

**Tetrabutylammonium cation expulsion versus perchlorate electrolyte anion uptake in the electrochemical oxidation of microcrystals of [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Cr(CO)<sub>5</sub>I] mechanically attached to a gold electrode: a voltammetric and quartz crystal microbalance study**

ABSTRACT

The electrochemistry of microcrystals of [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Cr(CO)<sub>5</sub>I] attached to a gold electrode which is placed in aqueous (lithium or tetrabutylammonium perchlorate) electrolyte media has been studied in detail by chronoamperometric, voltammetric and electrochemical quartz crystal microbalance (ECQCM) techniques. Whilst chronoamperometric and voltammetric measurements show that the expected one-electron oxidation of microcrystalline [Cr(CO)<sub>5</sub>I] solid to Cr(CO)<sub>5</sub>I occurs at the solid-electrode-solvent (electrolyte) interface, the ECQCM measurements reveal that charge neutralization does not occur exclusively via the expected ejection of the tetrabutylammonium cation. Rather, uptake of ClO<sub>4</sub><sup>-</sup> occurs under conditions where the solubility of sparingly soluble [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]ClO<sub>4</sub> is exceeded. This is the first time that uptake of an anion rather than loss of a cation has been detected in association with an oxidation during electrochemical studies of microcrystals attached to electrode surfaces. It is therefore now emerging that analogous charge neutralization processes to those encountered in voltammetric studies on conducting polymers are available in voltammetric studies of microcrystals attached to electrodes which are placed in contact with solvent (electrolyte) media. In the presence of LiClO<sub>4</sub> as the electrolyte, an ion exchange process occurs leading to formation of Li[Cr(CO)<sub>5</sub>I] · X H<sub>2</sub>O which then slowly dissolves in water at a rate that is strongly influenced by the electrolyte concentration, the relatively hydrophobic nature of the [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sup>+</sup> cation and the poor solubility of [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]ClO<sub>4</sub>.

**Keyword:** Electrochemical quartz crystal microbalance (ECQCM); Iodopentacarbonyl chromium(0) [Cr(Co)5I]<sup>-</sup>; Ion transfer; Voltammetry mechanically attached solid