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Application of FT-Raman spectroscopy to the study of the benzotriazole inhibition of acid copper corrosion

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Abstract—The initial stages of the corrosion protection of copper surfaces by benzotriazole in sulfuric acid solution are investigated using FT-Raman SERS and X-ray photoelectron spectroscopy. Spectra are measured in the presence of ppm levels of inhibitor on a copper surface *in situ*. The dependence of the adsorbate spectra on the electrode potential, solution pH, oxidation/reduction cycles and time is observed. Good spectra are obtained from copper electrodes prepared using *in situ* oxidation/reduction cycling in low pH sulfate solutions free from chloride at negative potentials.

Keywords: FT-Raman, NIR, copper, corrosion inhibition, benzotriazole.

INTRODUCTION

THE USE of chemical reagents to inhibit corrosion is an important technological procedure. The inhibitors minimize corrosion by interacting with the metal surface and preventing or retarding the rate of the electrochemical corrosion reactions. This inhibition is generally achieved using low concentrations of reagents in the parts per million range (ppm). There are few techniques which have the required sensitivity to directly investigate the interaction of inhibitors with a metal surface. Surface enhanced Raman scattering (SERS) is a useful method for investigating the interaction of inhibitors at appropriate metal surfaces. Using the technique it has been possible to obtain Raman spectra of inhibitor molecules as they interact with a metal surface in the inhibition process. There has been considerable interest in the theoretical basis of the enhancement of the Raman signal. Enhancement can be of the order of 10^6 times [1], and this has enabled the spectroscopic investigation of adsorbates at electrode and colloid surfaces. Benzotriazole (BTAH) is an effective inhibitor for copper corrosion and this system has been used to demonstrate the *in-situ* capability and sensitivity of the technique [2–4]. The recent development [5–7] of Fourier transform Raman spectroscopy (FT-Raman) instruments has simplified the collection of SERS data. The FT-Raman instrument allows the easy acquisition of high signal to noise data suitable for sophisticated data analysis. This access to information at the molecular interaction level, combined with electrochemical techniques, will lead to substantial advances in the understanding of the behaviour of inhibitors and plating additives.

The interaction of BTAH with a copper surface is interesting because the inhibition process involves the formation of a complex copper(I) BTA polymer [8–10]. This polymer formation may be preceded by reaction between copper and BTA^- [8, 11] or the adsorption of BTAH molecules onto the copper surface. The mechanism of the reaction is amenable to SERS investigation. Appropriate selection of solution pH and the applied copper electrode potential would enable the initial stages of the inhibition process to be observed using SERS. This is also assisted by the minor effect that sample fluorescence has on most systems studied with FT-Raman. At basic pH the BTAH molecule is predominantly ionized to form BTA^- ions which can react with the copper surface. At low pH the investigation of the initial stages of inhibition can be investigated prior to the formation of the thick polymeric inhibition film. The information obtained from the SERS spectra would be particularly valuable to assist with elucidating the nature of the initial chemical reaction which precedes the formation of the corrosion

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inhibiting BTA–Cu(I) film on the metal surface. This paper describes our investigation of the initial interaction of BTAH with a copper electrode surface in sulfuric acid solution.

EXPERIMENTAL

Electrochemistry

The working electrode (WE) was a 6 mm disc machined from a block of 99.99% purity electrorefined copper obtained from Copper Refineries Pty Ltd, Townsville. The WE was mounted on the end of an assembly constructed from Teflon and stainless steel and this assembly was held in turn in a Teflon B34 cone and sealed with neoprene O-rings. The cell was constructed from a 55 mm pyrex tube with a B34 socket on one end and an optically flat quartz window on the other end. The electrode surface could be moved relative to the quartz window when required. Three B14 connectors were located on the top of the tube for insertion of the Luggin capillary, gas inlet/outlet and a platinum counter electrode. A drain tap on the lower side of the tube enabled the cell electrolyte to be removed and the cell rinsed inside the spectrometer. The construction was similar to cells described by FLEISCHMANN *et al.* [6]. The electrode surface was wet abraded with successively finer grades of silicon carbide paper to 1200 mesh and rinsed with distilled deionized water prior to being used in the electrochemical cell. The reference electrode was a silver/silver chloride model MI 410 supplied by Microelectrodes Inc., Londonderry, NH. Electrode potentials were controlled by a MP81 Bank Elektronik potentiostat. All potentials listed are relative to the silver/silver chloride electrode.

Analar grade HNO_3, H_2SO_4, CuCl and KCl were used as supplied by Ajax chemicals, Sydney. BTAH was used as supplied by Hopkin and Williams Ltd, Chadwell Heath. All solutions were prepared using distilled deionized water. The cell, counter electrode and working electrode holder assembly were cleaned between experiments with AR nitric acid. The copper electrode surface required activation using oxidation reduction cycles (ORC) in order to obtain optimum SERS activity. The 2 M sulfuric acid electrolyte could be used to produce a suitable surface for use in the BTAH SERS investigation after 3–4 ORC switched between 0.3 and −0.5 V vs Ag/AgCl. The oxidation and reduction voltages were maintained for 20 s prior to reversing the potential. A minimum electrolyte volume of 50 cm^3 ensured that the solution pH was not altered by the ORC procedure. The electrode was generally activated in acid in the cell prior to addition of BTAH. Electrodes could be prepared in 2 M sulfuric acid electrolyte containing BTAH at the ppm level with similar effect. There appeared to be no SERS requirement for chloride ions in this system, and the presence of chloride ions was carefully avoided to ensure that competing surface reactions and possible formation of $CuClBTAH_2$ was prevented.

Solid Cu(I)Cl BTAH was prepared by the reaction of CuCl with BTAH in CH_2Cl_2 using a similar procedure to that described by RUBIM *et al.* [2].

Raman spectroscopy

Raman spectra were collected on a Perkin Elmer System 2000 FT-Raman spectrometer equipped with a Spectron Laser system SL301 Nd:YAG laser emitting at 1064 nm, a quartz beamsplitter and an InGaAs detector operated at room temperature. Typically the resolution was 8 cm^{-1} the mirror velocity was 0.1 cm s^{-1} and the laser power was 200 mW. Fifty scans were co-added to achieve spectra of acceptable signal to noise ratio. All spectra are uncorrected for instrument background. Any spectral data manipulation was performed with the Perkin Elmer infrared data manager (IRDM) software package.

Photoelectron spectroscopy

The X-ray Photoelectron Spectroscopy (XPS) spectra were recorded using a Perkin Elmer 560 ESCA/SIMS double-pass CMA with an angle resolvable aperture; Mg Kα X-ray radiation was obtained from a dual Mg anode source operated at 500 W, 15 kV. The band pass energy was 100 eV for survey and 50 eV when recording individual bands. The photoelectron signal obtained from a freshly sputtered gold coupon was used to calibrate the spectrometer in the region of interest. The Au $4f_{7/2}$ band was assumed to occur at an energy of 83.86 eV. Measurements were made under control of 560 MACS version VI software, and data was transferred to Macintosh Classic II for processing.