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Tetrabutylammonium cation expulsion versus perchlorate electrolyte anion uptake in the electrochemical oxidation of microcrystals of [(C₄H₉)₄N][Cr(CO)₅I] mechanically attached to a gold electrode: a voltammetric and quartz crystal microbalance study

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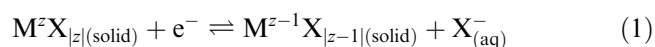
Abstract The electrochemistry of microcrystals of [(C₄H₉)₄N][Cr(CO)₅I] attached to a gold electrode which is placed in aqueous (lithium or tetrabutylammonium perchlorate) electrolyte media has been studied in detail by chronoamperometric, voltammetric and electrochemical quartz crystal microbalance (ECQCM) techniques. Whilst chronoamperometric and voltammetric measurements show that the expected one-electron oxidation of microcrystalline [Cr(CO)₅I]⁻ solid to Cr(CO)₅I 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 ClO₄⁻ occurs under conditions where the solubility of sparingly soluble [(C₄H₉)₄N]ClO₄ 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 LiClO₄ as the electrolyte, an ion exchange process occurs leading to formation of Li[Cr(CO)₅I] · X H₂O which then slowly dissolves in water at a rate that is strongly influenced by the electrolyte concentration, the relatively hydrophobic nature of the [(C₄H₉)₄N]⁺ cation and the poor solubility of [(C₄H₉)₄N]ClO₄.

Key words Iodopentacarbonyl chromium(0) [Cr(CO)₅I]⁻ · Electrochemical quartz crystal microbalance (ECQCM) · Ion transfer · Voltammetry · Mechanically attached solid

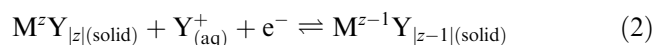
Introduction

In earlier studies undertaken in these laboratories it was demonstrated that the voltammetry of microcrystalline particles mechanically attached to electrodes and immersed in aqueous electrolyte media is different from conventional solution studies due to the associated ion transfer processes that accompany the electron transfer process [1–13]. More recently, the use of the electrochemical quartz crystal microbalance (ECQCM) has proved to be a powerful technique for determining mass changes in the vicinity of the electrode that correspond to these ion transfer processes, and considerable mechanistic information has been obtained [8, 11, 12].

In all the cases examined so far, a simple counter ion of the redox-active species is either expelled or incorporated into the redox-active microcrystalline solid as a result of the need to maintain electroneutrality throughout the crystal [2, 4–13]. Generally, it has been observed that the mechanism of the process can be determined from knowledge of the counter ion involved. When the counter ion is an anion, the general equation for a reduction/expulsion or an oxidation/inclusion reaction is



and when the counter ion is a cation, we have for a reduction/inclusion or an oxidation/expulsion reaction



where *z* is the charge of the redox-active species, *M*. The nature and concentration of the counter ion can strongly influence both the thermodynamic and kinetic aspects of

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these reactions [4, 6, 7, 9, 11, 12]. Other important considerations are solvent transfer [4, 11], counter ion exchange [5, 8, 11] and the solubility of the redox-active species in different oxidation states [6, 9, 10].

The importance of ion transfer reactions in conjunction with the use of chemically modified electrodes [14, 15] has enabled the development of an ion gate [16, 17], applications involving the electronically controlled release of ionic species from polymer films on electrode surfaces [18] and the development of preconcentration methods for analytical purposes [15]. The ion transfer mechanisms involved in these processes are analogous to those described in Eqs. 1 and 2 where the charge of the redox-active film is potentiostatically controlled and the ions of appropriate charge are transferred in order to maintain electroneutrality. Chemical reactions in the vicinity of the film can be induced from changes in the charge of the film and the subsequent inclusion or expulsion of ions; an example of this is the massive decrease in pH near a polypyrrole-coated electrode due to inclusion of OH^- upon oxidation of the film even though 0.1 M Br^- was present in solution [19]. A different mechanism has been encountered where a redox-active species is contained in a fixed charged polymer matrix. In one particular case, ferricyanide was reduced to ferrocyanide within a positively charged, cross-linked poly(vinylpyridinium) film and one molecule of ferricyanide was expelled from the film for every three molecules of ferrocyanide produced (See [20] and references therein).

In this paper, we have investigated the redox properties of the substituted chromium carbonyl salt, $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$, mechanically attached to gold electrodes in aqueous (electrolyte) solution using the ECQCM under both chronoamperometric and cyclic voltammetric conditions. A significantly different ion transfer mechanism for a solid crystalline compound attached to an electrode surface has been discovered, although analogous processes have been observed in systems containing immobilized charges within a polymer film. The concentration of the supporting electrolyte and its influence on fundamental solution behavior has proved to be a critical factor in the overall mechanism.

Experimental

Chemicals

$[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$ was synthesized based on the previously described method of Abel et al. [21]. Distilled water was used for the preparation of all of the aqueous electrolyte solutions, and all of the perchlorate salts were of analytical reagent or electrochemical grade. The acetone was HPLC grade (Mallinckrodt, Paris, Ky., USA).

Electrochemical apparatus and conditions

Simultaneous cyclic (staircase) voltammetric or chronoamperometric and mass balance experiments were obtained using an

electrochemical quartz crystal microbalance (ECQCM) consisting of an Elchema (Elchema, Potsdam, NY, USA) Model EQCN-701 nanobalance and Model PS-205 potentiostat. The system was controlled using a 486 PC running VOLTSCAN software (Intellect Software, Potsdam, N.Y., USA). The reference electrode for the aqueous experiments was Ag/AgCl (3 M KCl) and the auxiliary electrode was platinum wire. The reference electrode was calibrated using the $[\text{Fe}(\text{CN})_6]^{4-/3-}$ couple in aqueous 1 M KCl , and the $E_{1/2}$ was found to be 0.270 ± 0.002 V vs Ag/AgCl (3 M KCl); all potentials reported are given relative to this chemical system. The working electrode was one side of a 1.2-cm diameter AT-cut quartz crystal (Bright Star Crystals, Rowville, Victoria, Australia) which had gold disks (0.5-cm diameter) vapor deposited on each side and oscillated at a frequency of 10 ± 0.05 MHz. The calibration of the ECQCM was as previously described [12].

The ECQCM cell arrangement has been modified from previous reports [12] by grafting a flange with an 8-mm diameter silicone O ring onto the original Elchema cell and sandwiching the crystals onto the cell with another flange containing a silicone O ring. A loosened ball and socket clamp maintains a water-tight seal. This design has reduced the number of crystals damaged during assembly of the working electrode and also decreased the time for assembly and disassembly of the working electrode.

All experiments were undertaken at ambient temperatures ($20 \pm 1^\circ\text{C}$), and solutions were deoxygenated using high-purity nitrogen (BOC Gases, Chatswood, NSW, Australia).

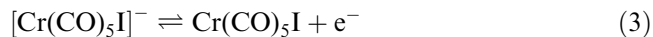
Electrode preparation

The $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$ compound was ground into a powder. The microcrystals were then adhered to the gold electrode by smearing the surface of the electrode with a cotton swab containing the material. The $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$ powder is quite soft, and the gold-coated crystal takes on a shiny film-like appearance. Electron micrographs revealed the presence of well-spaced, discrete crystals on the electrode surface. Data obtained from ECQCM experiments indicated that sample masses of 3–6 μg were transferred to the electrode surface (see later).

Results and discussion

Stability of $\text{Cr}(\text{CO})_5\text{I}$ in aqueous media

Previously, the solution voltammetry of $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$ has been examined in acetone [22, 23], dichloromethane [24], acetonitrile [25] and DMF [25]. It is generally agreed that, under voltammetric conditions, the dissolved $[\text{Cr}(\text{CO})_5\text{I}]^-$ anion is reversibly oxidized by one electron to form the neutral $\text{Cr}(\text{CO})_5\text{I}$.



On the longer synthetic time scale it has been shown that a solution of the neutral complex decomposes via a disproportionation reaction in acetone solution [23]. A recent study, in which the reactivity of $\text{Cr}(\text{CO})_5\text{I}$ with molecular oxygen was considered, showed that the $\text{Cr}(\text{CO})_5\text{I}$ was unaffected in acetonitrile and reacted only slightly in DMF [25]. However, there has been no indication of the stability of the $\text{Cr}(\text{CO})_5\text{I}$ in water. Consequently, before commencing the solid-state voltammetric experiments we examined the stability of $\text{Cr}(\text{CO})_5\text{I}$ on the voltammetric timescale in acetone with varying quantities of water. This preliminary study in-

involved dissolving the $[(C_4H_9)_4N][Cr(CO)_5I]$ in acetone (0.1 M $[(C_4H_9)_4N]ClO_4$) and following the cyclic voltammetric response at a gold electrode as a function of the percentage of water added. Both $[(C_4H_9)_4N][Cr(CO)_5I]$ and the electrolyte remained soluble on addition of 25% water to the acetone solution, and no change to the reversible voltammetric response was observed using water concentrations up to 25% when using scan rates over the range 20–500 $mV s^{-1}$. The conclusion was therefore reached that dissolved $Cr(CO)_5I$ does not react with water on the voltammetric timescale. Reaction of water with solid $Cr(CO)_5I$ will almost certainly be even slower, and solid state voltammetric studies of the $[Cr(CO)_5I]^{-/0}$ redox couple, when a gold electrode coated with mechanically attached $[(C_4H_9)_4N][Cr(CO)_5I]$ is placed in aqueous (electrolyte) media, therefore should be possible.

Solubility of $[(C_4H_9)_4N][Cr(CO)_5I]$ in aqueous (electrolyte) solution

It has been previously reported that the tetraethylammonium salt of the $[Cr(CO)_5I]^-$ anion is soluble in water, alcohols, chloroform and polyethers [21]. The solubility of $[(C_4H_9)_4N][Cr(CO)_5I]$ mechanically attached to an Au coated quartz crystal was examined at various concentrations of aqueous $LiClO_4$ electrolyte solutions using the ECQCM. A potential of $-0.17 V$ vs $[Fe(CN)_6]^{4-/3-}$ (1 M KCl) was applied to the electrode in order to establish an electrochemically relevant ionic environment (double layer) at the electrode surface. The interfacial electrode-microcrystal-solvent (electrolyte) region can have substantially different concentrations of ions compared with the bulk solution depending upon the applied potential [26]. No faradaic current was observed at the potential of $-0.17 V$, so the ECQCM presumably, at this potential, measures only mass changes associated with solid $[(C_4H_9)_4N][Cr(CO)_5I]$.

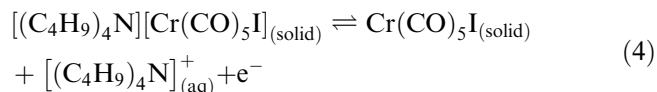
The $LiClO_4$ concentrations ranged from 0.05 to 1 M, and the results are shown in Fig. 1a–d. At the lowest two concentrations of 0.05 and 0.1 M (Fig. 1a, b) the rate of dissolution is essentially constant and has a value of approximately $0.3 ng s^{-1}$. In Fig. 1c, where a higher concentration of 0.5 M $LiClO_4$ was used, it appears that an initially faster rate of dissolution occurs, but after 300 s the rate of dissolution slows to the rate observed at the lower concentrations. At the highest electrolyte concentration examined (1 M $LiClO_4$), the initial rate of mass decrease is relatively fast, although once again, after 300 s, the rate of dissolution appears to return to the rate observed at lower concentrations. The ECQCM data suggest that an ion exchange process involving replacement of $[(C_4H_9)_4N]^+$ by Li^+ occurs in the solid, which leads to the formation of the more soluble $Li[Cr(CO)_5I]$ salt.

However, importantly, the rate of dissolution of $[Cr(CO)_5I]^-$ from the Au electrode is very slow on the time scale of the voltammetric experiments described in

the remainder of this paper. For example, a typical cyclic voltammogram measured with a scan rate of $100 mV s^{-1}$ is completed in 14 s, which would result in approximately 5 ng of mass being lost by dissolution out of a total initial mass of 3–6 μg . In percentage terms this corresponds to a $\sim 0.1\%$ loss per cycle.

Chronoamperometric and mass balance measurements associated with the oxidation of solid $[(C_4H_9)_4N][Cr(CO)_5I]$

The experiments described above were repeated, except that the potential was now stepped after 10 s from $-0.17 V$ to $0.53 V$ vs $[Fe(CN)_6]^{4-/3-}$ (1 M KCl). At $0.53 V$, faradaic current resulting from oxidation of the solid occurs. The interesting feature of all these potential step experiments was that the mass increased rather than decreased upon application of an oxidizing potential. The expected reaction



would result in a decrease rather than an increase in mass. The magnitude and duration of the mass increase can be directly correlated with the concentration of $LiClO_4$. Inspection of the data contained in Fig. 2a, b reveals that at the lower (0.05 and 0.1 M) concentrations of $LiClO_4$ the current approaches zero and the mass reaches an extended plateau region after approximately 250 s. Initially, current spikes greater than $100 \mu A$ are observed which then decay to a steady state current followed by a decay to zero. The extended plateau region in the mass observed after 250 s corresponds to almost, but not quite, total loss (see later) of the $[(C_4H_9)_4N][Cr(CO)_5I]$, so that these data enable estimates (3–6 μg) of the mass of mechanically attached compound to be obtained. Obviously, the rate of dissolution of the mechanically attached compound is greatly increased when an oxidizing potential is applied.

When higher $LiClO_4$ concentrations are present (Fig. 2c, d) the oxidative current spike also occurs but no steady-state current region can be detected. While the current decays to zero in approximately 300 s, the mass now takes substantially longer to reach the extended plateau region, and indeed for a concentration of 1 M $LiClO_4$ there are still small mass changes observable after 30 min. Clearly, at high concentrations of $LiClO_4$ the rate of the dissolution is strongly inhibited.

Cyclic voltammetric and mass balance measurements associated with the oxidation of $[(C_4H_9)_4N][Cr(CO)_5I]$

Historical effects can exert a considerable influence on the voltammetry of solids, and often many cycles of the potential are required to achieve a constant (steady

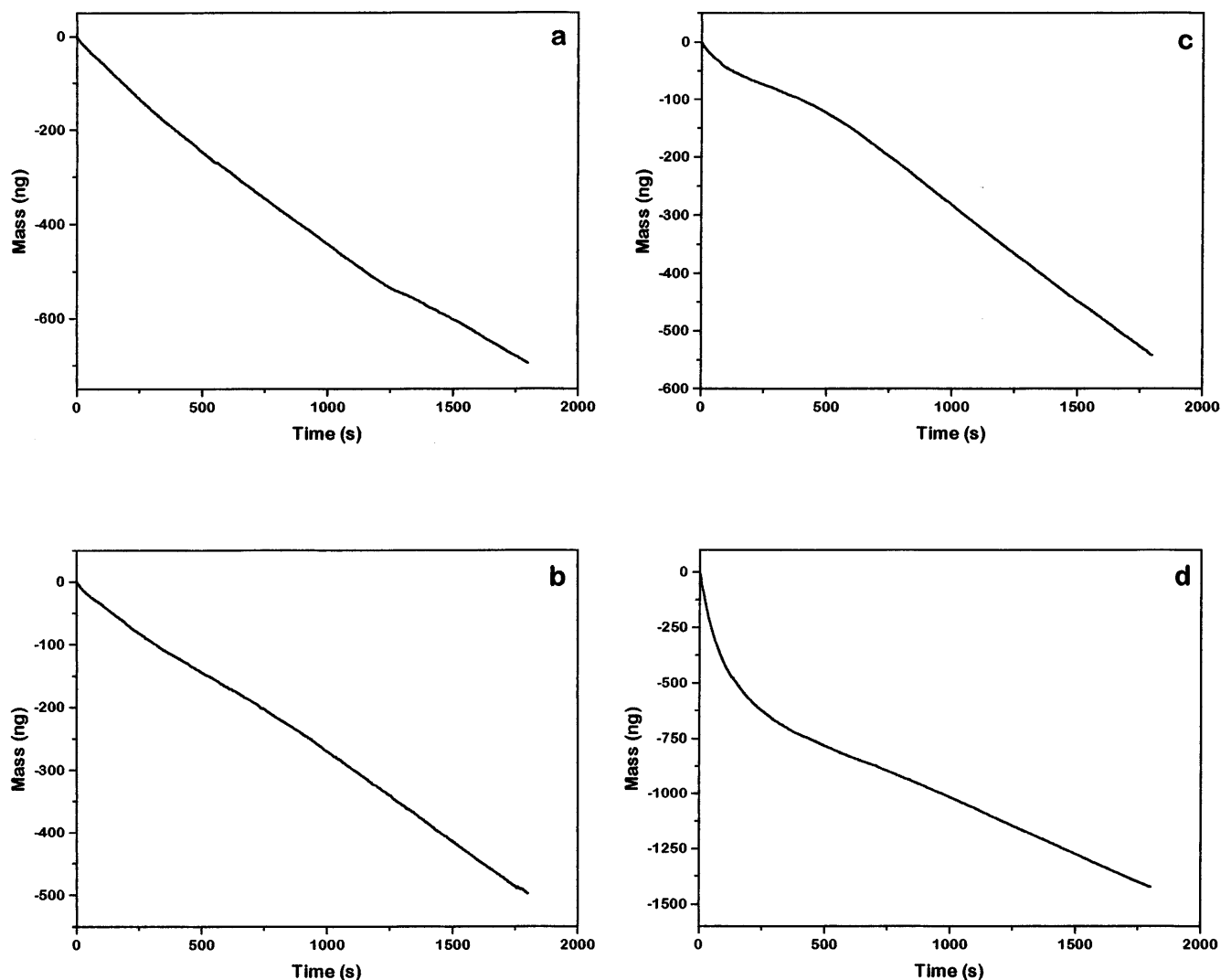
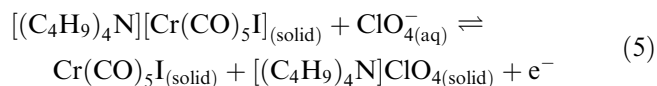


Fig. 1a–d Mass diagrams for the dissolution of $[(C_4H_9)_4N][Cr(CO)_5I]$ mechanically attached to an Au-coated quartz crystal electrode in aqueous solution containing **a** 0.05 M, **b** 0.1 M, **c** 0.5 M and **d** 1 M $LiClO_4$ as electrolyte. Applied potential was -0.17 V vs $[Fe(CN)_6]^{4-/3-}$ (1 M KCl)

state) response [12]. Because of an instrumental limitation, cyclic (staircase) voltammograms were measured in groups of five cycles to establish whether either a steady-state voltammetric or mass condition could be achieved via cycling of the potential.

The lower panels of Fig. 3a–d contain the first set of five scans corresponding to each of the $LiClO_4$ concentrations considered in the last section. In all cases, the first cycle in the cyclic voltammetric experiment is substantially different from the next four cycles. A common feature in the mass measurements (the upper panels of Fig. 3a–d) is that on the first oxidative cycle (these are denoted by a small arrow) the mass initially decreases when a potential of approximately 0.33 V is reached. However, the mass then increases before the switching potential of 0.53 V. This observation is consistent with a process where the $[(C_4H_9)_4N]^+$ is released into solution when $[Cr(CO)_5I]^-$ is initially oxidized to form the neutral complex as in Eq. 4. However, with

further oxidation, additional $[(C_4H_9)_4N]^+$ is generated until the presence of ClO_4^- in the vicinity of the electrode creates conditions where the solubility product for $[(C_4H_9)_4N]ClO_4$ is exceeded and precipitation of $[(C_4H_9)_4N]ClO_4$ or incorporation of ClO_4^- into the mechanically attached compound occurs in order to maintain electroneutrality. Under these latter conditions the major component of the electrode process can be written as



As for the data in the last section, the results can be segregated on the basis of the $LiClO_4$ electrolyte concentration. For the lower $LiClO_4$ electrolyte concentrations (Fig. 3a, b), the mass for the last four cycles shows an overall decrease. However, close examination of the voltammograms reveals that while a large mass

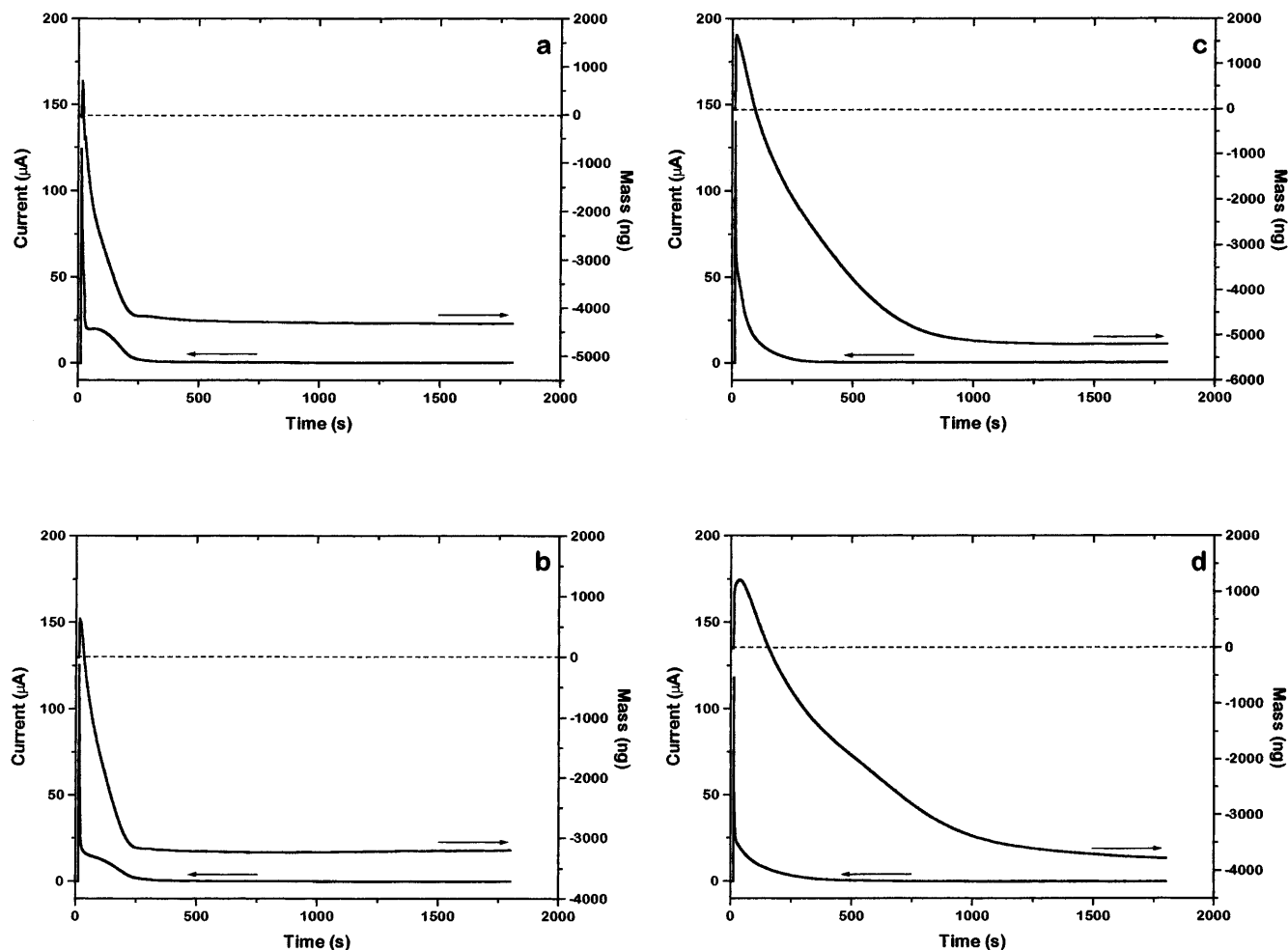


Fig. 2a–d Mass diagrams and chronoamperograms of $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$ mechanically attached to an Au-coated quartz crystal electrode in aqueous solution containing a 0.05 M, b 0.1 M, c 0.5 M and d 1 M LiClO_4 as electrolyte. Applied potential was 0.53 V vs $[\text{Fe}(\text{CN})_6]^{4-/3-}$ (1 M KCl)

decrease occurs when the solid is oxidized, on the reverse or reductive part of the cycle a smaller mass increase occurs. This behavior is consistent with oxidation leading to the $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ being released into solution at a concentration below the $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$ solubility product. This is followed by incorporation of the less massive lithium ion during the reductive component of the experiment. Fig. 4a, b, which represents cycles numbered 21–25, show this ion-exchange process more clearly, since a voltammetric steady state has been reached during cycles 21–25 but the net mass change is still negative. If a simple ion-exchange process occurs, then calculations, assuming the Sauerbrey equation is valid [27], show that the Li^+ ion would need to be hydrated by approximately six water molecules.

Under conditions where the LiClO_4 concentration is high (Fig. 3c,d), the voltammetry for cycles 2–5 is more complicated than for low concentration (Fig. 3a,b), and a large mass increase occurs during oxidation while a significant mass decrease occurs during reduction. This mass-potential behavior seen in scans 2–5 is the oppo-

site to that found for the lower concentrations of LiClO_4 but is consistent with the profile observed on the first cycle. These results can be explained by assuming that the amount of $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ released during each oxidation cycle remains sufficiently large, so that the solubility product of $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$ is exceeded and uptake of ClO_4^- rather than loss of $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ occurs to maintain electroneutrality. The peak potential associated with the oxidation process involving uptake of ClO_4^- is around 0.43 V, but is concentration dependent (compare Fig. 3c, d). In contrast, the peak potential associated with the loss of $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ at lower LiClO_4 concentrations occurs at around 0.31 V. Thus, while thermodynamically the loss of $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ is more favored than the uptake of ClO_4^- , solubility constraints override this feature. Kinetically, it is possible that the solubility limit can be exceeded and a supersaturated solution of $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$ can occur. However, the absence of any detectable nucleation process implies that transient supersaturated solutions, if formed, are stable, and the precipitation of a separate $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$

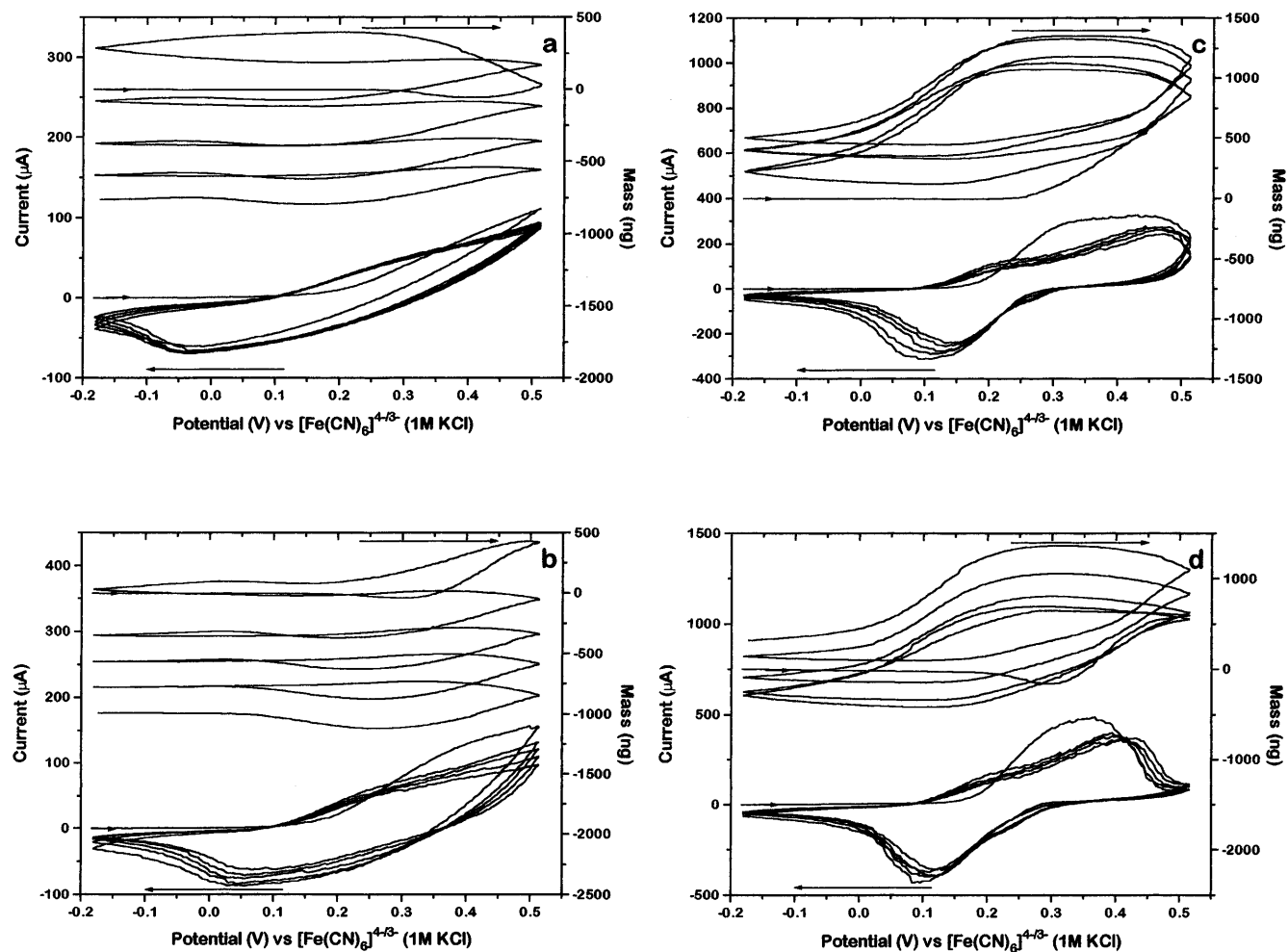


Fig. 3a–d Mass diagrams and cyclic voltammograms of $[(C_4H_9)_4N][Cr(CO)_5I]$ mechanically attached to an Au-coated quartz crystal electrode in aqueous solution containing a 0.05 M, b 0.1 M, c 0.5 M and d 1 M $LiClO_4$ as electrolyte. Cycles 1 to 5 obtained using a scan rate of 0.1 Vs^{-1}

crystalline phase on the electrode surface is therefore considered to be unlikely.

Fig. 4c,d contains cycles 21 through to 25 for the two highest concentrations of $LiClO_4$ electrolyte examined. Interestingly, in Fig. 4c, the two different processes of Eqs. 4 and 5 that are associated with the oxidation of $[Cr(CO)_5I]^-$ can be seen. Thus, the mass initially decreases at approximately 0.21 V but then again increases at 0.43 V. This result further demonstrates the critical nature of the concentrations of $[(C_4H_9)_4N]^+$ and ClO_4^- relative to the solubility product.

With the exception of the highest concentration of $LiClO_4$ examined, the $Cr(CO)_5I^{+/0}_{(solid)}$ redox system eventually reached a voltammetric steady state (Fig. 5a). Clearly not all the solid compound is lost from the electrode surface on repetitive cycling, since a well-defined steady-state voltammetric response is found. This steady-state response also was observed in the chronoamperometric experiments described in the last section. The corresponding mass change associated with each potential cycle when the voltammetric steady

state is achieved is shown in Fig. 5b, where each box represents one complete cycle. In the first half of each box, which represents the oxidation process, the mass increases, while in the second half of each box, where reduction occurs, the mass decreases. It is possible that under these voltammetric steady-state conditions the $[Cr(CO)_5I]^-$ anion may be specifically or non-specifically adsorbed. In this case, oxidation to the neutral $Cr(CO)_5I$ would require an anion to enter the double layer to maintain electroneutrality. Conversely, reduction would in turn lead to loss of the anion.

Cyclic voltammetric and mass balance measurements associated with the oxidation of $[(C_4H_9)_4N][Cr(CO)_5I]$ in saturated aqueous $[(C_4H_9)_4N]ClO_4$

$[(C_4H_9)_4N]ClO_4$ is not generally used as a supporting electrolyte in water due to its low solubility. However, even though there are problems with ohmic (IR) drop, voltammograms and the corresponding mass changes can be measured in a saturated $[(C_4H_9)_4N]ClO_4$ solu-

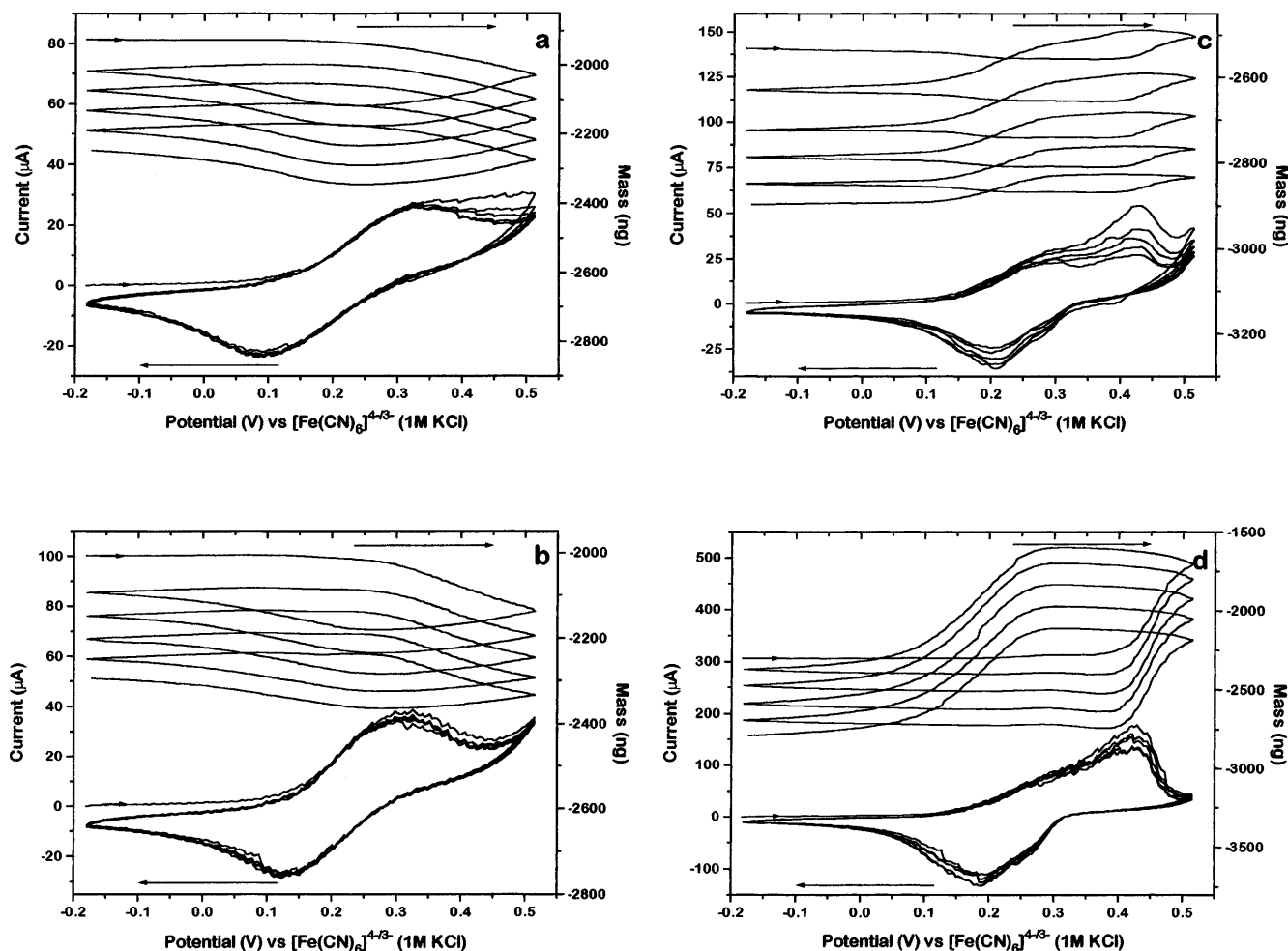


Fig. 4a–d Mass diagrams and cyclic voltammograms of $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$ mechanically attached to an Au-coated quartz crystal electrode in aqueous solution containing **a** 0.05 M, **b** 0.1 M, **c** 0.5 M and **d** 1 M LiClO_4 as electrolyte. Cycles 21 to 25 obtained using a scan rate of 0.1 V s^{-1}

tion without the complication of needing to introduce a foreign cation into the charge neutralization process. Since the saturated solution contains a low concentration of ClO_4^- , results are best compared to those obtained in 0.05 M LiClO_4 . Figure 6a shows cyclic voltammetric data for the first five cycles. Noteworthy are the much lower currents at a potential of 0.53 V than those observed when 0.05 M LiClO_4 is used as the electrolyte, the almost ohmic oxidation response and the increase in the magnitude of reductive peak current as the number of cycles increases. The first feature is attributed to the positive shift in peak potential expected at the very low ClO_4^- concentration. That is, only the foot of the oxidation wave is reached at 0.8 V, so that much smaller currents are observed. The mass changes associated with the voltammetry also are shown in Fig. 6a. As is the case when LiClO_4 electrolyte is employed, the mass initially decreases slightly, but then increases due to the addition of ClO_4^- . Interestingly, the mass continues to increase on subsequent cycles as does the magnitude of the reduction $\text{Cr}(\text{CO})_5\text{I}$

being released from the solid during the oxidation process and adsorbed on to the electrode as previously postulated. When reduction of $\text{Cr}(\text{CO})_5\text{I}$ occurs, additional $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ from solution precipitates to form solid $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$. The additional $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ must come from solution because release of $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ from the solid during the oxidation process is unlikely, as this would require the solubility product for $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$ to be exceeded. Perchlorate ions from solution must also be incorporated into the solid in this circumstance to replace expelled $\text{Cr}(\text{CO})_5\text{I}$ and maintain electroneutrality. It is the combination of all these factors that is believed to result in the net increase in mass.

Figure 6b contains cycles 91 to 95, and, after this lengthy period of cycling the potential, it is now noticeable that a small overall negative mass has been attained. Additionally, an oxidation peak is now apparent at 0.33 V which is associated with a mass decrease. These results are remarkably similar to the results in Fig. 4a,b indicating that the $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ cation is being cycled out of and into the mechanically

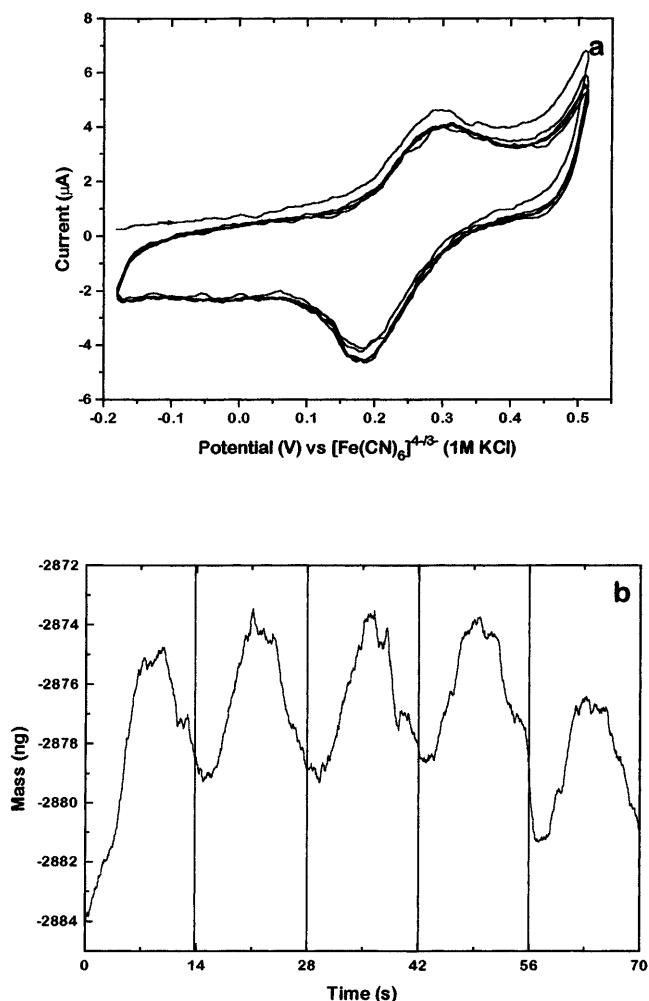


Fig. 5 a Cyclic voltammogram of $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$ mechanically attached to an Au-coated quartz crystal electrode in aqueous solution containing 0.05 M LiClO_4 as electrolyte. Cycles 66 to 70 obtained using a scan rate of 0.1 V s^{-1} . b Corresponding mass diagram

attached solid during the respective oxidation and reduction processes. Presumably, the localized concentration of $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ must be below the solubility limit of $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$ for this to occur.

Conclusions

All of the processes detected at the gold electrode-microcrystalline solid-aqueous (electrolyte) interface in the redox chemistry of the $[\text{Cr}(\text{CO})_5\text{I}]^{-/0}_{(\text{solid})}$ system can be described by Reaction Scheme 1. When commencing with the water-insoluble $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$ compound and in the presence of LiClO_4 as the electrolyte, the process proceeds towards the formation of $\text{Li}[\text{Cr}(\text{CO})_5\text{I}] \cdot \text{X H}_2\text{O}$, which can then dissolve in water. The rate at which this overall process occurs is strongly influenced by the concentration of ClO_4^- , the relatively

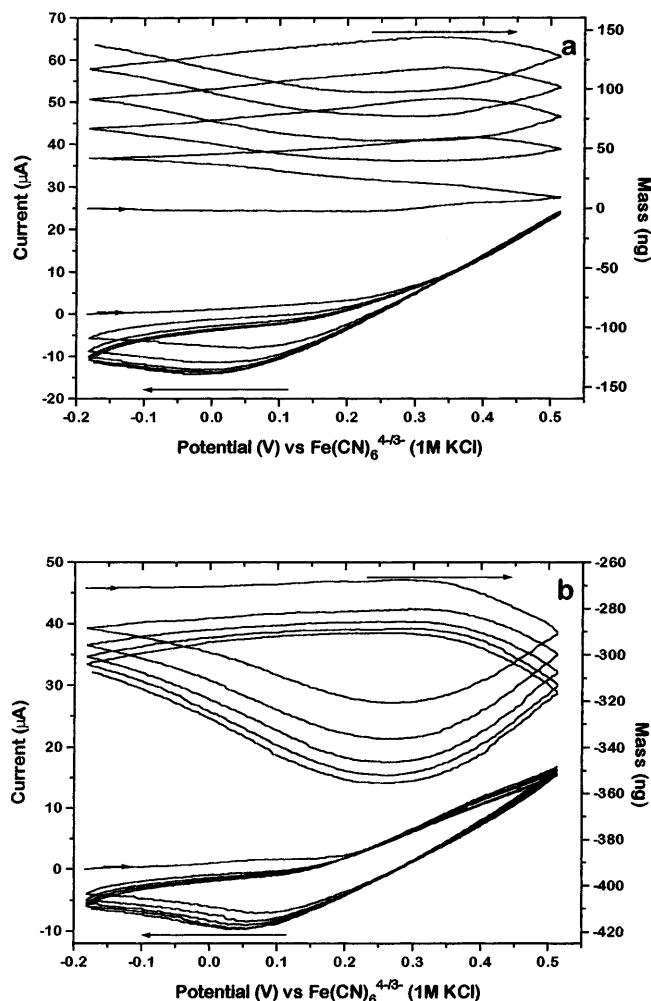
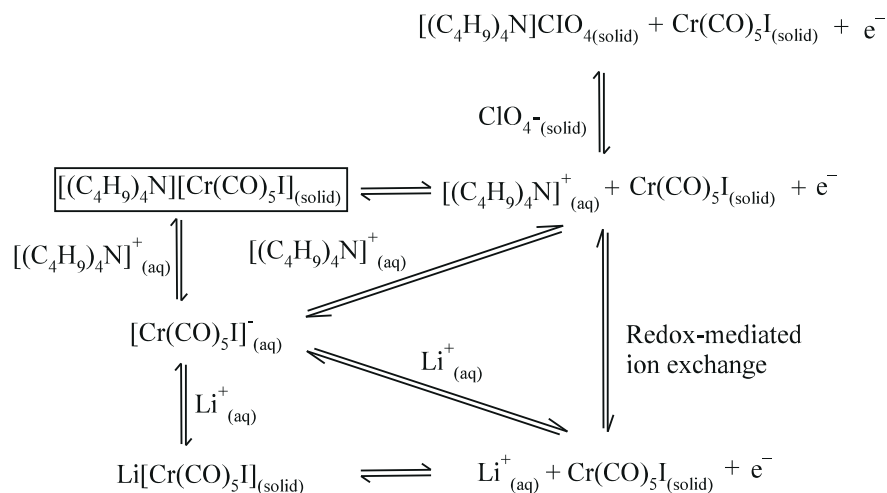


Fig. 6a, b Mass diagrams and cyclic voltammograms of $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{CO})_5\text{I}]$ mechanically attached to an Au-coated quartz crystal electrode in aqueous saturated $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$. a Cycles 1 to 5 and b cycles 91 to 95 obtained using a scan rate of 0.1 V s^{-1}

hydrophobic nature of the $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ cation and the solubility of $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$. The insolubility of $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$ in water leads to the possibility that addition of ClO_4^- rather than loss of $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ is associated with the charge neutralization process that must accompany oxidation of $[\text{Cr}(\text{CO})_5\text{I}]^-$ to $\text{Cr}(\text{CO})_5\text{I}$.

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 charge neutralization processes analogous 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.

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Reaction Scheme 1

References

- Bond AM, Scholz F (1991) *J Phys Chem* 95: 7640
- Bond AM, Scholz F (1991) *Langmuir* 7: 3197
- Bond AM, Scholz F (1992) *J Geochem Expl* 42: 227
- Dueber RE, Bond AM, Dickens PG (1992) *J Electrochem Soc* 139: 2363
- Bond AM, Colton R, Daniels F, Fernando DR, Marken F, Nagaosa Y, Van Steveninck RFM, Walter JN (1993) *J Am Chem Soc* 115: 9556
- Bond AM, Marken F (1994) *J Electroanal Chem* 372: 125
- Bond AM, Colton R, Marken F, Walter JN (1994) *Organometallics* 13: 5122
- Dostal A, Meyer B, Scholz F, Schröder U, Bond AM, Marken F, Shaw SJ (1995) *J Phys Chem* 99: 2096
- Bond AM, Cooper JB, Marken F, Way DM (1995) *J Electroanal Chem* 396: 407
- Downard AJ, Bond AM, Hanton LR, Heath GA (1995) *Inorg Chem* 34: 6387
- Shaw SJ, Marken F, Bond AM (1996) *J Electroanal Chem* 404: 227
- Shaw SJ, Marken F, Bond AM (1996) *Electroanalysis* 8: 732
- Bond AM, Fletcher S, Marken F, Shaw SJ, Symons PG (1996) *J Chem Soc Faraday Trans* 92: 3925
- Inzelt G (1994). In: Bard AJ (ed) *Electroanalytical chemistry: a series of advances*, vol 18. Dekker, New York, pp 90–241
- Murray RW (1984) In: Bard AJ (ed) *Electroanalytical chemistry: a series of advances*, Vol 13. Dekker, New York, pp 192–368
- Burgmayer P, Murray RW (1982) *J Am Chem Soc* 104: 6193
- Burgmayer P, Murray RW (1984) *J Phys Chem* 88: 2515
- Shinohara H, Aizawa M, Shirakawa H (1985) *Chem Lett* 179
- Shinohara H, Kojima J, Aizawa M (1989) *J Electroanal Chem* 266: 297
- Doblhofer K, Braun H, Lange R (1986) *J Electroanal Chem* 206: 93
- Abel EW, Butler IS, Reid JG (1963) *J Chem Soc* 2068
- Bond AM, Bowden JA, Colton R (1974) *Inorg Chem* 13: 602
- Bond AM, Colton R (1976) *Inorg Chem* 15: 446
- Lloyd MK, McCleverty JA, Orchard DG, Connor JA, Hall MB, Hiller IH, Jones EM, McEwan GK (1973) *J Chem Soc Dalton Trans* 1743
- Fehlhammer WP, Fritz M, Floner D, Moinet C (1997) *Electrochim Acta* 42: 1549
- Bard AJ, Faulkner LR (1980) *Electrochemical Methods*. Wiley, New York, Chap. 12
- Buttry DA (1991) In: Bard AJ (ed) *Electroanalytical chemistry: a series of advances*, vol 17. Dekker, New York, pp 1–85