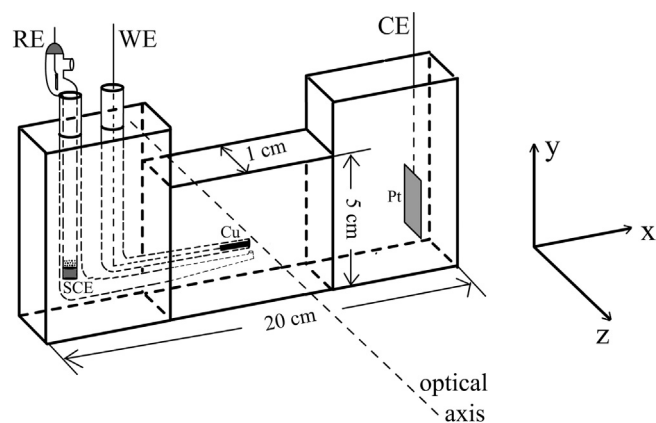Fig. 1. Schematic illustration of the optical system.

Fig. 2. Schematic diagram of the electrochemical cell. RE, reference electrode; WE, working electrode; CE, counter electrode.

During the measurement, the solution concentration and its refractive index near the surface of the copper electrode were changing with the reactions proceeding. The variations of RI led to change of optical path length of the object beam, which gave rise to deformations of the interference fringes. When the electrochemical reactions were carried out, the interferograms were recorded by a CMOS image sensor and then processed by a personal computer.

2.2. Theoretical background

Several components coexist in electrolytes in most electrochemical systems, thus the concentration change of individual species cannot be determined by the interferometer. As a substitute, the RI changes closely related to concentration change can be determined quantitatively. The main cause of the RI changes can be tracked for the exploration of reaction mechanisms. The interferometric principle is based on the change in RI when there is a change in concentration or temperature. In the absence of large pressure fluctuations, the RI n of a multi component mixture is a function of its concentration C, temperature T and the wavelength of the incident light λ [19].

$$n = n(C, T, \lambda) \tag{1}$$

Hence the change of RI Δn for a multi component mixture, for small changes in the concentration, temperature and wavelength is given by,

$$\Delta n = \frac{\partial n}{\partial C}\Delta C + \frac{\partial n}{\partial T}\Delta T + \frac{\partial n}{\partial \lambda}\Delta \lambda \tag{2}$$

For a monochromatic light source like laser, $\Delta\lambda \approx 0$. In the current study, the concentration of soluble species at the electrode/electrolyte might change with the time during the electrochemical reactions while the temperature of electrolyte changes slightly. Thus, the latter two terms can be deleted in Eq. (2). The change in the phase of the object beam is brought about by the change in the RI inside the cell, which is associated with the changes of concentration caused by the electrochemical reaction. The relationships among the solution RI (Δn), the phase difference ($\Delta\phi$) and the solution concentration (ΔC) was formulated as,

$$\Delta n = (\lambda_0/2\pi d)\Delta\phi = (1/k)\Delta C \tag{3}$$

where k is the concentrative refractivity; λ_0 is the wavelength of the laser light; d means the geometrical path length where the RI variation exists. Generally, several components are present in the solution in most cases. Thus, the RI variation in the cell is the summation of the effect of each species' concentration,