

Transient adsorption of sulfate ions during copper electrodeposition

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Adsorption of a variety of species, including the anions of the electrolyte employed, can significantly influence the morphology of electrodeposits. A knowledge of adsorption of sulfate, therefore, is important in understanding the electrowinning and electrorefining of copper. SERS spectroscopy can be used to detect sulfate adsorption and modern instrumentation is sufficiently sensitive for measurements to be made in real time.

A Raman spectrum obtained from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is shown in Fig. 1. The major feature is a band at 983 cm^{-1} due to the symmetrical stretching vibration of the SO_4^{2-} group. Bending and antisymmetric stretching vibrations of sulfate give rise to the band at 615 cm^{-1} , and the band at 465 cm^{-1} is assigned to a bending mode. Fig. 1 also presents a Raman spectrum from 1 mol dm^{-3} sulfuric acid; it displays corresponding sulfate bands at 983 cm^{-1} , 595 cm^{-1} and 434 cm^{-1} together with bands at 1050 cm^{-1} and 898 cm^{-1} arising from stretching vibrations of the SO_3 group and the OH group components of the bisulfate.

A typical spectrum from a copper surface in 1 mol dm^{-3} sulfuric acid at potentials in the region of stability of the metal is also shown in Fig. 1. The spectrum displays bands of low intensity at the same wavenumbers as expected from the 1 mol dm^{-3} sulfuric acid electrolyte itself. This spectrum could have arisen from the solution in the roughened electrode surface or from adsorbed species.

When the potential of the copper electrode was taken into the dissolution region and then returned to the region of stability, either on a potential scan or a potential step function, SERS spectra were observed, a typical example of which is shown in Fig. 1. This spectrum has a single band at 972 cm^{-1} , which is assigned to a surface sulfate species. The adsorption of sulfate, but not bisulfate, on copper from sulfuric acid solutions was previously reported by Brown and Hope [1]

The adsorbed sulfate spectrum was observed to disappear over a period of a few minutes when the potential was held in the metal stability region. This indicates that the adsorbed sulfate is a transient species associated with copper being deposited. The sulfate band appeared at all potentials in the Cu^0 stability region following an excursion to dissolution potentials or the addition of copper ions to the solution.

Sulfate ions have also been shown [2] to co-adsorb in the underpotential deposition (UPD) of copper on platinum and gold and that it is sulfate and not bisulfate that is on the surface [3]. The structure and composition of copper ad-layers have been extensively studied by a variety of experimental techniques and it is well established that a honeycomb ($\sqrt{3} \times \sqrt{3}$) phase is formed in UPD Cu on Au(111) consisting of $2/3$ monolayer of Cu and $1/3$ monolayer of SO_4 . The copper is considered [4] to have a partial positive charge and this induces the adsorption of sulfate anions which themselves become partially discharged.

It is possible that the initial copper deposit formed on copper retains a partial charge analogous to that for UPD copper layers and, similarly, induces the co-adsorption of sulfate ions into the surface. The subsequent discharge of the partially charged copper atoms would complete the

electrode reaction and the surface layer would reconstruct to form the stable copper structure. The sulfate ions would then be desorbed.

The SERS spectrum displays only the symmetrical stretching vibration of sulfate; the antisymmetrical vibrations are suppressed. This would indicate that each SO_4 is sited with three oxygen atoms close to surface copper atoms with the fourth vertically above the surface. The symmetrical stretching band is blue-shifted by $\sim 11 \text{ cm}^{-1}$ from the corresponding band from H_2SO_4 or hydrated CuSO_4 . This could arise from bonding between the adsorbed sulfate and surface copper atoms.

The sulfate band did not appear on similar experiments in which the 1 mol dm^{-3} sulfuric acid solution contained 10 ppm chloride. This suggests that the transient adsorbed sulfate ions are replaced by chloride ions in the growing copper electrodeposit.

Studies have also been carried out on the influence of nitrate and of thiourea on the transient adsorption of sulfate

References

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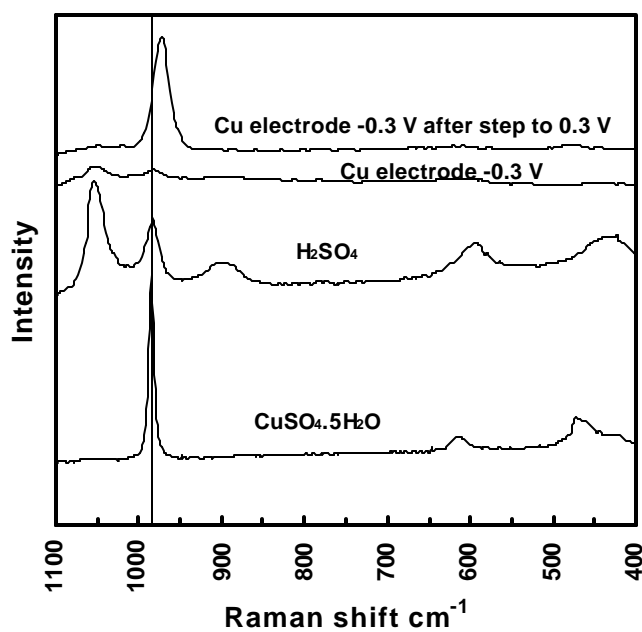


Fig. 1. Raman spectra from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 1 mol dm^{-3} H_2SO_4 , copper electrode at -0.3 V in 1 mol dm^{-3} H_2SO_4 and a copper electrode at -0.3 V following a potential step to 0.3 V . Vertical line is 983 cm^{-1} , which is the position of the sulfate symmetrical stretch band for position of the CuSO_4 and H_2SO_4 .