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Graphite screen printed electrodes for the electrochemical sensing of chromium(VI)

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We demonstrate that graphite screen printed macroelectrodes allow the low ppb sensing of chromium(VI) in aqueous solutions over the range 100 to 1000 μg L^{-1} with a limit of detection of 19 μg L^{-1}. The underlying electrochemical mechanism is explored indicating an indirect process involving surface oxygenated species. The drawbacks of using hydrochloric acid as a model solution to evaluate the electrochemical detection of chromium(VI) are also pointed out. The analytical protocol is shown to be applicable for the sensing of chromium(VI) in canal water samples at levels set by the World Health Organisation. The protocol is simplified over existing analytical methodologies and given its analytical performance and economical nature, holds promise for the de-centralised screening of chromium(VI).

1. Introduction

The ability to detect trace amounts of toxic chromium species has always been of vast interest while remaining a challenge in its own right due to the numerous oxidation states in which the element can reside.[1] With regard to the environment and health, there are two valence states that have considerable impact, Cr(III) and Cr(VI).[1] Reported to be the second major inorganic contaminant in hazardous waste sites[2] and owing to its high chemical oxidation potential, a provisional World Health Organisation guideline value of 50 μg L^{-1} (50 ppb) has been introduced for hexavalent Cr in groundwater.[3] The chromate anions pass readily through cell membranes and are easily reduced inside the cell to Cr(III) which binds more effectively to DNA, causing detrimental impairment to cellular components.[4]

A number of sensitive techniques have been employed for the determination of Cr, such as atomic adsorption spectrophotometry,[5,6] plasma mass spectrometry,[7] spectrofluorimetry,[8] spectrophotometry,[9] and chemiluminescence,[10,11] but each of these processes is time consuming and necessitates expensive equipment. Various advantages are demonstrated when electrochemical methodologies are utilised for the determination of Cr including speed of analysis, good selectivity and sensitivity, which have resulted in a variety of highly responsive systems, utilising platinum[12] and gold[12–14] to be fashioned. Primarily mercury electrodes were used for the electrochemical detection of Cr(VI),[15–19] while demonstrating to be extremely sensitive, its application in analytical practice is limited due to its potential toxicity. The electrochemical characteristics of Cr(VI) are well documented for various electrode substrates such as gold, glassy carbon, platinum and boron doped diamond.[12,20,23,29]

Compton *et al.* have extensively explored the electrochemical reduction of Cr(VI) in aqueous solutions at a range of macroelectrodes.[20] It was demonstrated that gold macroelectrodes exhibited the greatest electrochemical reversibility over glassy carbon and boron doped diamond macroelectrodes.[20] Recently Hood *et al.* have explored the electro-analytical sensing of Cr(VI) at gold ultra-microelectrodes arrays where it was demonstrated that the spacing between neighbouring ultra-microelectrodes is critical in allowing analytical useful measurements.[21] Current state-of-the-art for Cr(VI) sensing has been reported by Jena and Raj who claim sub-ppb level detection employing amperometry at gold nanoparticle sol gels.[22]

The development of screen printed electrodes has lead to the assembly of intelligent sensors which can be integrated into portable systems, a significant requirement of analytical methods intended for direct analysis of a sample in its "natural environmental conditions" without alteration.[23] Screen printed electrodes are mass produced and have scales of economy and may be used as a one shot sensor which precludes problems that may be encountered with memory effects and alleviates the need for electrode pre-treatment.[24,25]

Herein we revisit the electrochemical reduction of Cr(VI) and report for the first time, non-modified, non-metallic, graphite screen printed electrode for the electroanalytical sensing of low ppb levels of Cr(VI) in aqueous solutions at levels set by the World Health Organisation (WHO). The methodology is demonstrated to be possible for the electro-analytical sensing of Cr(VI) in water samples and holds promise for high throughput screening.

2. Experimental section

All chemicals used were of analytical grade and were used as received without any further purification and were obtained from Sigma-Aldrich. All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm^{-1}.

Voltammetric measurements were carried out using a μ-Autolab III (ECO-Chemie, The Netherlands) potentiostat. All measurements were conducted using a screen-printed three electrode configuration with a geometric working electrode area of 3 mm diameter. Connectors for the efficient connection of the screen printed electrochemical sensors were purchased

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from Kanichi Research Services Ltd (UK).[26] Screen-printed carbon electrodes were fabricated in-house with appropriate stencil designs using a microDEK 1760RS screen-printing machine (DEK, Weymouth, UK). A carbon–graphite ink formulation was first screen printed onto a polyester flexible film (Autostat, 250 μm thickness) defining the carbon contacts, counter and working electrodes. This layer was cured in a fan oven at 60 degrees for 30 minutes. Next a silver/silver chloride reference electrode was included by screen printing Ag/AgCl paste (Gwent Electronic Materials Ltd, UK) onto the plastic substrate, which after curing at 60 degrees for 30 minutes is ready to use. Note that in the work presented in this paper, we chose to use a Saturated Calomel Electrode (SCE) as the reference electrode to allow a direct comparison with literature reports. Last a dielectric paste ink (Gwent Electronic Materials Ltd, UK) was printed to cover the connections and define the 3 mm diameter graphite working electrode. After curing at 60 degrees for 30 minutes the screen printed electrode is ready to use. These electrodes have been characterised electrochemically in a prior paper and have heterogeneous rate constants of 1.7×10^{-3} cm^2 s^{-1}.[27] Fig. 1 displays SEM images of the graphite screen printed electrochemical sensor where a well defined electrode surface[27,28] is observed from randomly orientated graphite particles bound together with a inert polymeric binder which is free from cracks and holes. Canal water was sampled in Bury, Lancashire which was simply acidified to pH 1 before electroanalytical measurements. Carbon powder was used as received and was purchased from Gwent electronic materials Ltd. Amperometry was performed using a stirrer bar rotating at ~250 rpm.

Scanning electron microscope (SEM) images and surface element analysis were obtained with a JEOL JSM-5600LV model.

3. Results and discussion

Chromium(VI) can exist, depending on its speciation in aqueous solutions in a variety of forms. Based on the possible reactions that may occur, the dissociation and complexation constants may be defined as:

$$K_a = \frac{[HCrO_4^-][H^+]}{[H_2CrO_4]} \quad (1)$$

$$K_1 = \frac{[HCrO_4^-][Cl^-][H^+]}{[CrO_3Cl^-]} \quad (2)$$

$$K_2 = \frac{[HSO_4^-][HCrO_4^-]}{[CrSO_7^{2-}]} \quad (3)$$

Literature values are: $K_a = 0.18$ M;[29] $K_1 = 0.09$ M^2;[30] $K_2 = 0.24$ M.[31] Eqn (1)–(3) allow the calculation of different concentrations of monochromate anions in aqueous solutions in either H_2SO_4 or HCl. Typically obtained results are summarised in Table 1 where it can be readily observed that in 0.1 M H_2SO_4 the $HCrO_4^-$ species is the most dominant.

A literature survey reveals that Welch and Compton found equivalent sensitivity in acid electrolytes (0.1 M HCl, 0.1 M H_2SO_4 and 0.1 M HNO_3) towards the sensing of Cr(VI) with gold electrodes.[32] Additionally it was noted glassy carbon should not be recommended as a working electrode for analytical purposes for the sensing of Cr(VI) in HCl.[32] Conversely, Danilov and Protsenko reported that the sensitivity in various electrolytes diminished in the following order: H_2SO_4 > HCl > HNO_3.[13] Results reported by Pezzin *et al.*[33] suggest that the reduction of Cr in oxidising acids, not involving a conventional reducing species such as chloride, advocates that the proton may be the defining reagent in the reduction pathway. In discussing the reduction of Cr(VI) in formic acid, Archundia *et al.*[34] concluded that the process is promoted by H^+ and is conceivably independent to the nature of the acid anion, thought the latter may contribute to the formation of CrL_n-type species, whose stability may manipulate the overall kinetics of the acid-reduction process and the consequential product distributions.

Given the information derived above we turn to exploring the electrochemical detection of Cr(VI) at a range of commercially

Table 1 Estimated concentration of species calculated for H_2SO_4 and HCl within a 0.1 M solution

	$K_a = 0.18$ M	$K_1 = 0.09$ M^2	$K_2 = 0.24$ M
H_2SO_4	$HCrO_4^-$	H_2CrO_4	$CrSO_7^{2-}$
0.1 M	50.4%	30. 7%	18.9%
HCl	$HCrO_4^-$	H_2CrO_4	CrO_3Cl^-
0.1 M	60.0%	33.3%	6.7%

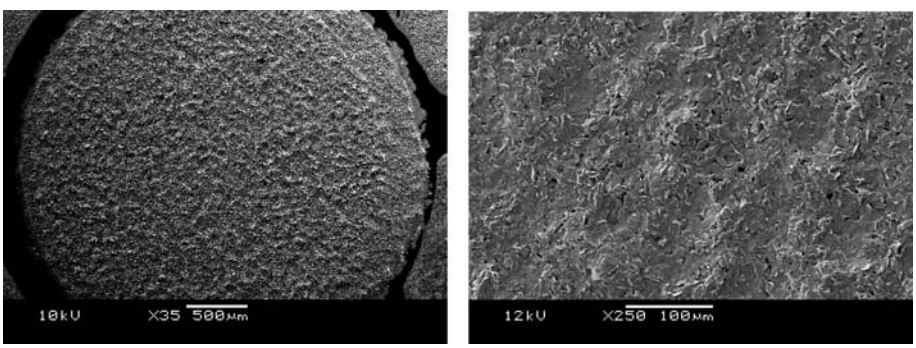

Fig. 1 SEM images of a graphite screen printed electrochemical sensor.

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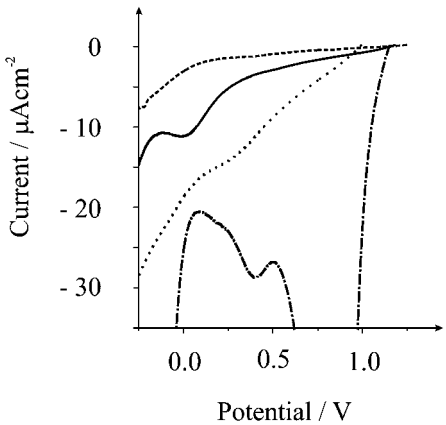

Fig. 2 Linear sweep voltammograms using gold (dot-dashed line), glassy carbon (dotted line) and boron doped-diamond (dashed line) electrodes with that of the non-modified graphite screen printed sensor (solid line) in an aqueous solution of 0.1 M H_2SO_4 containing 1000 μg L^{-1} Cr(VI). All scans recorded at a scan rate of 50 m V s^{-1} (*vs.* SCE).

available electrodes in 0.1 M H_2SO_4[21] using linear sweep voltammetry. Fig. 2 depicts the voltammetric profiles where at the gold electrode a large reduction wave is observed at approx. +0.85 V (*vs.* SCE) due to the electrochemical reduction of gold oxide and a reduction wave at approx. +0.45 V (*vs.* SCE). Based on previous reports,[21,32] the reaction mechanism on the gold electrode likely involves the electrochemical reduction of Cr(VI) to Cr(V) with the transfer of one electron and one proton with follow up chemical steps.[32] Also shown in Fig. 2 is the response of screen printed and glassy carbon electrodes which exhibit reduction waves at approx. +0.075 V and approx. +0.32 V (*vs.* SCE) respectively. Note that no voltammetric waves are observed on the boron-doped diamond electrode.

Inspection of Fig. 2 reveals that the gold electrode appears to exhibit a more reversible electrochemical process over that of the glassy carbon and screen printed electrodes. If we consider the change in reversibility, as is possible through the careful choice of electrode substrates, the ratio of the voltammetric peak current resulting from a reversible electrochemical reduction, I_p^{rev}, and that of a irreversible reduction, I_p^{irr}, can be defined by the appropriate Randles–Ševčík expression:[35]

$$\frac{I_p^{rev}}{I_p^{irr}} = \frac{2.69 \times 10^5 ACD^{1/2}\upsilon^{1/2}}{2.99 \times 10^5 \beta^{1/2} ACD^{1/2}\upsilon^{1/2}} \approx 1.27 \quad (4)$$

Clearly an improvement in the reversibility of the electrochemical reaction by applying gold as an electrode material is observed but theoretically only increases the magnitude of the voltammetric peak current by only a factor of ~1.3. This implies that a change in reversibility is not always beneficial in electroanalysis but what is most appropriate is where in relation to inteferents these voltammetric signatures occur. Given that the voltammetric signal observed at the screen printed electrode is around ~0 V (*vs.* SCE), which is well resolved from likely interferents and the low cost of production and disposable nature compared to the glassy carbon and gold electrodes, screen printed electrodes are highly desirable for the portable screening of Cr(VI). We now turn to exploring the electroanalytical performance of the screen printed electrodes towards the sensing of Cr(VI).

Using linear sweep voltammetry, additions of Cr(VI) were made into a 0.1 M H_2SO_4 aqueous solution and as depicted in Fig. 3 the magnitude of the electrochemical signal increases as a function of added Cr(VI) concentrations. Analysis of the peak current (I_p) reveals a linear response is observed over the range 100 to 1000 μg L^{-1} ($I_P/A = 7.9 \times 10^{-10}$ A/μg $L^{-1} - 3.6 \times 10^{-9}$ A; $R^2 = 0.999$; $N = 11$) with a limit of detection (3σ)[36] found to correspond to 19 (±0.5) μg L^{-1} respectively. The inter-reproducibility of the sensor evaluated from five separate measurements using new screen printed electrodes was found to produce a % Relative Standard Deviation of 4.8%.

Next the electrochemical sensing of Cr(VI) in canal water was explored, allowing a comparison of performance in that of natural environmental conditions and to determine if any materials present could hinder the screen printed sensors ability to detect trace amounts of Cr(VI). As described in the experimental section the canal water sample was acidified to pH 1 with additions of Cr(VI) made into the sample. As shown in Fig. 4, the addition of Cr(VI) is observed to be linear over the range 100 to 1000 μg L^{-1} ($I_P/A = 7.3 \times 10^{-10}$ A/μg $L^{-1} + 1.2 \times 10^{-8}$ A; $R^2 = 0.999$; $N = 11$) with a limit of detection (3σ)[36] found to correspond to 21 (±0.7) μg L^{-1} which is close to the guideline limit set by the WHO (50 μg L^{-1}) in groundwater.[3] In comparison with that depicted in Fig. 3, it is interesting to note that there is no decrease in the sensitivity for the sensing of Cr(VI) in the water sample using the screen printed sensors which likely arises due to the position of the electrochemical signal in the potential window. We note that copper, usually present in water samples,

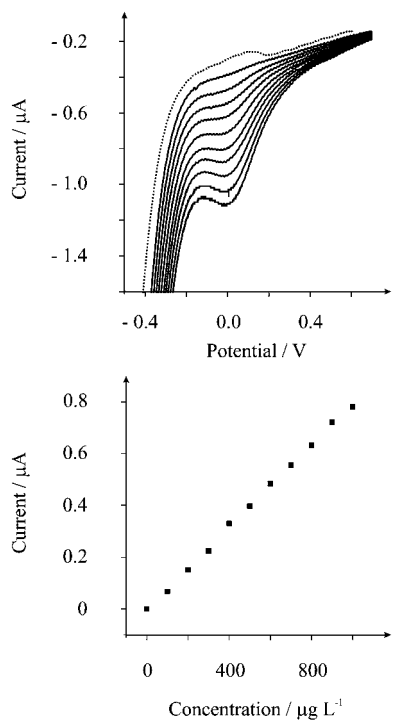

Fig. 3 Linear sweep voltammograms using a screen printed sensor resulting from additions of Cr(VI) into a 0.1 M H_2SO_4 aqueous solution. Scan rate: 50 m V s^{-1}.

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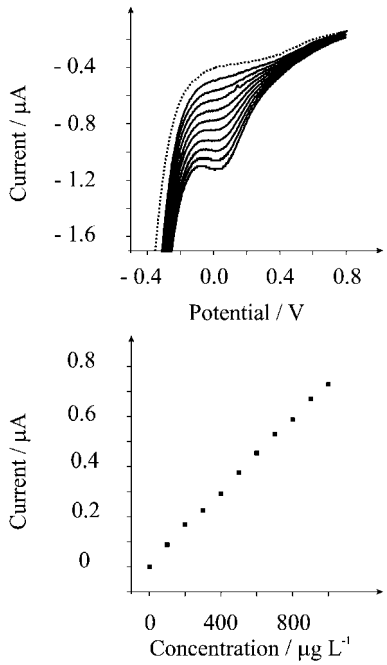

Fig. 4 Linear sweep voltammograms using a screen printed sensor resulting from additions of Cr(VI) into a canal water sample (pH 1). Scan rate: 50 m V s^{-1}.

appears to not interfere with our methodology and caution should be used when using this methodology that the voltammetric potential is not scanned too negative so as to induce the electrochemical reduction of copper ions to copper metal such that the corresponding stripping peak, which usually occurs at ~0 V, does not interfere with the voltammetric signal for the sensing of Cr(VI).

Last we turn to exploring the analytical performance using unoptimised amperometry. Fig. 5 shows the response of 25 μM additions of Cr(VI) made in the canal water sample with analysis of the current as a function of added Cr(VI) concentration depicted in Fig. 6 where a linear range is observed over the range

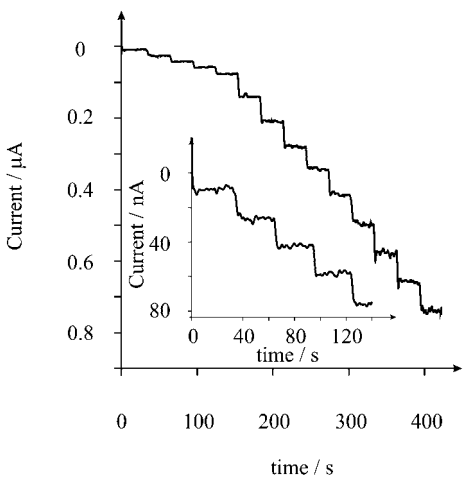

Fig. 5 Amperometric response using a screen printed sensor resulting from additions of Cr(VI) into a canal water sample (pH 1). Potential held at + 0.025 V.

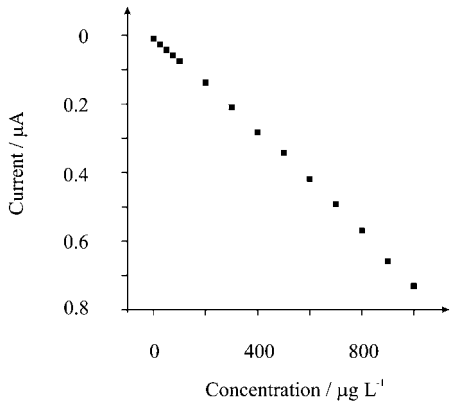

Fig. 6 Analysis of the amperometric data presented in Fig. 5.

25 to 1000 μg L^{-1} ($I_P/A = 7.6 \times 10^{-10}$ A/μg $L^{-1} - 8.4 \times 10^{-10}$ A; $R^2 = 0.99$; $N = 13$). Note that the inset of Fig. 5 shows the response of the lower additions clearly indicating that the sensing of Cr(VI) at levels below the WHO is possible.

In considering the concept of interferents it is clear that in the intended application of sensing Cr(VI) in water samples, it appears that this protocol is extremely promising and has clear advantages over existing analytical and electroanalytical techniques. One potential interferent is the use of water softeners to remove the hardness from water which is used in a plethora of applications through the introduction of chloride salts. The chloride present can, in the presence of Cr(VI), be oxidised to chlorine:

$$2Cr^{6+} + 6Cl^- \rightleftharpoons 2Cr^{3+} + 3Cl_2 \quad (5)$$

Fig. 7 displays the electrochemical reduction of Cr(VI) in a 0.1 M H_2SO_4 aqueous solution using a glassy carbon electrode and after the addition of sodium hypochlorite which releases chlorine gas in acidic media:

$$NaOCl + H^+ + Cl^- \rightarrow NaOH + Cl_2 \quad (6)$$

It is clearly evident that the magnitude of the initial voltammetric peak is considerably increased following the addition of sodium hypochlorite which produces chlorine gas in aqueous solution with the electrochemical processes now due to the electrochemical reduction of chlorine gas:

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad (7)$$

The potential of the electrochemical reduction wave in the voltammetric window, which we attribute to the electrochemical reduction of chlorine, is in excellent agreement with that reported by Lowe *et al.*[37] who have studied the electrochemical sensing of chlorine in aqueous solutions at a range of commercially available electrode substrates. Thus we suggest that: (i) in aqueous solutions other than H_2SO_4, the electrochemical reduction of Cr(VI) may not actually be that as suggested previously[32] but is actually an indirect methodology, which is especially true when using electrolyte solutions such as HCl; (ii) in solutions and real samples, where high levels of chloride may be present, care needs to be taken to ensure the true origin of the electrochemical signal which would become particularly evident in real samples, for

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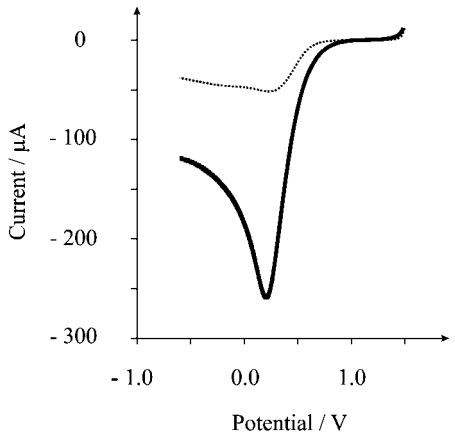


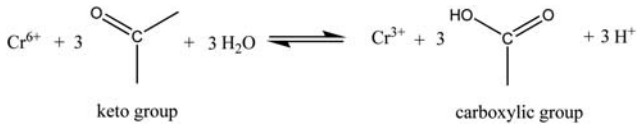
Fig. 7 Linear sweep voltammograms of a GC electrode in an aqueous solution of 0.1 M H_2SO_4 containing 1000 μg L^{-1} Cr(VI) (dotted line) and in the presence of 100 μL (thick solid line) sodium hypochlorite (10–13%). Scan rate: 50 m V s^{-1} (*vs.* SCE).

example in trying to determine Cr(VI) in sea water, but this indirect methodology (eqn (5)–(7)) might prove analytically useful.

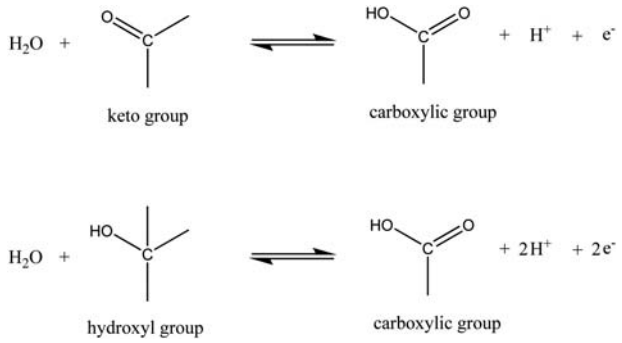
Returning to the analytical performance of the screen printed sensors towards Cr(VI) sensing, to gain an insight into the electrochemical mechanism, the effect of scan rate over the range 0.1 to 1 V s^{-1} using an aqueous solution of 0.1 M H_2SO_4 containing 1000 μg L^{-1} Cr(VI) using a screen printed electrode was explored. Analysis of the current as a function of scan rate and square-root of scan rate revealed a linear response only in the former case ($I/A = 3.3 \times 10^{-6}$ A/V s^{-1} + 2.0×10^{-8} A; $R^2 = 0.995$). It should also be noted that when applying fast scan rates (>400 mV s^{-1}) a distinctive pre-wave was observed indicating that the electrochemical reaction may be adsorption controlled, which might likely proceed *via* a CE route. Thus, in the case of the screen printed electrode, the mechanism is different to that above (not involving Cl^-/Cl_2) since it involves a surface bound species.

Reactive surface groups and a vast surface area make carbon an effective reductant for Cr(VI).[37] The interaction of Cr(VI) with carbon has a two phase mechanism: the sorption of Cr(VI) and the resulting reduction of Cr(VI) to Cr(III) *via* the oxidation of functional groups.[38] IR spectra were obtained for carbon black used in fabrication of the electrodes, to distinguish the surface functional groups responsible for Cr(VI) reduction. Bands at 1604, 1737, 2725, 2850 and 3400 cm^{-1} were observed within the IR spectrum. Assignment of the band at 1604 cm^{-1} was accredited to the stretching of conjugated C–C bonds. The C=O stretching of aldehyde and ketone functional groups was present at 1737 cm^{-1} while the vibrations from the C–H bonds within alkyl groups contribute to the band shown at 2725 and 2850 cm^{-1}. Finally the intense band at 3400 cm^{-1} was assigned to the presence of O–H from either alcohol or phenol active groups. It is feasible to theorize that the absorbed Cr(VI) is reduced to Cr(III) with the oxidation of the functional groups C–H, C–OH and C=O. Results published by Yue *et al.* provide additional data that support this hypothesis.[39]

To quantify these results, a commercially available carbon powder abrasively modified glassy carbon electrode was explored towards the sensing of Cr(VI) which had previously shown a limited response to the presence of Cr(VI). Fig. 8 depicts the pertinent voltammetric profiles where a substantial improvement in the electrochemical signal towards Cr(VI) sensing is revealed through the introduction of surface oxygen rich carbon powder. This observation coupled with the current being proportional to the scan rate employed leads us to believe that the mechanism involves active functional groups found on carbon which are oxidised by Cr(VI):



which are electrochemically reduced, generating the observed electrochemical signal due to the following processes:



which allows for the indirect measurement of Cr(VI) using the screen printed sensor. The electrochemical reduction of surface functional groups is consistent with the observation above from the scan rate data. Returning to Fig. 2 it is evident that the glassy carbon and boron-doped diamond electrodes have less surface active groups resulting in a poor electrochemical signal. Such observations have never been reported before in the literature and the screen printed sensor, while providing the required sensitivity yet is cost effective, lends itself towards the

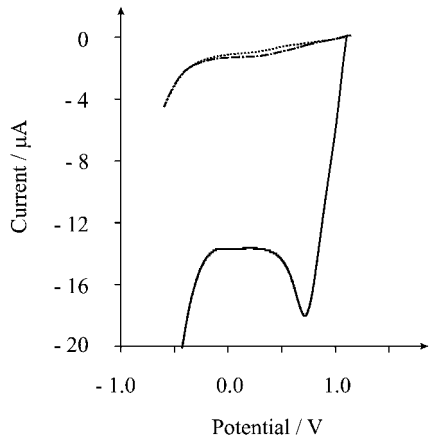


Fig. 8 Linear sweep voltammograms of a glassy carbon electrode in an aqueous solution of 0.1 M H_2SO_4 in the absence (dotted line) and in the presence (dot-dashed line) of 1000 μg L^{-1} Cr(VI) and a carbon powder abrasively modified glassy carbon electrode (solid line) in the presence of 1000 μg L^{-1} Cr(VI). Scan rate: 50 m V s^{-1} (*vs.* SCE).

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de-centralised testing of Cr(VI) in water samples. Further work in this area is underway.

4. Conclusions

We have explored the electrochemical reduction of Cr(VI) and reported for the first time, non-modified, non-metallic, graphite screen printed electrode for the electroanalytical sensing of low ppb levels of Cr(VI) in aqueous solution which are at WHO levels. The methodology is demonstrated to be possible for the electroanalytical sensing of Cr(VI) in water samples. Investigation of the electrochemical mechanism indicates that the electroanalytical protocol is an indirect sensing approach involving surface oxygenated species. Given the analytical performance and low cost of the screen printed sensors, this protocol holds promise for the portable sensing of the toxic pollutant Cr(VI) in water samples.

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