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Electrochemical reduction of nitrogen oxyanions in 1 M sodium hydroxide solutions at silver, copper and $CuInSe_2$ electrodes

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The reduction of nitrate and nitrite ions was studied in 1 M NaOH supporting electrolyte. Voltammetric investigations show that, on silver cathodes, nitrate reduction begins at potentials about 500 mV more positive than nitrite reduction, the latter being superimposed on hydrogen evolution. Electrolyses of nitrate solutions at −1.4 V/SCE give nitrite with good selectivity. On copper cathodes, nitrate and nitrite reductions occur in the same region of potentials and show similar voltammetric profiles. The dominant product of nitrite reduction is ammonia, whereas nitrate may be reduced to nitrite at −1.1 V/SCE and to ammonia with high yields at −1.4 V/SCE. Reduction of nitrogen oxyanions may also be performed on $CuInSe_2$ (photo)cathodes. Photoassisted reductions of nitrate performed on p-$CuInSe_2$ at −1.4 V/SCE gave mixtures of ammonia, nitrite and hydrogen.

1. Introduction

The electrochemical reduction of nitrogen oxyanions in aqueous solutions is of interest for several purposes, among which are: (i) developing sensitive and selective methods of analysis of these ions [1], (ii) synthesizing useful chemicals like hydroxylamine [2] and ammonia, and (iii) developing techniques for treatment of waste solutions, the most important being radioactive solutions originating from nuclear plants [3, 4].

Much literature is available for processes in acidic media, in which several metals are efficient cathodes [5]. Conversely, only a small number of investigations has been performed in modern times in alkaline media, which appear less favourable [5]. However, alkaline media are the best indicated for sustained large-scale processes, since the reduction reactions produce hydroxyl ions. In order to lower the required overvoltage, various strategies have been proposed, including (i) the use of electrode materials with catalytic properties, (ii) the addition of catalysts in solution [6] and (iii) their incorporation into the electrode surface [7].

Concerning the first strategy, interesting results were recently reported for metal cathodes like nickel [3] and zinc [4]. Ability to reduce nitrite to ammonia was also reported for suspensions of some large-gap semiconductors, under illumination [8]. The performances of silver and copper electrodes in alkali were investigated in a few early papers with galvanostatic experiments [9], but the modern literature is limited and focused on neutral media [10, 11].

This paper reports investigations in 1 M NaOH based on cyclic voltammetry and constant potential electrolyses. Considering the catalytic properties of copper, the investigations are extended to electrodes of $CuInSe_2$, a copper-containing semiconductor, particularly suitable for harvesting solar energy [12] and which may operate as a photocathode.

2. Experimental details

Metal electrodes for voltammetric investigations were slices 2 mm thick (surface area about 0.10 cm^2) cut from silver and copper rods (Johnson Matthey Puratronic), fixed with silver epoxy to a brass holder and sealed with epoxy resin (Scotchcast 3M 10/XR5241). The resulting electrode surface was exposed vertically to the electrolyte. The $CuInSe_2$ electrodes, with geometric areas in the range 0.10 to 0.20 cm^2, were prepared similarly, according to a procedure reported in detail elsewhere [13].

Cyclic voltammetry was carried out in a single compartment cell, with the reference electrode (SCE, to which all potentials are referred) connected by an adjustable Luggin capillary. Coulometric experiments (constant potential electrolyses or CPE) were performed in two compartment cells. Large-area silver and copper foils (2 cm × 5 cm × 0.1 cm, Johnson Mattey Puratronic) were used as working electrodes and platinum foils of comparable area as counter-electrodes. Prior to each experiment, the working electrodes were polished with 0.3 μm Al_2O_3 (Buehler) and rinsed with distilled water.

All solutions were prepared from certified A.C.S. grade reagents (Carlo Erba) dried before use according to literature procedures [14], and were deaerated prior to electrolysis with a nitrogen stream. Hydroxylamine solutions were prepared from the sulphate salt.

The electrochemical apparatus consisted of an Amel 553 potentiostat modulated by a 568 function generator and coupled to a 731 digital integrator. Recordings were taken on a Philips PM 8272 recorder.

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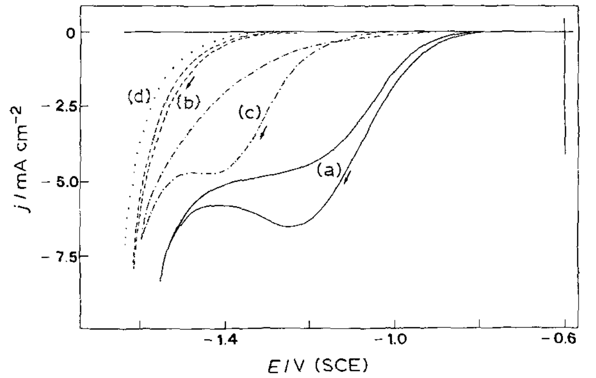

Fig. 1. Cyclic voltammograms ($10\,\mathrm{mV\,s^{-1}}$) for reduction at a stationary silver electrode of: (a) 50 mM $NaNO_3$; (b) 50 mM $NaNO_2$ and (c) 50 mM NH_2OH. Curve (d): background current in base electrolyte.

In photoelectrochemical experiments, performed under white light illumination, a 100 W W-Hal lamp was used as the light source.

The variations of nitrite concentration resulting from electrolysis were assessed, with an estimated accuracy of ± 2%, by measuring the absorbance at 354 nm on a Perkin–Elmer spectrophotometer (mod. Lambda 15). Ammonia yields were determined either by the Nessler method [15] or by distilling the reaction mixture, absorbing the expelled ammonia in acid and back titrating the acid [16], with an overall accuracy estimated as ± 5%. The amounts of ammonia lost during electrolysis appeared to be low but were not quantitatively determined. Hydroxylamine was determined by potentiometric titration with ferricyanide [17].

3. Results and discussion

3.1. *Voltammetric investigations*

3.1.1. Silver. In the presence of NO_3^- a broad reduction peak is observed in the voltammogram at $E = -1.2$ V (Fig. 1a). The peak shape, changing appreciably with cycling, is not typical of diffusion limited processes. Peak current i_p increases with increasing scan rate (v_s) but is not linear with $v_s^{1/2}$. Setting the potential negative to the peak, for example, at -1.4 V, the current at a rotating disc electrode varies little with rotation rate. All these facts indicate that the current is controlled by kinetics as well as diffusion, and suggest the presence of catalytic phenomena.

The voltammograms in the presence of NO_2^- show the onset of a reduction process in the region of hydrogen evolution (Fig. 1b). The observed current increases with increasing concentration of NO_2^-, suggesting that the latter species is indeed reducible on silver. The voltammograms relevant to NH_2OH show a sluggish wave in a region of potentials intermediate to the onset of NO_2^- and NO_3^- reduction (Fig. 1c). Marked hysteresis between the two half-cycles indicates that surface modifications, important for electrode kinetics occur upon polarization at the negative potential limit.

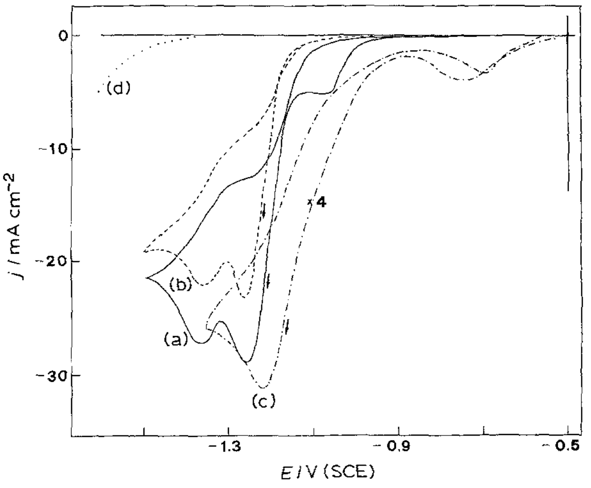

Fig. 2. Cyclic voltammograms ($10\,\mathrm{mV\,s^{-1}}$) for reduction at a stationary copper electrode of: (a) 50 mM $NaNO_3$; (b) 50 mM $NaNO_2$ and (c) 50 mM NH_2OH. Curve (d): background current in base electrolyte.

3.1.2. Copper. The voltammograms for reduction of NO_2^- and NO_3^- show similar patterns, except for a comparatively small wave at $E = -1.1$ V, which is only observed for the NO_3^- species (Fig. 2a and b).

A double peak is observed in both cases around -1.3 V. Peak currents, i_p, recorded during the first cycle after polishing, show a dependence on scan rate v_s close to that expected for a diffusion controlled reaction. However, the current at a fresh copper RDE polarized in the potential region of the peaks, or more negative, decreases with time and, after stabilizing, it shows a limited dependence on rotation speed. These facts, together with the significant dependence of the shape of the voltammogram on electrode treatment (discussed below) again indicate the role of catalytic properties in defining electrode kinetics.

As regards NH_2OH species, reduction starts at more positive potentials as compared with oxyanions (Fig. 2c). The voltammogram shows a small current maximum around -0.7 V for both sweep directions, with a region of negative slope. The diffusive peak occurs around -1.2 V, just before the peaks for reduction of oxyanions. The relatively easy reduction of hydroxylamine on copper cathodes in alkali may be compared with its resistance to reduction in acid medium [18].

As already mentioned, the voltammetric pattern recorded for reduction of NO_2^- and NO_3^- on copper depends significantly on electrode treatment. This dependence is illustrated in Fig. 3 for the case of NO_3^-. The first voltammogram after polishing (Fig. 3a), starting from an open circuit potential of about -0.55 V, shows a small reduction peak in the region of redox processes involving copper oxides [19, 20]. Proceeding in a negative direction beyond -0.9 V (note change of scale), the peak at -1.1 V is observed, which persists with a gradual decrease if the potential is cycled over the range -0.9 to -1.15 V. At more

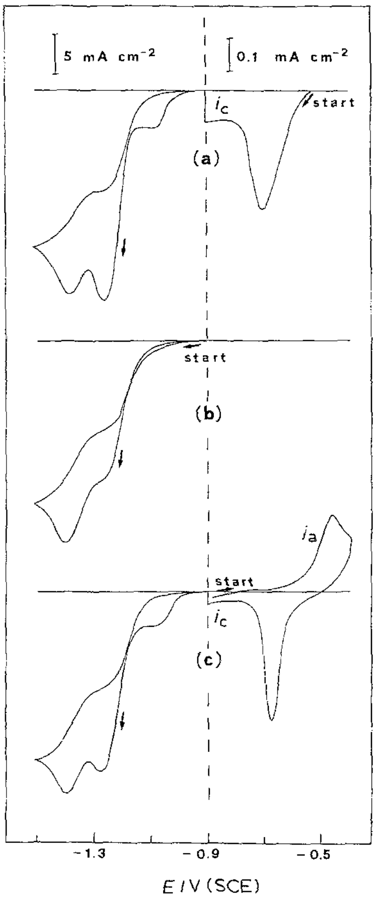

Fig. 3. Cyclic voltammograms between -0.9 V and -1.5 V ($10 \mathrm{mV\,s^{-1}}$), after different electrode treatment, at a stationary copper electrode. Electrolyte: 1 M NaOH containing 50 mM $NaNO_3$. From top to bottom: (a) sweep from open circuit potential to -0.9 V, then a cycle; (b) second cycle; (c) preliminary cycle between -0.9 V to -0.4 V, then third cycle.

negative potentials, two peaks in the region of -1.3 V are observed, the first (at about -1.25 V) being somewhat larger than the second.

If the cycle is completed, reaching the negative limit of -1.5 V and then sweeping the potential up to -0.9 V, in the subsequent cycle (Fig. 3b) the voltammetric profile shows two major variations: (i) the peak at -1.1 V disappears and (ii) the peak at about -1.25 V is much lower and appears as a shoulder. If the potential is now cycled between -0.9 and -0.4 V (Fig. 3c, right), the subsequent cycle (Fig. 3c, left) shows a pattern approaching that of the freshly polished electrode (Fig. 3a). In the potential region around -1.3 V, results similar to those of Fig. 3 are also observed for NO_2^-.

As shown in Fig. 3c, right side (note current magnification), during the cycle to -0.4 V and backwards a redox process occurs, also observed in 1 M NaOH without added nitrate; this represents oxidation of copper metal to oxides (mainly Cu_2O, see [19] and [20]) and back-reduction in a single peak. The integrated charge, 2 to $3 \mathrm{mC\,cm^{-2}}$, indicates that several monolayers are involved. A reduction peak of comparable size is also observed during the first cycle at the freshly polished electrode (Fig. 3a, right side) and may be attributed to reduction of oxides forming on the electrode surface during polishing in air.

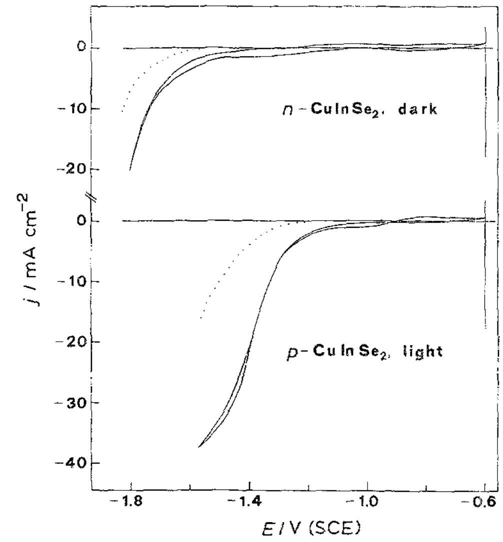

Fig. 4. Cyclic voltammograms ($10 \mathrm{mV\,s^{-1}}$) for reduction of 50 mM $NaNO_3$ in 1 M NaOH at n-$CuInSe_2$ in the dark (top) and p-$CuInSe_2$ under illumination (bottom, white light from a 100 W W-Hal lamp). Dotted curves: background current in base electrolyte.

It may be concluded that the peaks of NO_3^- reduction at -1.1 V and -1.25 V are enhanced after reduction of surface oxides produced by mechanical polishing or mild anodization, and decreased after polarization at sufficiently negative potentials. The changes of voltammetric pattern observed in Fig. 3 for NO_3^- reduction cannot be attributed to the presence or absence of a copper oxide film on the electrode surface, since at potentials negative to -0.9 V the copper oxides have already been reduced in any case. The observed variations may be attributed, in general terms, to surface modifications affecting interfacial properties of relevance to catalytic behaviour, although we do not possess a sufficient basis to go further into mechanistic details.

3.1.3. $CuInSe_2$. Figure 4 compares the voltammograms for NO_3^- reduction recorded at the n-type material in the dark (top) and the p-type material under illumination (bottom). The p-type semiconductor operates as a photocathode: electrons are promoted to the conduction band by incident photons and driven to the interface by the applied field. Light energy is thereby converted into electronic energy [21] and reduction processes may occur at less negative potentials than those required in the dark.

The photon-assisted process at p-$CuInSe_2$ offers an advantage of about 400 mV as compared with the process at n-$CuInSe_2$ in the dark (Fig. 4), but performances remain lower than those of copper metal (Fig. 2), due to the lower catalytic properties of the semiconductor. For the same reason, the latter material offers a lower selectivity as compared with the metals: reduction of nitrate is superimposed on hydrogen evolution (Fig. 4), and even more so reduction of nitrite and hydroxylamine (not shown).

3.2. *Constant potential electrolyses*

A series of 3 to 5 runs were performed for some

Table 1. Results of CPE of NO_3^- and NO_2^- in 1 M NaOH

Electrode	E/V(SCE)	Starting species*	Reduction/%	Current efficiency/%†	
				NO_2^-	NH_3
Ag	−1.4	NO_3^-	50	90–94	1–3
Cu	−1.1	NO_3^-	20	90–95	4–7
Cu	−1.4	NO_2^-	40	-	90–96
Cu	−1.4	NO_3^-	40	4–8	80–88
p-$CuInSe_2$‡	−1.4	NO_3^-	5	20–35	25–40

* 50 mM initial concentration.

† Charge used to generate given product over total charge. The interval between minimum and maximum values obtained in 3 to 5 runs is given.

‡ Under illumination with a 100 W W-Hal lamp.

selected experimental conditions. The results are shown in Table 1.

CPE of NO_3^- at −1.4 V on silver cathodes produces predominantly NO_2^-, small amounts of NH_3 and no detectable NH_2OH (Table 1). The current yield of ammonia increases appreciably, and that of nitrite decreases correspondingly, increasing the amount of charge passed during an experiment.

The results may be interpreted in the light of the voltammetric data indicating, at the given potential, reduction rates in the order $NO_3^- \gg NH_2OH \gg NO_2^-$ (Fig. 1). The main reaction is

$$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^- \quad (1)$$

and the formed nitrite accumulates, except for a small fraction which is further reduced to ammonia:

$$NO_2^- + 5H_2O + 6e^- \longrightarrow NH_3 + 7OH^- \quad (2)$$

This fraction obviously increases during electrolysis as a result of the increasing ratio between the concentrations of NO_2^- and NO_3^- competing for reduction.

Concerning copper cathodes, reduction of NO_2^- at −1.4 V proceeds to a large extent according to Reaction 2, with production of NH_3 (Table 1). Reduction of NO_3^- at the same potential also leads essentially to ammonia, according to the reaction:

$$NO_3^- + 6H_2O + 8e^- \longrightarrow NH_3 + 9OH^- \quad (3)$$

formally resulting from addition of Reactions 1 and 2. Considering the presence in the latter case of significant amounts of NO_2^- after electrolysis, and the fact that nitrite is the main product of CPE at −1.1 V, the occurrence at −1.4 V of Reactions 1 and 2 in sequence appears very likely even from a mechanistic standpoint. No significant amount of NH_2OH is found after electrolyses of either NO_2^- or NO_3^-. This fact may mean either that hydroxylamine, formed as an intermediate of Reactions 2 and 3, is readily reduced at the applied potential, a conclusion compatible with voltammetric data of Fig. 2; or that hydroxylamine is not formed during the reactions. The latter conclusion seems to apply to the reduction of nitrogen oxyanions to ammonia in acid medium: hydroxylamine was not found among the reaction products, despite its strong resistance to reduction [18].

CPE of NO_3^- were also performed at p-$CuInSe_2$ (photo)cathodes, at −1.4 V under illumination. The electrode was the same as that used for voltammetric investigations and, due to its small surface area, a limited fraction of the starting species was processed. The main products of NO_3^- reduction are NO_2^- and NH_3, each accounting for a comparable fraction of the integrated charge, with values rather scattered between 20% and 40% (Table 1). The remaining reduction charge may be essentially attributed to hydrogen evolution, indicated by the development of gas bubbles at the polarized electrode in both the presence and absence of NO_3^-. These data confirm the lower selectivity of the cathodic processes at the semiconductor as compared to copper, already shown by voltammetric data.

Formation of nitrogen gas, with efficiencies of a few percent, during reduction of nitrogen oxyanions at silver and copper electrodes is compatible with the data presented in Table 1 – the main products account for less than 100% of the charge. However, given the uncertainties of determination of the mentioned products, only direct analytical evidence would be reliable.

4. Conclusions

Electrochemical reduction of nitrogen oxyanions in alkaline media may be achieved without surface modifications on certain metal cathodes, including silver and copper (present data), nickel [3] and zinc [4]. The fact that these metals are close in the periodic table may be a clue to the identification of the parameters crucial to catalytic behaviour, although the correlation may not be trivial [6]. With proper choices of electrode material and applied potential various products may be obtained with good selectivity: NO_3^- may, for instance, be reduced to NO_2^- (Ag), NH_3(Cu, Zn) and N_2(Ni).

The behaviour of the catalytic materials is worth further investigation, for example comparing the performances in prolonged electrolysis. Being relatively noble, copper should have superior stability as compared for instance to zinc and iron, which are vulnerable to corrosion [4].

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