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The adatom/incipient hydrous oxide mediator model for reactions on silver in base

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The adatom/incipient hydrous oxide mediator model for electrocatalysis at a metal/solution interface is outlined in a general manner and examined with particular reference to the behaviour of silver in base. A low level transition, involving less than 0.1% of the surface metal atoms, was observed at ~ 0.4 V (RHE). Above this value (where Ag adatoms are assumed to oxidise to hydrous oxide) anodic reactions, e.g. HCHO oxidation or Ag dissolution in the presence of CN^-, take place; below this value (where the adatom is unoxidized) cathodic processes, e.g. nitrobenzene or nitrate ion reduction, are catalysed at adatom sites. The role of subsurface oxygen, which may be an inhibiting factor in the case of nitrate reduction, is a feature requiring further investigation.

1. Introduction

Attention was drawn recently [1] to the important role of both adatoms and incipient hydrous oxides in noble metal electrocatalysis. Adatoms are considered here as surface metal atoms of low bulk metal lattice coordination number residing at defect sites or on ledges; there may well be a range of such species and since many of their coordination sites are exposed to the solution they are considered to be partially hydrated. Such species oxidize at potentials well below that required for regular monolayer oxide formation and the product obtained is a hydrous oxide species, not the conventional OH_{ads} entity which is the species formed on the majority of surface metal atoms that are of relatively high lattice coordination number.

The basic ideas of this theory have already been outlined for gold [1, 2], platinum [1, 3], silver [4] and quite recently for a wide range of noble metals [5]. The response for adatom oxidation is often difficult to detect; these adatoms are metastable, high energy and, consequently, low coverage species; their voltammetric response on oxidation is therefore quite low and may be spread, for various reasons (variation of adatom coordination number, formation of slightly different product species, electrostatic repulsion between product species, slow preceding reactions, etc.) along the voltage axis. The main point, with regard to electrocatalysis, is that for electrocatalytically demanding electrode processes oxidation reactions of solution species are triggered or mediated on the anodic sweep at the potential of adatom oxidation (the mediating species being the incipient hydrous oxide) whereas reduction reactions of solution species (at least those requiring adatom sites) commence on the cathodic sweep in the region where the incipient hydrous oxide is reduced to form adatoms. This approach has already been outlined for platinum [1, 6] and gold [6]. Support for the view that a hydrous oxide, rather than OH_{ads}, species is involved in oxidation processes was established recently [5] by showing that for hydrazine on gold the onset/termination potential for oxidation dropped by ~ 90, rather than 60, mV per unit increase in solution pH ($T = 25°C$); the 90 mV per pH unit shift (pH-independent scale) is a characteristic feature of adatom/hydrous oxide transitions [7] for systems where the oxidation state of the central metal ion in the oxide is greater than 1.

The object of the present work is to extend this approach to silver; the mediation of formaldehyde oxidation by incipient hydrous oxide species generated on this metal in base has already been reported [4]. However, before describing the present results in detail a general scheme for the interfacial mediator model of electrocatalysis will be outlined.

The basis of the model is given in Fig. 1. The full line in this diagram represents the conventional cyclic voltammogram for a metal such as platinum: it shows the usual three regions, namely, hydrogen adsorption (H_a)/desorption (H_d), double layer (DL) and oxide (OH_{ads} or O_{ads}) formation (O_f)/removal (O_r). No attempt is made here to show fine structure in the hydrogen and oxygen regions; it must also be borne in mind that some metals, for example silver and gold, do not chemisorb hydrogen (in which case the H_d and H_a section in the diagram should be absent) while for others, for example ruthenium and iridium, the hydrogen and oxygen regions tend to overlap [8].

The dotted line (· · ·) in this diagram illustrates the response for the reversible adatom/incipient hydrous oxide transition – this has been discussed earlier for gold [2], platinum [3] and silver [4]. The response here is frequently quite low (due to low adatom coverage); however, in some cases the potential for this transition may be determined by noting the quite large peak – the dashed (– – –) line in Fig. 1 – for the reduction of a thick hydrous oxide layer produced by potential cycling [7]. This large response, as discussed earlier for

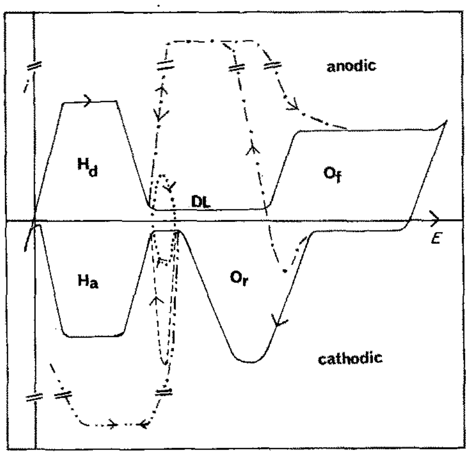

Fig. 1. A generalised presentation of the i/E response for adatom/incipient hydrous oxide mediated electrocatalysis; see text for details.

platinum [3], is usually only seen on the first reduction sweep in the case of the oxide-coated electrode; the hydrous oxide on reduction yields adatoms (Pt*) but the majority of the latter decay rapidly in a post-electrochemical step by increasing their lattice coordination number to form lattice atoms (Pt_l), i.e. the latter step, Pt* → Pt_l, is a major source of irreversibility. The main point with regard to electrocatalysis is that oxidation of solution species commences (anodic sweep) and terminates (cathodic sweep) in the region of the reversible adatom/hydrous oxide transition – see the upper line (—·—); conversely, reduction of electrocatalytically demanding solution species commences (cathodic sweep) and terminates (anodic sweep) at approximately the same region – see the lower line (—··—) in this diagram.

The following important points should be borne in mind:

1. The ideal behaviour outlined here is not observed with processes which lead to deactivation of the surface, for example CO_{ads} is a common deactivating species formed in the course of organic oxidation on Pt [9].

2. A kinetic treatment for this mode of electrocatalysis has been published [4] and the limiting current is often reaction controlled at the interfacial redox centre.

3. Regular monolayer oxide deposits (OH_{ads}) tend to be deactivating, but the surface reactivates as such films commence reduction.

4. The initial stages of monolayer film formation in the case for instances of platinum [10] and gold [11] appear to involve hydrous oxide species; thus there may be an indication of high activity in this region due to the high mediator coverage; in fact if the solution species, for example N_2H_4 [1], is highly reactive the monolayer oxide may not attain a high coverage and marked inhibition may not be observed.

5. Some inhibition may also be seen in some cases in the cathodic sweep as the potential enters a region of high hydrogen coverage. The origin of this effect is uncertain; the high hydrogen coverage may inhibit chemisorption of the solution species or decrease the activity or coverage of the mediator.

2. Experimental details

The working and counter electrode consisted of lengths of silver wire (Koch-Light Laboratories, Ltd., 1 mm diam., ~0.75 cm^2 exposed area) sealed directly into soda glass. The electrodes were cleaned before use by brief (10 s) immersion in concentrated HNO_3 followed by mild abrasion with fine grade emery paper; they were then rinsed with triply distilled water. Potentials were measured, and are reported, with respect to a hydrogen reference electrode in the same solution; a Luggin capillary was used to minimise errors due to iR drop in the solution.

The electrochemical equipment consisted of a Potentiostat (Wenking, Model PGS 81) controlled by a function generator (Metrohm VA Scanner, Model E612). Cyclic voltammograms were recorded using a Rikadenki, Model RW-21T, X-Y recorder. The solution around the working electrode was purged with a flow of nitrogen gas; cyclic voltammograms were generally recorded using unstirred solutions; due to the low solubility of nitrobenzene in water the behaviour of this compound was investigated using a mixed (water/ethanol) solvent. All charge and current density values are given with respect to geometric surface area.

3. Results and discussion

As pointed out earlier [4] regular monolayer oxide film formation on silver in base commences, dashed line in Fig. 2, at ~1.1 V(RHE); two peaks (corresponding to an Ag(0)/Ag(I) and Ag(I)/Ag(II) transition) are observed on both the anodic and cathodic sweep. However, by restricting the upper limit of the sweep to 1.0 V and increasing the recorder sensitivity minor peaks (referred to hereafter as premonolayer peaks), attributed to adatom (Ag*)/incipient hydrous oxide transitions, were observed at lower potentials (solid line in Fig. 2). The level of response here is quite low; as discussed in more detail later the adatom coverage involved is estimated to be less than 0.1% of a mono-

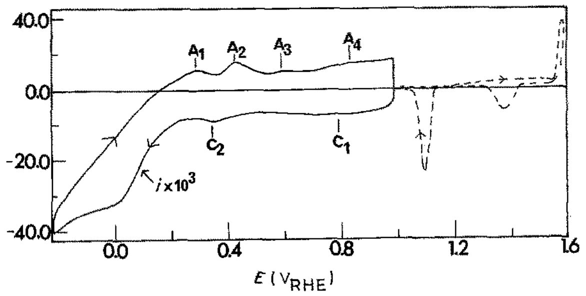

Fig. 2. Typical cyclic voltammogram (- - -) for a silver electrode in N_2-degassed 1.0 mol dm^{-3} NaOH at 25°C (0–1.6 V, 10 mV s^{-1}); at the recorder sensitivity used here no peaks were evident below 1.0 V(RHE). The full line (——) was recorded later for the same electrode using a reduced upper limit (−0.2, 1.0 V, 10 mV s^{-1}) and increased recorder sensitivity.

layer. Adatoms are regarded as high energy, metastable species that decay readily by increasing their lattice coordination number (LCN value). If an electrode surface is allowed to rest after cycling the majority of adatoms are assumed to relax, i.e. to attain a state of high LCN value and become inactive with regard to premonolayer oxidation. However, a very small percentage of adatoms are assumed to become trapped in surface states of low to intermediate LCN value from which on cycling they readily attain the adatom, and hence the hydrous oxide, state. As pointed out earlier [4] the response for silver in base in the premonolayer region is rather variable; the factors influencing the response may include such parameters as the level of trapped oxygen and the degree to which the outer layers of the metal lattice are disturbed (for example, the density of metal atom vacancies, etc.).

On the anodic sweep minor peaks were observed at ~0.30 V(A_1), 0.43 V(A_2), 0.61 V(A_3) and 0.84 V(A_4); all these peaks were minute relative to the response for monolayer-type oxide formation – the upper two, A_3 and A_4, are particularly small but larger peaks at approximately the same potential values can be seen in curve A, Fig. 3, in [4]. On the subsequent cathodic sweep there was an indication of a broad peak at ~0.76 V(C_1) and another at ~0.36 V(C_2) – the latter appeared to be the cathodic counterpart of A_2. A dramatic feature in this voltammogram, also reported earlier [4], was the presence of significant cathodic current, even on the anodic sweep, at potentials below ~0.2 V. This is attributed to reduction of an oxysilver species present either as a weakly adherent species at the electrode surface or suspended, in colloidal form, in the solution close to the electrode surface. On prolonged cycling a black deposit, presumably Ag_2O, was observed on the floor of the cell; somewhat similar behaviour to that found here with silver was reported earlier for one of the less corrosion resistant noble metals – namely ruthenium in base [12]. There are reports that Ag_2O is more soluble in base than in distilled water [13]; the oxide suspension in water is also reported to be strongly basic [13] – a similar conclusion was drawn recently [14] from studies of the potential/pH behaviour of oxide films on copper, silver and gold electrodes. On the basis of the latter it is assumed here that the effective oxidant for formaldehyde oxidation on silver in base is some form of low coverage, surface bound, hydrated cationic species which may be formulated as $(Ag^+ \cdot nH_2O)_{ads}$. As pointed out recently in the case of platinum [5] the binding of such ions to the surface may involve subsurface oxygen species.

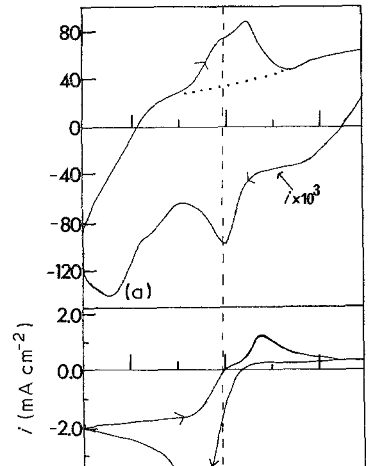

Fig. 3. (a) Cyclic voltammogram (–0.2 to 1.0 V, 100 mV s^{-1}) for an Ag electrode in N_2-degassed 1.0 mol dm^{-3} NaOH at 25°C; (b) cyclic voltammogram (–0.2 to 1.0 V, 20 mV s^{-1}) for an Ag electrode in N_2-degassed 1.0 mol dm^{-3} NaOH containing 1 × 10^{-2} mol dm^{-3} $PhNO_2$ at 25°C; the solvent used here was 90% (by volume) C_2H_5OH in water; and (c) cyclic voltammogram (–0.2 to 1.0 V, 20 mV s^{-1}) for an Ag electrode in N_2-degassed 1.0 mol dm^{-3} NaOH containing 0.1 mol dm^{-3} CN^- at 25°C.

If the general theory of electrocatalysis, as outlined in Fig. 1, is valid then the onset of oxidation on the anodic sweep, and reduction on the cathodic sweep, should show some coincidence with the minor peaks shown (full line) in Fig. 2. An example is shown here in Fig. 3. Figure 3a here shows again the voltammogram for silver in pure base; the low level peaks in this case are not particularly well resolved but the major anodic/cathodic (adatom/incipient hydrous oxide) transition can be seen at ~0.4 V. In the presence of nitrobenzene in the solution, Fig. 3b significant reduction current commenced (cathodic sweep) and terminated (anodic sweep), as expected, at ~0.4 V. Similarly, with cyanide present in solution, Fig. 3c, significant oxidation current commenced (anodic sweep) and terminated (cathodic sweep) in the same region. The cyclic voltammograms shown here in Figs 3b and c may be considered as the steady state behaviour; the responses shown correspond to the third cycle – generally the difference between cycles (especially after the first) was trivial. Vigorous nitrogen stirring significantly increased the reduction current in the case of the nitrobenzene reaction, Fig. 3b. The onset/termination potential was unaltered but the decrease in current after the peak at ~0.3 V on the cathodic sweep was not as pronounced; the rate of reduction at lower potentials was virtually double in stirred, as compared with unstirred, solution. The onset/termination potential behaviour establish the crucial role of adatom/incipient hydrous oxide transitions in electrode reactions at metal surfaces. The fact that the flow of current in Figs 3b and c involve participation of the solution species is borne out by the fact that for both the nitrobenzene (Fig. 4) and cyanide (Fig. 5) the current in the active region is proportional to the bulk concentration of the reactant.

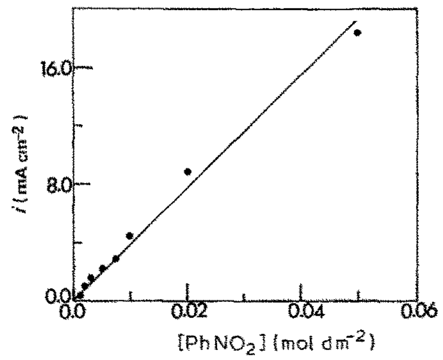

Fig. 4. Variation of i_{max} (cathodic sweep, $E \simeq 0.33$ V) with PhNO$_2$ concentration for PhNO$_2$ reduction at Ag in N$_2$-degassed 1.0 mol dm^{-3} NaOH (in 90% C$_2$H$_5$OH in water) at 25°C; the data were taken from cyclic voltammograms recorded at 20 mV s^{-1}, -0.2 to 1.0 V(RHE).

As pointed out in [4] the interfacial mediator model for electrode processes has much in common, especially from a kinetic viewpoint, with enzyme-catalysed reactions. In both cases there is a changeover from first-order to zero-order kinetics with increasing concentration of the reactant. This was demonstrated earlier in the case of HCHO oxidation on silver [4]; it is not expected in the case of the CN$^-$ reaction (Fig. 5) as this species is involved in a dissolution, rather than an electrocatalytic, reaction; however, it may be expected in the case of nitrobenzene reaction at Ag* sites (Fig. 4). One problem with the latter is that nitrobenzene has only a limited solubility in aqueous media; it may be noted here that the data in Fig. 3b was obtained using nitrobenzene in 90% (by volume) of ethanol in water; attaining concentration levels sufficient to observe the transition to zero-order kinetics (without encountering solubility problems) was difficult. Zero-order kinetics corresponds to saturation of the active regions of surface with the reactant. The concentration level at which the changeover occurs depends on the ability of the dissolved reactant to react with the surface; a strongly adsorbing species will reach a limiting coverage, and hence a changeover to zero-order behaviour, at a lower concentration than a weakly adsorbing species. Formaldehyde, which exists in base [4] in the anionic, gem-diolate form ($H_2CO \cdot OH^-$) may be assumed to interact strongly with the interfacial mediator which in the case of oxidation on silver is believed to be a cationic species, $(Ag^+ \cdot nH_2O)_{ads}$. Formaldehyde adsorption in this case is assumed to be enhanced due to electrostatic forces and the changeover to zero-order reaction is observed [4] at a HCHO concentration of ~0.02 mol dm^{-3}. For nitrobenzene reduction the mediator is postulated as being the neutral adatom Ag*; since there is no major electrostatic force in this case favouring adsorption saturation coverage, and hence the changeover to a zero-order rate law, is expected to occur at a significantly higher reactant concentration (evidently above the limiting value for nitrobenzene solubility).

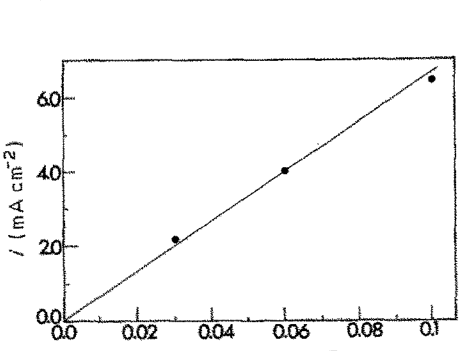

Fig. 5. Variation of i_{max} (anodic sweep, $E \simeq 0.6$ V) for Ag dissolution with CN$^-$ ion concentration in N$_2$-degassed 1.0 mol dm^{-3} NaOH (+CN$^-$) at 25°C: the data were taken from cyclic voltammograms recorded at 20 mV s^{-1}, -0.2 to 1.0 V(RHE).

The detailed mechanism of nitrobenzene reduction on silver in base is not the primary concern of the present work. This reaction has been investigated in some detail by Nishihara and Shindo [15]: they reported two reduction peaks, one at ~ −0.3 V(SCE) and the other at ~ −0.8 V(SCE) on the cathodic sweep (these values correspond to ~ +0.4 and −0.1 V(RHE), respectively) — there was no indication of the lower peak on the subsequent anodic sweep (it is possible that this feature was due to reduction of either subsurface oxygen or weakly adherent oxide — see the broad wave in this regon, ~ −0.1 V(RHE), in the cathodic sweep in Fig. 3a — where there was no nitrobenzene present in the solution). We suggest that nitrobenzene reduction is an inhibited process which required the intervention of silver adatoms; the latter must be in the reduced state, i.e. the reaction can only occur below the adatom/incipient hydrous oxide transition — the rise in reduction current as the potential drops below the latter value is quite dramatic (see Fig. 1 in [15]). The reaction path for nitrobenzene reduction is quite complex (the products include [15] azobenzene, aniline and phenylhydroxylamine) and clarification will require a separate, detailed investigation.

The reaction of cyanide with silver, Fig. 3b, is a metal dissolution, not an electrocatalytic, process. However, these two types of processes seem to have much in common; for instance as shown earlier [4], and also discussed here later in connection with Fig. 6, the onset/termination potential for formaldehyde oxidation on silver in base is also in the region of 0.4 V. The assumption here in the case of the cyanide reaction is that oxidation of adatoms to form the hydrous oxide is followed by a ligand displacement reaction resulting in the formation of soluble silver cyanide species, namely,

$$Ag^* + nH_2O \xrightarrow{-e^-} [Ag^+ \cdot nH_2O]_{ads} \xrightarrow{+2CN^-} [Ag(CN)_2^-]_{aq} + nH_2O \quad (1)$$

A further illustration of the electrocatalytic behaviour of silver in base is outlined in Fig. 6. In this case both the oxidizable (HCHO) and reducible (NO_3^-) species were present in the same solution. During the course of the potential sweep major anodic currents for formaldehyde oxidation were observed just above 0.4 V(RHE) whereas major cathodic currents due to nitrate reduction were observed below 0 V(RHE).

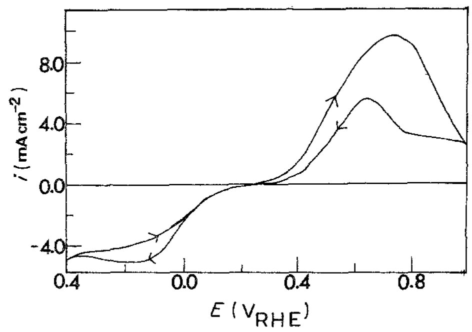

Fig. 6. Cyclic voltammogram (-0.4 to 1.0 V, 10 mV s^{-1}) recorded for an Ag electrode in N_2-degassed 1.0 mol dm^{-3} NaOH solution which also contained HCHO (0.1 mol dm^{-3}) and NO_3^- (0.1 mol dm^{-3}), $T = 25°C$.

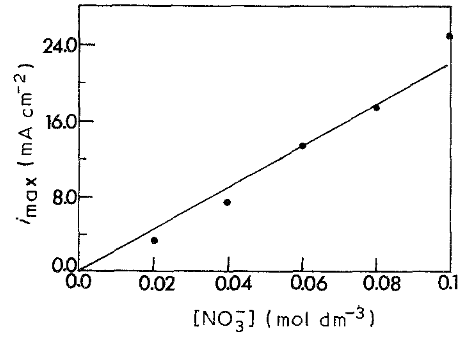

Fig. 8. Variation of i_{max} (cathodic sweep, $E \simeq 0.25$ V) with NO_3^- concentration for NO_3^- ion reduction at Ag in N_2-degassed 1.0 mol dm^{-3} NaOH ($+NO_3^-$) at 25°C; the data were taken from cyclic voltammograms recorded at 10 mV s^{-1}, -0.5 to 1.0 V.

The nitrate reduction process appeared to be significantly more inhibited (or more electrocatalytically demanding) than the corresponding reaction with nitrobenzene. It may be noted that in Fig. 6 cathodic currents were observed below $\sim +0.25$ V(RHE); the onset/termination potential for NO_3^- ion reduction, in the absence of HCHO, rose significantly with increasing NO_3^- concentration. It may well be that in this case subsurface oxygen had an inhibiting effect; loss of this oxygen from the surface of the lattice below ~ 0.2 V, Fig. 3a, leads to a rise in activity for NO_3^- reduction — eventually giving a peak on the anodic sweep (Fig. 7) at ~ -0.2 V(RHE). Hydrogen gas evolution in this case only became significant below ~ -0.4 V(RHE). In the case of the nitrate reduction the rate of reaction at constant potential was a linear function, Fig. 8, of the concentration of NO_3^- — at relatively low concentrations of the latter; similar behaviour was demonstrated earlier for HCHO oxidation on Ag in base [4].

4. Conclusions

The objective of this work was to demonstrate, in terms of the general diagram shown in Fig. 1, the importance of the adatom/incipient hydrous oxide approach in electrocatalytic processes at metal electrodes. For silver in base the crucial region for generation of low coverage mediating species (adatoms on the cathodic sweep, incipient hydrous oxides on the anodic sweep) was shown, Fig. 2a, to be ~ 0.4 V(RHE); however, the response for premonolayer oxidation was somewhat dependent on the electrode pretreatment. Electrocatalytically demanding oxidation (and metal dissolution) processes tend to occur above this value whereas the corresponding reduction processes occur at lower potentials; this approach to electrocatalysis is relatively novel — the main theories of electrocatalysis at metal surfaces to date emphasize the importance of chemisorption phenomena. While we do not assume the latter approach to be invalid, it seems necessary to consider both approaches (chemisorption and mediation by low coverage species) when examining electrocatalytic processes at metal electrodes.

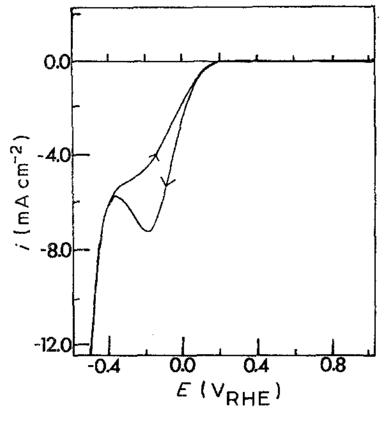

Fig. 7. A typical cyclic voltammogram (-0.5 to 1.0 V, 10 mV s^{-1}) for an Ag electrode in N_2-degassed 1.0 mol dm^{-3} NaOH + 0.04 mol dm^{-3} NO_3^- solution, $T = 25°C$.

One of the major problems in the development of the mediator approach to electrocatalysis is the very low coverage, and nebulous character, of the active species at the interface; comparing for instance the charge associated with the doublet in the lower region (i.e. above the dotted line in the case of the anodic sweep in Fig. 3a) with that for monolayer Ag(I) oxide or hydroxide formation (i.e. the net anodic charge associated with the peaks observed between 1.18 and 1.58 V(RHE), the dashed line in Fig. 2 only ~ 0.08% of the surface metal atoms seem capable of undergoing the adatom/incipient hydrous oxide transition at ~ 0.4 V. Other complications include the relatively poor reproducibility of the i/E response in the premonolayer region, the uncertain role of subsurface oxygen or weakly adherent oxide, and the difficulty of controlling the coverage of mediator species at the interface. These topics are obviously fertile ground for future research.

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