

## SHORT COMMUNICATION

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**Mechanism of activation of glassy carbon electrodes by cathodic pretreatment**

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**Abstract** The performance of carbon electrodes depends on the surface pretreatment methods. An exclusively cathodically pretreated glassy carbon electrode (GCE) shows very good activity towards monomeric molybdate(VI) ion adsorption and its reduction. X-ray photoelectron spectroscopy studies reveal the creation of  $>C-O-$  surface groups on cathodisation. A strong interaction between the Mo(VI) ion and these  $>C-O-$  surface groups with the formation of Mo(V) is responsible for the activation of the cathodically pretreated GCE surface.

**Key words** Activation · Cathodic pretreatment · Glassy carbon electrode · Monomeric molybdate(VI) ion

**Introduction**

The method of electrode surface pretreatment, either electrochemical or non-electrochemical, for a glassy carbon electrode (GCE) can cause a wide alteration in the heterogeneous electron transfer rate constant of a variety of redox systems, often by many orders of magnitude [1]. This is true even for redox systems which proceed through adsorption and a subsequent electron transfer step [2, 3]. While methods like application of square wave pulses several times between two extreme potentials, potential cycling between two preset potentials, static polarisation at an anodic potential, static anodic polarisation followed by short time cathodic polarisation, etc., have been reported as prominent electrochemical pretreatment methods for GCEs, no report is available regarding the exclusive use of pre-cathodisation as a pretreatment method. We have recently observed that an exclusively cathodically

pretreated GCE shows improved adsorption of monomeric molybdate(VI) and its subsequent electroreduction. Surprisingly, the most effective pretreatment method of anodisation is found to be detrimental. The mechanism of activation of the cathodically pretreated GCE with respect to monomeric molybdate(VI) and a comparison of this with an anodically pretreated sample is presented here.

**Experimental**

Electrochemical experiments were carried out with a Wenking potentiostat (ST 72) and a Wenking voltage scan generator (VSG 83) coupled with a Graphtech XY recorder (WX 2300). The potentials were referred with respect to SCE. The GCE working electrodes (3 mm dia) were firstly hand polished to a mirror finish by successively fine grades of emery paper, degreased with trichloroethylene and washed with double distilled water. Then the electrodes were pretreated as follows: (1) for cathodisation the electrode was polarised at  $-1.5$  V (SCE) for 2 min (pre-cathodised electrode); and (2) for anodisation the polished electrode was polarised at  $+1.5$  V (SCE) for 2 min (pre-anodised electrode). Both the pretreatments were carried out in  $0.1$  M  $H_2SO_4$ . X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ESCALAB MK II spectrometer.

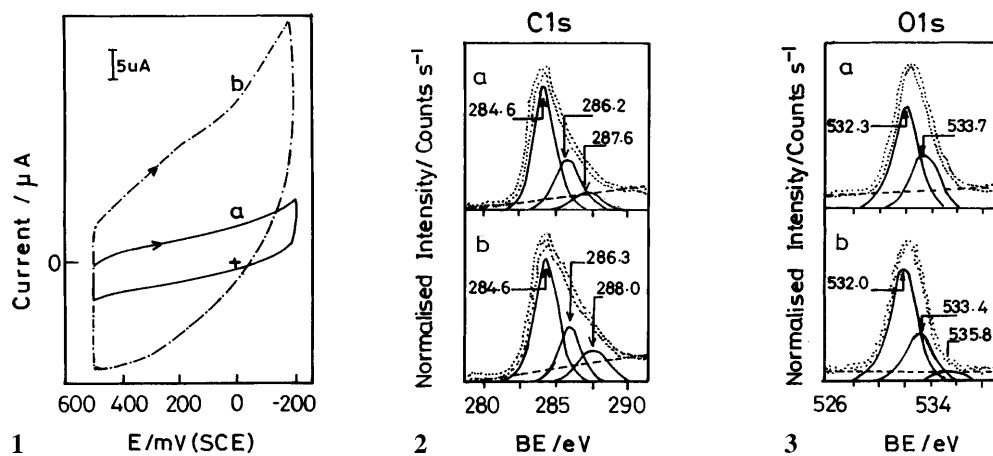
**Results and discussion**

The cyclic voltammograms (CV) of the first cycle of both pre-cathodised and pre-anodised electrodes in  $0.1$  M  $H_2SO_4$  are illustrated in Fig. 1. The magnitude of the background current is highly sensitive to the type of electrochemical pretreatment. It is small for the cathodised electrode, but in the case of the anodised electrode a very high capacitive-like background current is observed. It is known that the background current for carbon electrodes varies greatly with the surface history and nearly always contains components from a double layer charging process and a faradaic process like oxidation/reduction reaction of surface functional groups.

**Fig. 1** Cyclic voltammetry (CV) in 0.1 M H<sub>2</sub>SO<sub>4</sub> of a glassy carbon electrode (GCE): *a* cathodised; *b* anodised ( $v = 100 \text{ mV s}^{-1}$ )

**Fig. 2** X-ray photoelectron spectroscopy (XPS) of C 1s for a GCE: *a* cathodised; *b* anodised

**Fig. 3** XPS of O 1s for a GCE: *a* cathodised; *b* anodised



Broad anodic and cathodic surface waves in current potential curves have been generally reported for anodised GC electrodes [1–5]. While these waves have been attributed by many (cf. [1, 4]) to a redox reaction of surface oxidised functional groups of phenol and quinol forms introduced by electrochemical treatment, Nagaoaka et al. [5] have assigned the waves to the uptake and release of protons by the oxidised surface carbons. Alternatively, Barbero et al. [2] have proposed that the anodised GCE surface behaves like a surface modified polymeric film containing uniformly distributed anchored sites which may be oxidised and reduced, giving rise to well-defined peaks. However, in our case, the background voltammograms are mostly flat and featureless for the anodised electrode. As the anodic treatment used in the present work is relatively mild, this may account for the lack of creation of highly reactive oxygen containing surface functional groups and oxidised carbons following anodisation.

The surfaces of the pretreated electrodes have been analysed by XPS. The C 1s and O 1s levels are given in Figs. 2 and 3, respectively. XPS shows a relatively smaller surface oxygen concentration for the cathodised sample (O/C atomic ratio = 0.19) and substantial increase in the oxygen content upon anodisation (O/C = 0.54). This indicates that surface functionalisation has occurred on

anodisation, and consequent to this, we suggest that these oxygen surface sites have probably redox transitions which are quite slow to spread over a wide potential range, resulting in a higher background current.

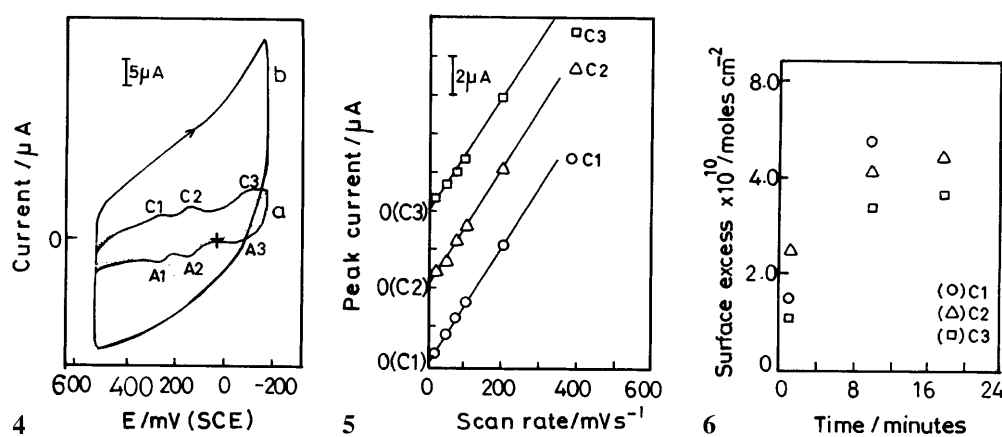
Figure 4 illustrates the CV of the two pretreated electrodes in 2 mM Mo(VI) containing 0.1 M H<sub>2</sub>SO<sub>4</sub>. While the cathodised electrode gives three well-defined redox peaks (C1/A1, C2/A2 and C3/A3), the anodised electrode totally fails to yield any such redox peaks. These peaks are characterised to be surface waves as they show the following characteristics: (1) peak current is linear with  $v$  up to  $200 \text{ mV s}^{-1}$  for all the three peaks (Fig. 5); (2) anodic to cathodic peak potential separation is  $< 20 \text{ mV}$ ; (3) anodic and cathodic peak potentials are invariant with  $v$ . The strength of adsorption of Mo(VI) on precathodised GCE is so strong that the Mo(VI) adsorption layer can be easily formed on the GCE surface by simply soaking the electrode in Mo(VI) containing 0.1 M H<sub>2</sub>SO<sub>4</sub> solution. Indeed, the surface coverage depends on the dip time, as shown in Fig. 6. The saturation surface coverage is achieved within 5 min. Even in this case the preanodised electrode does not show any Mo(VI) adsorption.

The electrochemical processes of the three redox pairs of peaks on a cathodised GC electrode have been analysed elsewhere [6], using CV, controlled potential elec-

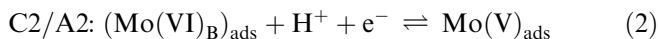
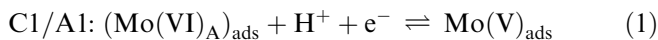
**Fig. 4** CV of 2 mM Mo(VI) in 0.1 M H<sub>2</sub>SO<sub>4</sub> of a GCE: *a* cathodised; *b* anodised ( $v = 100 \text{ mV s}^{-1}$ )

**Fig. 5**  $i_p$  versus  $v$  for C1, C2, C3 peaks of 2 mM Mo(VI) in 0.1 M H<sub>2</sub>SO<sub>4</sub> at a cathodised GCE

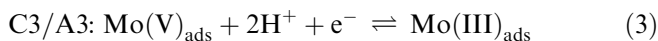
**Fig. 6**  $\tau_{\text{Mo(VI)}}$  on a cathodised GCE versus electrode exposure time in 2 mM Mo(VI) in 0.1 M H<sub>2</sub>SO<sub>4</sub>



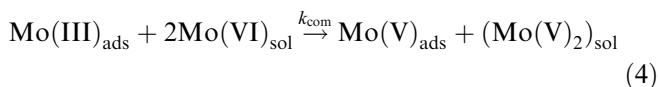
tolysis, UV spectroscopy and XPS techniques. Briefly, two forms of monomeric molybdate(VI) species, Mo(VI)<sub>A</sub> and Mo(VI)<sub>B</sub>, which are in equilibrium in solution, undergo  $1e^-$ ,  $1H^+$  reduction to Mo(V) in an adsorbed state at C1 and C2:



The products of C1 and C2, viz., Mo(V)<sub>ads</sub>, subsequently undergo  $2e^-$ ,  $2H^+$  reduction at C3 as follows:



The electroactive species Mo(VI)<sub>A</sub> and Mo(VI)<sub>B</sub> have been identified as Mo(OH)<sub>6</sub> and Mo(OH)<sub>5</sub> (O<sup>-</sup>). While the charge transfer mechanisms at C1 and C2 remain the same at all Mo(VI) concentrations and potential sweep rates, the process at C3 is seen to become a reversible charge transfer step (reaction 3) followed by the comproportionation electron exchange between adsorbed Mo(III) and dissolved Mo(VI), regenerating Mo(V)<sub>ads</sub> at the GCE/solution interphase (reaction 4):



The catalytic comproportionation rate constant,  $k_{com}$ , has been estimated to be  $0.60 \pm 0.15 \times 10^3 M^{-1} s^{-1}$  from experimental CV data following the method proposed by Andrieux and Saveant [7] as done in the previous studies [8, 9]. The details on the mechanistic aspects will be published separately.

The different behaviour of the precathodised and preanodised electrodes could be unraveled by studying the surface composition changes of the GCE with pretreatment. The high resolution C 1s spectra for both the anodised and cathodised GCE (Fig. 2) are deconvoluted for three different C species [10]: (1) graphite or hydrocarbon (with binding energy (BE) = 284.6 eV); (2) alcohol, phenol, ether or quinolic carbon (BE = 286.2 eV); and (3) carbonyl carbon (BE = 287.6 eV). Similarly, the O 1s spectra of both the electrodes (Fig. 3) could be deconvoluted into two peaks at BE = 532.0 eV due to  $>C=O$  and at 533.7 eV mainly due to the  $>C-O-$  species [11]. The quantitative analysis of these spectra reveals the following facts. First, the relative C 1s area associated with the functional groups alcohol, phenol, ether or peroxide (BE = 286.2 eV) relative to the total oxidised C (expressed as the ratio of alcohol C/oxidised C) is higher: 0.70 for the precathodised sample but 0.6 for the anodised GCE. Most importantly, the relative intensity of the O 1s peak at 533.7 eV (due to  $>C-O-$ ) to total O 1s intensity is higher, namely 0.35 for the precathodised electrode but only 0.18 for the preanodised electrode. These observations provide a useful clue to the activation of the cathodically treated GC electrode to Mo(VI) ion adsorption. Presumably, formation of the specific functional group  $>C-O-$  on cathodic treatment facilitates the Mo(VI) adsorption.

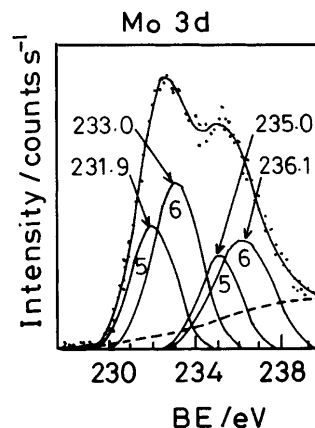
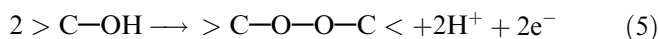


Fig. 7 XPS of Mo 3d for monomeric molybdate adsorbed on a cathodised GCE; 5 and 6 denote the assigned oxidation states

The Mo(VI) adsorbed on the precathodised GCE surface (prepared by the dip coating method at open circuit conditions) has been examined by XPS for the Mo 3d energy level [12]. Analysis of the Mo 3d level reveals the presence of Mo(VI) and also, surprisingly, Mo(V), as shown in Fig. 7. In the case of anodised GCE, neither Mo(VI) nor Mo(V) has been noticed. Thus Mo(V) formation during Mo(VI) adsorption at open circuit seems to be specific for the cathodised electrode. The specific functional group ( $>C-O-$ ) created on precathodisation should be responsible for the Mo(V) formation. The likely cause of the formation of Mo(V) on the cathodised GCE is the reduction of Mo(VI) adsorbed on the surface and the simultaneous oxidation of the  $>C-O-$  functional group by a mixed potential mechanism. This suggestion stems from the fact that the redox potential of the  $>C-OH$  group oxidation to  $>C-O-O-C<$  is  $-0.87$  to  $-0.44$  V (SCE) [13], negative to the reduction potential of surface bound Mo(VI) reduction to Mo(V) [ $+0.24$  V(SCE)], fulfilling the requirement for the mixed potential mechanism to be operative [14]. The following reactions can, therefore, be considered to occur during Mo(VI) adsorption on a precathodised GCE:



Thus, as far as Mo(VI) adsorption on a precathodised GCE is concerned, the spontaneity of the coupled reactions 5 and 6 seems to be the prime activating factor of precathodised GCE. The ratio Mo(V)/Mo(VI) is 0.64 on the above treated GCE (Fig. 7), and this ratio must depend on the duration of precathodisation and the polarisation potential as per the mechanism proposed. These aspects are being examined at present in detail and will be communicated shortly.

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