

Spectroelectrochemistry of gold in thiosulfate solution

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The oxygen-driven dissolution of gold in thiosulfate is a very slow reaction and requires catalysis by ammonia and Cu(II). [1] The solution chemistry becomes complicated due to the dependence of the dissolution potential on the ratio of Cu(II)/Cu(I) and the simultaneous catalysis of thiosulfate oxidation to tetrathionate. The process is further hindered by an intransigent passivation of undetermined nature, possibly due to a surface process. [2] Surface-enhanced Raman spectroscopy (SERS) is a technique that greatly increases the scattering intensity of species in close proximity to, and adsorbed upon, the surface of suitably activated coinage metal surfaces. Minimal inference by the inherently weak Raman scattering of water makes the technique particularly suited to in-situ studies of gold dissolution processes, and here the technique has been used to interrogate the electrochemical interface of the Au-thiosulfate dissolution system.

This study reports SERS of a gold electrode under potential control in uncatalysed solutions of 0.1 and 1.0 mol dm⁻³ Na₂S₂O₃ in a pH 9.2 borate buffer in equilibrium with air. Figure 1 shows SERS spectra in 0.1 mol dm⁻³ thiosulfate solution at OCP 114 mV (vs SHE). A band due to S-S stretching, ν_{SS} , is observed at 457 cm⁻¹ which is considerably lower than the ν_{SS} of S₈ sulfur at 470 cm⁻¹ and higher than ν_{SS} of solution thiosulfate at 445 cm⁻¹. A characteristic thiosulfate SO₃ symmetric stretch ν_{SO} expected at 1000 cm⁻¹ is not seen at this concentration. A shoulder at 313 cm⁻¹ appears in a region in which Au-S bonding has been previously reported. [3] A similar spectrum of Au in 10⁻³ mol dm⁻³ Na₂S in borate also presented in figure 1 may indicate the formation of a similar surface sulfide layer in both systems

Figure 2 shows the effect of increasing the potential of the SERS electrode in 0.1 mol dm⁻³ thiosulfate. A decrease of the 314 cm⁻¹ shoulder, but no change in the frequency of the surface ν_{SS} , is observed with increased potential up to 510 mV. At 560 mV the 457 cm⁻¹ band disappears in the shoulder of the characteristic 470 cm⁻¹ ν_{SS} of S₈. The presence of S₈ is further confirmed by the S-S-S bending mode, δ_{SS} , at 220 cm⁻¹.

SERS spectra of 1.0 mol dm⁻³ solution are shown in figure 3. At the OCP of 56 mV, ν_{SS} due to thiosulfate is superimposed over a broader ν_{SS} band, with the characteristic thiosulfate ν_{SO} present at 1000 cm⁻¹. A broad band at 320 cm⁻¹ may indicate bonding between the thiosulfate and gold. This band reaches maximum intensity at 350 mV and the first appearance of tetrathionate, indicated by a ν_{SO} band at 1030 cm⁻¹, is also noted at this potential. At 460 mV strong characteristic tetrathionate bands are seen at 1040 & 385 cm⁻¹. The ν_{SS} band originally due to thiosulfate is seen to grow in intensity and shift to higher frequencies with potential, reaching a limiting value of 457 cm⁻¹ by 560 mV, similar to that seen in the 0.1 mol dm⁻³ solution. Characteristic S₈ bands appear at 610 mV. By 710 mV, bands due to thiosulfate and tetrathionate diminish in intensity, but are

seen to return after 30 min at 810 mV, following significant conversion of the surface layer to S₈ sulfur. This may indicate that conversion to S₈ allowed solution species to regain access to the gold surface after breakdown of the surface sulfur layer. A small band at 985 cm⁻¹ confirms the presence of sulfate as an oxidation product at 810 mV.

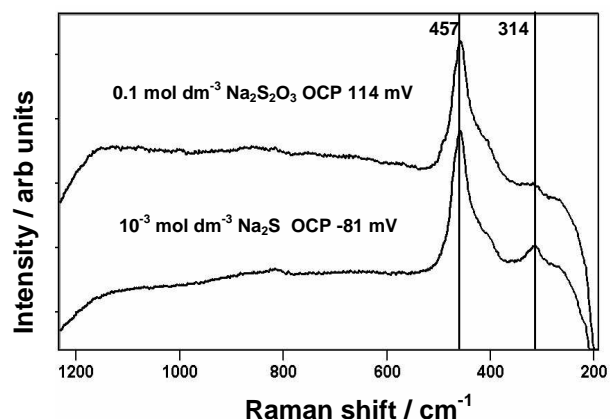


Figure 1: SERS of Au at OCP in (a) 0.1 mol dm⁻³ Na₂S₂O₃, 114 mV and (b) 10⁻³ mol dm⁻³ Na₂S, -81 mV

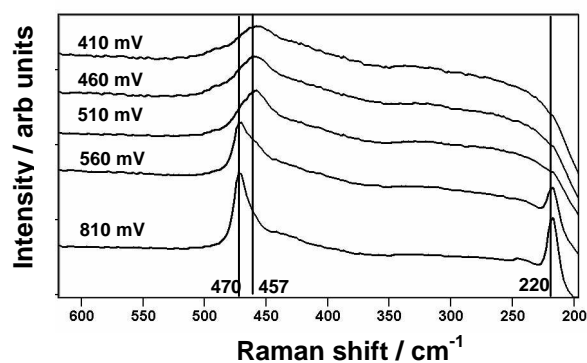


Figure 2: SERS of Au in 0.1 mol dm⁻³ Na₂S₂O₃

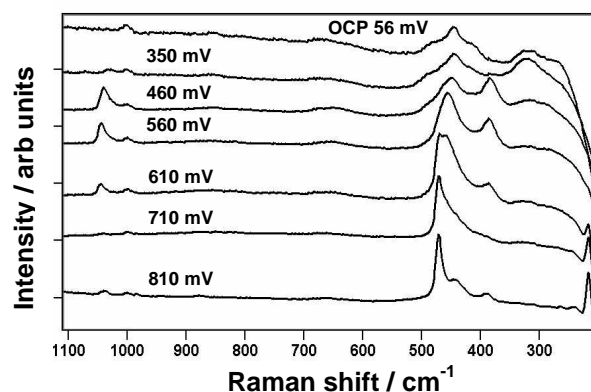


Figure 3: SERS of Au in 1.0 mol dm⁻³ Na₂S₂O₃

1. P. L. Breuer and M. I. Jeffrey, *Minerals Engineering*, **13**, 1071 (2000)
2. M. G. Aylmore and D. M. Muir, *Minerals Engineering*, **14**, 135 (2001)
3. X. Gao, Y. Zhang and M. J. Weaver, *Langmuir*, **8**, 668 (1992)