Raman Spectra from Electrode Surfaces

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Summary The Raman spectra of electrochemically deposited Hg_2Cl_2, Hg_2Br_2 and HgO on Hg/Pt substrates have been observed.

The development of analytical techniques which are capable of detecting and characterising the small quantities of species present at electrode surfaces during electrochemical reactions is of fundamental importance to the study of electrode processes. Although a number of methods involving reflectance spectroscopy using visible radiation have been developed in recent years[1] the clear potential of vibrational Raman spectroscopy to give a specific analytical 'fingerprint' of species at electrode surfaces has not been explored. The relatively recent revival in Raman spectroscopy, due mainly to the advent of laser sources, has seen the use of this technique extended into new areas, for example, the study of adsorbed species at the solid/gas interface.[2] This latter development suggests that the detection of species at electrode surfaces should now be feasible. We report a series of experiments giving spectra from the mercury–aqueous electrolyte interface.

The Raman spectra were recorded on a Cary 82 Raman spectrometer. A Spectra Physics 165 Ar^+ laser operating at *ca.* 100 mW power at the sample and at 5145 Å or 4880 Å was used for the Hg_2Cl_2/Hg and Hg_2Br_2/Hg experiments while a Spectra Physics 125 He/Ne laser of *ca.* 70 mW at 6328 Å was employed for the HgO/Hg system. The electrochemical cell had an optical flat at one end for the incident laser beam and a flattened wall section to facilitate the collection of radiation scattered at 90°. The Hg/Pt electrode was prepared by electrolytic nucleation of mercury from a mercury(I) nitrate solution[3] onto a small disc of platinum foil. The surface of the electrode, consisting of small droplets of mercury with a dull grey appearance, was arranged in the cell at *ca.* 45° to the incident laser beam. The subsidiary electrode, a small platinum disc, and the Luggin capillary to the reference electrode were arranged outside the optically significant area. The potential of the Hg/Pt electrode was controlled by a Chemical Electronics Potentiostat type TR 70/2A. Spectra were recorded at constant potential and the quantity of material on the surface was estimated by integrating cathodic current-time transients.

The spectrum of mercury(I) chloride was obtained using $0{\cdot}1$ mol dm^{-3} HCl as electrolyte and maintaining the potential of the mercury electrode 150 mV anodic with respect to a saturated calomel reference electrode. Under these steady-state conditions the 168 cm^{-1} band of Hg_2Cl_2 gave a signal-to-noise ratio of 30 for $3{\cdot}0\,\mu g$ Hg_2Cl_2 cm^{-2} of electrode. Comparison of the spectra obtained with that of crystalline mercury(I) chloride shows that the spectra of a few molecular layers of material are essentially those of the material in bulk. To date, no spectral shifting at very low coverages has been observed. When the potential of the mercury electrode was switched to 50 mV cathodic, where the calomel on the surface was reduced, the spectrum disappeared. The analogous bromide system produced similar behaviour. The spectra of the chloride (strong bands at 41 and 168 cm^{-1} and a weak band at 273 cm^{-1}) and the bromide (strong bands at 36 and 135 cm^{-1} and a weak band at 218 cm^{-1}) compare closely with those published by Durig *et al.*[4] The spectrum of mercury(II) oxide was obtained using $0{\cdot}1$ mol dm^{-3} NaOH as the electrolyte and maintaining the potential of the mercury electrode 100 mV anodic with respect to a HgO/Hg reference electrode. A strong band at 330 cm^{-1} and a medium intensity band at 567 cm^{-1} were observed.

Thus it is clear that Raman spectra can be recorded from electrode surfaces and that the films formed on the surfaces may be characterised *in situ*. The species studied are known to be particularly effective Raman scatterers and extension of the method will demand an increased sensitivity using, for example, modulation techniques.

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