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Spectroelectrochemical investigations of flotation reagent–surface interaction

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Abstract

Surface enhanced Raman scattering (SERS) spectroscopy at surfaces under electrochemical control has been applied to elucidate the adsorption of thiol collectors. SERS spectroelectrochemical studies at coinage metal electrodes have been carried out on ethyl xanthate, and three isoxanthates, *O*-isopropyl-*N*-ethylthionocarbamate, 2-mercaptobenzothiazole, diisobutyldithiophosphinate and butylethoxycarbonylthiourea. For each collector, adsorption occurs via charge transfer to form a metal–sulfur bond and, in situations for which the reversible potential of the formation of the bulk phase is known, at underpotentials. Mercaptobenzothioazole was detected on chalcopyrite after immersion in a solution of the collector after the deposition of gold to induce SERS.

Keywords: Flotation collectors; Redox reactions; Mineral processing; Surface modification; Sulphide ores; Chalcopyrite

1. Introduction

The key chemical step in the flotation process is the adsorption of the organic collector on selected mineral surfaces. It is now well established that the interaction of thiol collectors with sulfide minerals takes place through an anodic oxidation reaction involving the collector that renders the mineral hydrophobic, coupled with a cathodic process, which is usually the reduction of oxygen. Electrochemical techniques provide valuable information on the kinetics and mechanisms of processes occurring at the solid/solution interface, but electrochemical characterization alone lacks the molecular specificity required to give unequivocal identification of species formed at electrode surfaces. For this reason, a number of in situ, and ex situ spectroscopies have been applied to augment electrochemical approaches and provide information on the elemental and molecular composition, the atomic geometry, and the electronic structure of the interface. The spectroelectrochemical techniques that have been most widely applied to flotation systems have involved Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) and the application of these techniques has been able to distinguish chemisorption from bulk compound formation (Buckley et al., 2003).

Raman spectroscopy is complementary to infrared; both techniques give spectra resulting from transitions between the vibrational energy levels of molecules, but different selection rules apply. Raman has an advantage over infrared techniques that the incident and scattered radiation can have wavelengths in the region that is not absorbed strongly by water and in which glass is transparent. Thus, in situ investigations in aqueous media can be carried out using conventional glass cells. Surface enhancement occurs with appropriately roughened copper, silver or gold electrodes (Fleischmann et al., 1974) enabling Raman spectra to be obtained from adsorbed species at the sub-monolayer level. These coinage metals provide model surfaces for SERS spectroelectrochemical studies of the adsorption behaviour of collectors. While surface products formed on metal sulfides can be detected by Raman spectroscopy,

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the sensitivity is such that only substantial layers can be characterised (Parker et al., 2003). Decorating the surface of the mineral with gold promotes surface enhancement of Raman scattering similar to that of coinage metal electrodes and greatly increases surface sensitivity. This paper presents a summary of SERS studies at Griffith University upon the interaction of thiol flotation collectors with electrochemically roughened coinage metal surfaces under potential control. SERS studies of surface species observed on a chalcopyrite-collector interface activated by gold decoration are also reported.

2. Experimental

Copper and gold electrodes were prepared from metal of 99.99% purity, and fashioned into slugs of 6 mm that were fitted into a Teflon-coated electrical contact/support prior to study. The surface of the copper electrode was electrochemically roughened prior to obtaining SERS investigations by oxidation–reduction cycling (ORC) in 2 mol dm^{-3} H_2SO_4. This procedure involved the application of 4–5 cycles between -0.3 and 0.7 V with a polarisation period of approximately 30 s before reversing the polarity. With gold, ORC was carried out between -0.3 and 1.2 V in 1 mol dm^{-3} KCl acidified to pH 1 with HCl. In the case of the silver working electrode, a flag electrode attached to silver wire was used. The electrode was roughened by applying ORC in 1 mol dm^{-3} KCl acidified with HCl between potentials of -0.2 and 0.6 V after initially reducing at -0.5 V. Gold and silver electrodes were subject to a final clean by heating in a furnace at 450 °C for 16 h to remove any organic species.

Spectroelectrochemical studies were generally carried out used an electrochemical cell constructed of borosilicate glass with an optically flat transparent window. For experiments with copper and gold, the working electrode was mounted on an assembly constructed from PTFE and was positioned close to the window. It follows the design devised by Fleischmann et al. (1990). Potentials were measured against a Ag–AgCl–KCl (saturated) reference electrode and converted to the standard hydrogen electrode (SHE) scale by taking the potential of the reference to be 0.21 V on this scale. All potentials are presented vs. SHE. Glassware used in these experiments was cleaned in 7% HNO_3 (Analar) for 48 h and rinsed repeatedly with de-ionized water. Solutions were made with AR grade chemicals, synthesized xanthates, or other flotation reagents (donated by Cytec) and made up with de-ionized reagent water (EC < 0.1 μS/cm).

In addition to spectra recorded in situ under potential control, spectra have been recorded on emersed electrodes and on electrodes ex situ. For measurements on emersed electrodes, spectra were recorded after the solution had been drained from the cell. The removal of solution was carried out under a constant flow of nitrogen to avoid ingress of oxygen from the atmosphere during emersion and the recording of spectra. In the last situation, the electrode was removed from the cell and washed with pure water to remove any cell solution from the electrode surface prior to examination in the spectrometer. This procedure provided information on the tenacity of attachment of species to the electrode surface as well as the identity of adsorbates.

Real-time SERS studies were conducted on a Renishaw 100 system Raman spectrometer using 632.8 nm red excitation from a HeNe laser (Au and Cu) or 514.5 nm green excitation from a Ar ion laser (Ag). The laser spot size was ~50 μm with power at the sample measured at ~6 (red) and ~20 mW (green). The scattered light was detected with a Peltier-cooled CCD detector with spectral resolution, 2 cm^{-1}. The laser and scattered radiation were focused through an ultralong working distance ×20 Olympus Plan Fl lens (NA = 0.4). Spectral manipulation such as baseline adjustment, smoothing and normalization was performed with GRAMS32 software (Galactic Industries, Salem, NH, USA).

To induce surface enhancement on mineral surfaces, gold films were vapor-deposited onto the exposed electrode surface. In the case of the chalcopyrite electrodes, fine gold (99.5% Au) was thermally evaporated for 2–4 min yielding discontinuous gold films. Coverage was in the range of nanometers as evidenced by comparison of the color of the gold layer deposited simultaneously on glass slides with gold films of known thickness.

3. SERS studies of collector adsorption

The present authors have carried out SERS spectroelectrochemical studies of the interaction of a number of sulfide mineral collectors with coinage metal surfaces and these are summarized in Table 1. In each case, the bulk compounds were characterized using both Raman and NMR spectroscopies.

Voltammetric studies by (Woods, 1996) showed that the interaction of ethyl xanthate with a number of sulfide minerals and with silver and copper have a prewave which occurs at potentials below the region where the metal xanthate is thermodynamically stable. This underpotential prewave has been identified with chemisorption of a monolayer of xanthate on to metal sites in the surface. The adsorption of ethyl xanthate on silver was studied by Buckley et al. (1997) using FT-Raman spectroscopy to confirm the nature of the underpotential layer. The surface was investigated ex situ to enable direct comparison with XPS data. The presence in the SERS spectra of bands arising from each of the functional groups of the xanthate molecule at wavenumbers similar to those of silver ethyl xanthate confirmed that xanthate retains its molecular integrity in the chemisorbed monolayer. This finding also validated the conclusion reached from XPS investigations (Buckley and Woods, 1995) that the absence of core electron energy shifts can be used to distinguish between chemisorption and compound formation.

Work at Griffith University (Woods et al., 1998a,b,c) extended these investigations to include the interaction of