SERS Investigation of dissolution of gold in cyanide

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Electrochemically roughened silver, copper and gold surfaces greatly enhance the intensity of Raman scattered light from molecules adsorbed upon, or in close proximity to, the metal surface. The technique of surface-enhanced Raman scattering (SERS) provides an excellent in-situ method of observing the vibrational characteristics of surface species during gold dissolution processes. The SERS technique allows rapid acquisition of spectra during voltammetric scans, allowing vibrational characteristics of surface and solution species to be observed in real-time during electrochemical events.

Potential dependent SERS scans show a variation of vibrational frequency with potential, known as Stark-tuning. This phenomenon provides qualitative information regarding the nature of the chemical bonding and orientation of the surface species. A significant variation of Raman background intensity is also seen during the acquisition of potentiodynamic SERS spectra. Elucidation of relationships between the Raman background and optical properties of the adsorbate-modified gold surface may facilitate the development of a novel surface-sensitive technique.

Cyclic voltammetry in pH 11 buffered 0.01 mol dm^{-3} NaCN solutions show a solution cyanide species Stark-tuning linearly at 55 cm^{-1}V^{-1} with ν_{CN} ranging from 2075 cm^{-1} at -1.4 V, to 2105 cm^{-1}. Adsorption is evidenced at the onset of cyanidation, -0.8 V, by the appearance of low frequency modes ν_{AuC}, 350 cm^{-1} and δ_{AuCN}, 290 cm^{-1}. Passivation of the oxidation is seen at –0.2 V, with a decrease in Stark-tuning of ν_{CN}. At +0.7 V ν_{CN} reaches a limiting value of 2130 cm^{-1}, attributable to a surface adsorbed dicyanoaurate.[1] With increased potential, the band was seen to disappear concurrently with the low frequency modes. A new band was seen to emerge at 2165 cm^{-1} attributable to solution dicyanoaurate, followed by surface cyanide bands at 2110 cm^{-1} and the appearance of low frequency bands at 580 cm^{-1} attributable to Au_2O_3.

In the cathodic direction, spectroscopic evidence of the oxide layer remained until a reduction +0.2 V. Below this potential a rapid oxidation was observed, with the return of both the solution species and adsorbed dicyanoaurate. An increase in SERS intensity was observed during the cathodic scan. Three linear Stark-tuning ν_{CN} curves were seen during the cathodic ramp. These may be tentatively assigned to the adsorbed dicyanoaurate, adsorbed cyanide and free cyanide.

Observed electrochemical behavior of the dissolution process in the presence of impurities agreed with the results of Jeffrey and Ritchie in their system purity studies, with respect to peak positions for Ag & Pb impurities in the cyanide system.[2,3] However, no spectroscopic evidence was found for the existence of a passivating AuCN surface polymer as suggested by these authors.[4] This may be attributed to the use of AR grade reagents during this work, rather than the high purity reagents employed by Jeffrey & Ritchie.

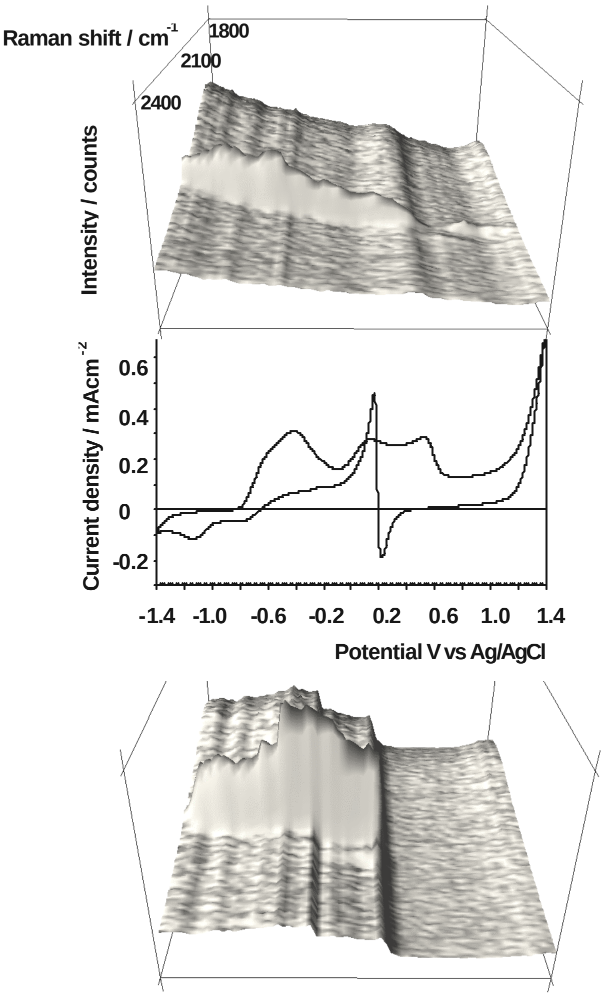

Fig. 1. Potential dependent SERS spectra and voltammetry of gold in 0.01mol dm^{-3} NaCN. Upper figure SERS acquired during anodic scan, lower figure during cathodic scan. Scan rate 10 mVs^{-1}.

References

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