JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1993) 471-476

Preparation and use of a nickel foam electrode for the production of diacetone-2-keto-L-gulonic acid from diacetone-L-sorbose in vitamin C production

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Received 7 October 1991; revised 5 February 1992

This paper deals with the electrochemical oxidation of diacetone-L-sorbose (DAS) to diacetone-2-keto-L-gulonic acid (DAG) at a nickel foam electrode in alkaline medium. DAG is an intermediate compound in Vitamin C production. Cyclic voltammetry in 1 M KOH was undertaken with a nickel foam electrode submerged in a stirred cell; the potential conditions for the nickel peroxidation were localized around 450 mV/SCE, and the temperature influence was investigated between 2° C and 60° C. The voltammetric study was extended to a 1 M KOH solution containing DAS (weight concentration varying from zero to 10%), by using successively a rotating disc nickel anode and a nickel foam electrode submerged in a stirred cell. The adherence of the nickel peroxide, the oxidation potential for the DAS to DAG reaction, the influence of the DAS concentration on this potential, and the electrode stability were investigated.

1. Introduction

As our previous studies on nickel foam electrodes were essentially oriented towards basic understanding such as material characterization, mass transfer, and potential distribution, they were restricted to the use of an electrochemical reaction of academic interest [1-3]. The applicability of this material to the oxidation of diacetone-L-sorbose (DAS) to diacetone-2-keto-L-gulonic acid (DAG) which is an intermediate in Vitamin C production is now described. This transformation from DAS to DAG may follow a chemical or electrochemical route.

Concerning the chemical route, the work of Zolotarev *et al.* [4] used a mixture of potassium manganate and permanganate as the oxidizing agent. Nondek *et al.* [5], and Hronec *et al.* [6] carried out the oxidation in an alkaline medium, with gaseous oxygen and a metallic catalyst (Pt, Pd, or Pb–Bi) supported by a carbon matrix. However, probably that the most promising chemical route was that using alkaline hypohalogenides as oxidizing agents; for example, Iacobescu *et al.* [7] and Kunugiza and Kamiya [8] used NaClO in an alkaline medium (NaOH 2–3%) with a concentration of active chlorine around 14%.

Previous work describes an electrochemical route through the indirect oxidation of DAS by sodium hypohalogenides (bromides or chlorides) electrolytically generated *in situ* from solutions of sodium bromide or chloride; in such cases, the anode was made of graphite, platinum or alloyed (with Nb, Ti, . . .) cast iron [9-13]. Probably Vertes *et al.* [14, 15], taking inspiration from the work of Briggs *et al.* [16] on the preparation of Ni–Cd batteries, were the first to propose the direct electrochemical oxidation of DAS at a nickel peroxide (NiOOH) electrode from such batteries. A similar idea was applied by Aurutskaya *et al.* [17] and Mulina *et al.* [18]. Generally, the active nickel peroxide electrode was prepared at the surface of a support of nickel; in the works of Robertson *et al.* [19, 20], the anodic material of the Swiss-Roll electrochemical cell consisted of thin sheets of peroxidized nickel.

The present paper reports results for the electrode preparation and use for the direct oxidation of DAS to DAG at a nickel foam electrode.

2. Preliminary experimental studies

According to Robertson *et al.* [19, 20], the anodic oxidation of DAS to DAG (in the form of the corresponding sodium salt) at a nickel electrode in a highly basic medium (pH ~ 14) has the following overall mechanism:

$$\mathrm{Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O} + e^- \quad (1)$$

$$\mathrm{NiOOH + DAS \rightleftharpoons Ni(OH)_2 + DAG} \quad (2)$$

This is similar to that proposed by Fleischmann *et al.* [21, 22] for the oxidation of aliphatic alcohols to carboxylic acids.

The experimental study of the DAS to DAG transformation at a nickel foam electrode required the previous solution of two problems: first, the availability of a sufficient amount of DAS, second the control of the NiOOH formation and stability at the nickel electrode.

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2.1. *DAS production*

DAS was prepared by acetonation of L-sorbose catalysed by H_2SO_4 [23, 24]; the acetonation process was followed up by T.L.C. on MERK silicagel 60 F_{254} sheets and by u.v. spectrophotometry, in accordance with the methods proposed by Ilner [25] and Devyatnin [26], respectively. The DAS was crystallized and purified according to [27]. The elementary chemical analysis of the crystals gave [C(55%; H(7.9%)], while the theoretical values are [C(55.4%); H(7.7%)]. By N.M.R. analysis it was demonstrated that the crystallized product was effectively diacetone-sorbose (DAS). It was concluded that the DAS was produced with a 95% purity; the impurity was monoacetone-L-sorbose.

2.2. *Preparation of the NiOOH electrode*

According to Reaction 1, nickel peroxide NiOOH results from nickel hydroxide $Ni(OH)_2$ in an alkaline medium, while Reaction 2 again generates this hydroxide together with DAG. The preparation of a NiOOH adherent layer on a nickel electrode is a problem closely connected with the charging of Ni–Cd batteries. The technique proposed by Briggs *et al.* [16] and applied by Vertes *et al.* [14, 15] was used in the present work for the electrode preparation; such a prepared NiOOH electrode is termed the 'activated electrode' in the rest of this text.

In the experiments, nickel foam of grade 100 (100 p.p.i.), previously characterized in the laboratory [28], was used as the material supporting the nickel peroxide. The preparation of NiOOH was carried out in a small and very simple magnetically stirred batch electrochemical cell; the volume of solution in the cell was 250 cm^3. The anode was a rectangular sheet (5 cm × 3 cm × 0.21 cm) of nickel foam, equidistant from two rectangular cathode sheets of expanded stainless steel (5 cm × 3 cm); a saturated calomel electrode was used as reference electrode. This classical 3-electrode system was associated with a Tacussel PRT-20-2 potentiostat for linear sweep voltammetry, and a recorder.

The cyclic voltammetry in 1 M KOH (which was the supporting electrolyte used for the DAS to DAG transformation, as presented below) led to the curves of Fig. 1. The presence of a maximum current followed by a minimum, between +400 and +500 mV/SCE, is associated with the Flade potential. Beyond this minimum, the current increases with the anodic potential, up to oxygen evolution, which occurs around +600 mV/SCE. The 'camel back' region of the curve, around +450 mV, can be related to the formation of NiOOH from $Ni(OH)_2$ [20, 22]. Towards less anodic potentials, a peak appears around +200 mV/SCE. In accordance with the observations of other authors [19, 21, 22, 29], this may be explained as corresponding to the electrochemical reduction of NiOOH according to Reaction 1 from right to left.

2.3. *Influence of temperature*

The influence of temperature (between 2° C and 60° C) on the NiOOH electrode stability was investigated in the magnetically stirred batch cell. Starting with an activated electrode (i.e. a nickel peroxide electrode prepared according to Vertes *et al.* [14, 15]), the anodic current-potential curve was registered at each temperature. In Fig. 2, where all the curves are given, it can be observed that at a constant potential, the higher the temperature, the higher the current density. Such a temperature influence explains why, both in the chemical [7, 8] and electrochemical [9, 22] routes, the experiments were made between 50° C and 90° C; this last temperature was used in pressurised experiments. Between 30° C and 50° C, the potential range corresponding to NiOOH formation moves towards less anodic potentials. The position of the maximum changes from approximately +500 mV/SCE to +400 mV/SCE, a conclusion which agrees with the results of Barnard *et al.* [30, 31].

3. Voltammetric study in the presence of DAS

Most work on the reaction DAS–DAG, either at laboratory or industrial scale [10, 12, 14], used 0.5–1.0 M NaOH (or KOH) as the supporting electrolyte. Indeed, an alkaline medium allows DAS hydrolysis to be avoided and ensures that the DAG formed remains in solution. In other respects, it is well known that the presence of nickel ions in the solution prevents loss of activity of the NiOOH [19, 32]. This is why the 1 M KOH supporting electrolyte used in the experiments reported below was prepared with 1.4 g dm^{-3} Ni introduced in the form of dissolved nickel sulphate.

Two classes of anodes, rotating disc and foam, were used in the experiments carried out in the same cell as for the NiOOH preparation; in each experiment, the cell contained 250 cm^3 of solution. Depending on the anode used, the cell was (case of the nickel foam anode) or not (case of the rotating disc) magnetically stirred.

3.1. *Rotating disc anode*

A polished nickel rotating disc, 2.5 cm in diameter, was used. Its surface was prepared, i.e. 'activated', as previously indicated for the nickel foam electrode. The disc electrode was rotated using E.D.I. Tacussel equipment, at an angular velocity between 500 r.p.m. and 2000 r.p.m. The experiments were made at 20° C. The definitive choice of the rotating disc velocity was a consequence of a series of experiments made using a solution containing 2 wt % of DAS. It was observed [27] that the peak current in the voltammogram changes by less than 1 mA when the rotation speed was changed. This was in agreement with Robertson *et al.* [19], but also with other authors [20, 22, 29], for the oxidation of different types of aliphatic alcohols, and reveals that the process was not diffusion limited.

At rotation velocities higher than 1000 r.p.m., the

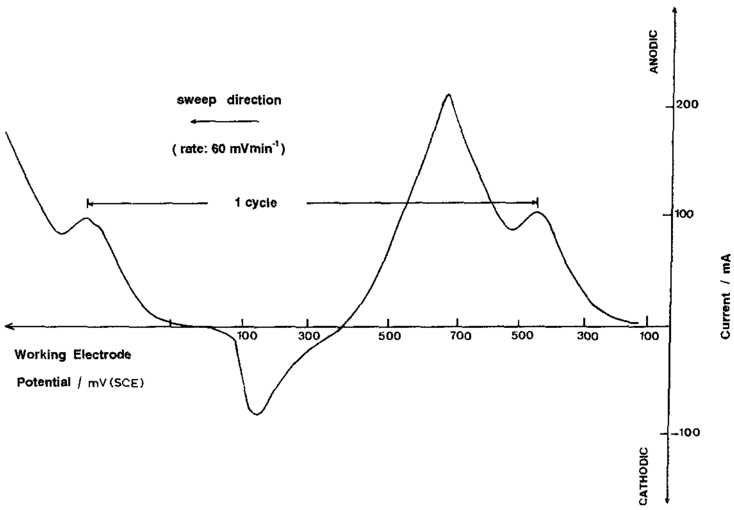

Fig. 1. Cyclic voltammogram obtained with a nickel foam anode in 1 M KOH at 29° C.

NiOOH layer was progressively removed from the smooth surface of the disc, an observation which highlights the problem of adherence of such a layer to any nickel matrix in highly turbulent flow. Thus a rotation speed of 500 r.p.m. was selected for the experiments on the influence of the DAS concentration. Cyclic voltammograms were obtained between 100 and 650 mV/SCE, at a potential sweep rate of 60 mV min^{-1} and for DAS concentrations varying between zero and 4% (by weight). From these voltammograms, shown in Fig. 3, it can be deduced that:

(i) The peak around 350 mV/SCE, and corresponding to the NiOOH formation, is less and less clear as the DAS concentration is increased. This disagrees with the results of Robertson *et al.* [19]. From computer controlled cyclic voltammetry, using a stationary electrode submerged in an agitated cell, these authors obtained curves where the peak remained unaffected by the DAS concentration.

(ii)For more anodic potentials than the potential of the peroxidation peak, there exists a second wave with a more or less accentuated 'camel back' region. This wave, which corresponds to the oxidation of DAS to DAG, is situated between 450 and 550 mV/SCE; it moves towards more anodic potentials, and at the same time is better defined, when the DAS concentration is increased. The current corresponding to the maximum of the 'camel back' region of the curve is proportional to the DAS concentration, as shown in Fig. 4. The correlation coefficient of this line is high; the fact that the line does not pass through the origin may be explained by the existence of a residual current due to the supporting electrolyte and/or to DAS impurities.

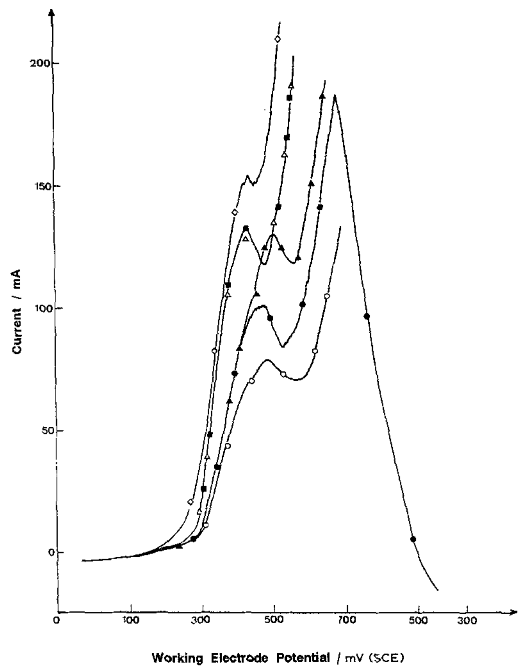

Fig. 2. Influence of temperature on the current–potential sweep (for a nickel foam anode in 1 M KOH). Temperature: (○) 2° C, (●) 20° C, (▲) 30° C, (△) 40° C, (■) 50° C and (◇) 60° C.

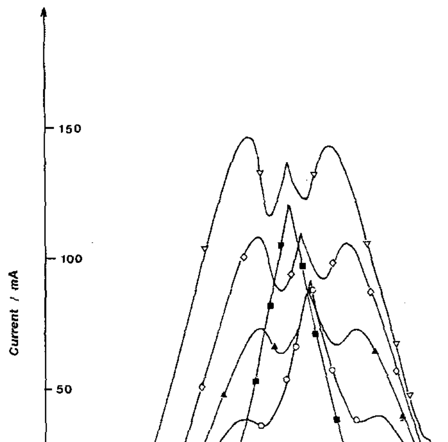

Fig. 3. Cyclic voltammograms obtained with a rotating nickel disc electrode (at 500 r.p.m.). Influence of DAS concentration in 1 M KOH at 20° C: (■) 1 M KOH; (○) 1 M KOH + DAS 1.0 wt %; (▲) 1 M KOH + DAS 2.0 wt %; (◇) 1 M KOH + DAS 3.0 wt %; (▽) 1 M KOH + DAS 4.0 wt %.

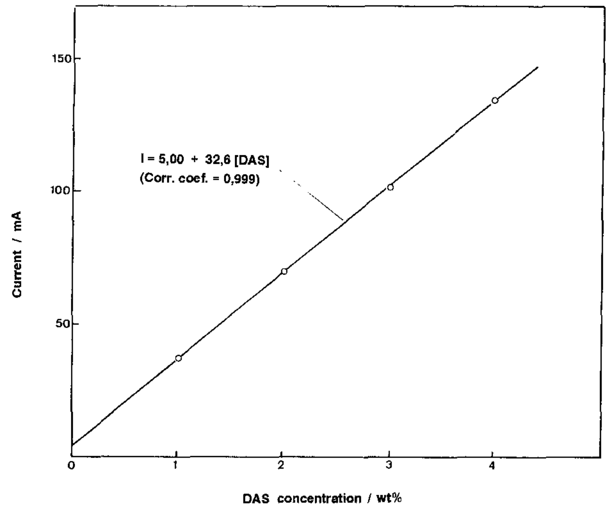

Fig. 4. Linear dependence of maximum peak current on DAS concentration.

3.2. *Case of a submerged nickel foam anode*

Figure 5 gives two voltammograms obtained with an activated electrode: curve (a) which corresponds to the supporting electrolyte alone, is similar to the voltammogram of Fig. 1, and curve (b) was registered immediately after (a), and after the addition of DAS (10 wt %) to the supporting electrolyte. These experiments were made at 29° C.

Along the part of curve (b) corresponding to increasing anodic potentials, there is no peak characterizing the nickel peroxidation, an observation which agrees with the disappearance of such a peak when the DAS concentration is increased (Fig. 3). However, the maximum anodic potential reached was 700 mV/SCE. The reverse sweep towards less anodic potentials still reveals the peak corresponding to the peroxide reduction (around 200 mV/SCE), but it is smaller than in curve (a). Thus, in summary, DAS oxidation hides the peroxide formation, but this peroxide remains present.

It is interesting to highlight the difference between the voltammogram curve (b) of Fig. 5 and the corresponding curve obtained by Robertson *et al.* [19]. These authors presented current-potential sweeps with a well defined peak followed by a 'camel back' region associated with the transformation of DAS to DAG. The peak and the 'camel back' do not appear in Fig. 5; an explanation may be found in the value of the DAS concentration, nearly 3% in [19] but 10% in the case of Fig. 5.

3.3. *Electrode stability*

In the experiments of Robertson *et al.* [19], the nickel electrodes of the Swiss-Roll cell were smooth and were in direct contact with the turbulence promoting cloths, so that the nickel peroxide was not firmly attached and was then easily removed from the nickel surface. In spite of the fact that this point was not commented upon in [19], it could have explained the electrode deactivation observed when a nickel salt was not present in the electrolyte.

Electrode stability was assumed to be synonymous with a permanent electrochemical activity and a good adherence of the peroxide on the nickel matrix. In their work on the electrochemical oxidation of $Ni(OH)_2$, Barnard *et al.* [30, 31] proposed that a heterogeneous crystalline system composed of a mixture of $Ni(OH)_2$ and NiOOH could be formed. According to this work, the peak we observed around 200 mV/SCE (Figs 1, 3 and 5) would be due to a non-equilibrium process leading to the elimination of crystalline defects in order to obtain a stable $Ni(OH)_2$ structure.

The current-potential sweep of Fig. 6 corresponds to the conditions of curve (b) of Fig. 5, but was registered after three experiments – with a total operating time of 60 h – of DAG production from DAS at a nickel foam electrode previously activated and working at a constant potential. It is seen that the curve of Fig. 6 is not regular. After a sufficiently long operation time, the solution became black due to nickel peroxide in suspension. As the electrode was not corroded, such a suspension probably resulted from the oxidation of $Ni(OH)_2$ without integration into the crystalline network deposited on the foam. After the experiments, no potential was imposed on the electrode kept submerged in the solution; then the

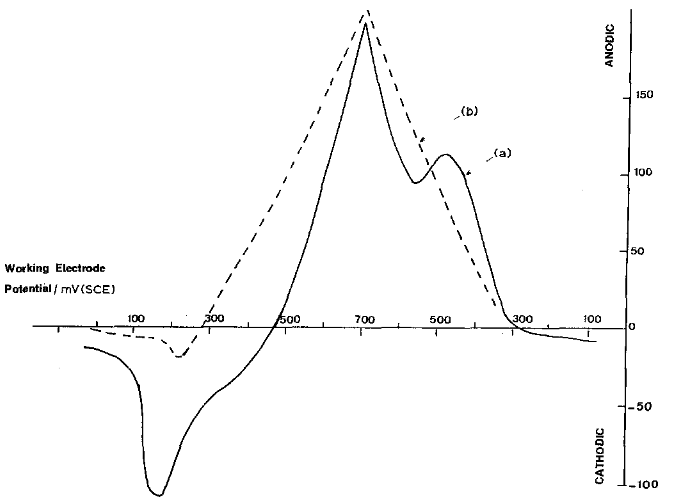

Fig. 5. Comparison of cyclic voltammograms obtained with a nickel foam anode at 29° C: (a): supporting electrolyte alone; (b): with dissolved DAS (10 wt %).

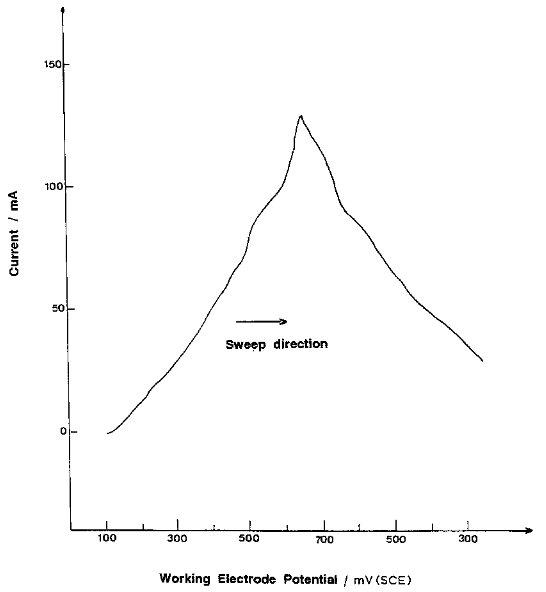

Fig. 6. Cyclic voltammogram registered after 60 h of operation (nickel foam electrode) 1 M KOH; initial DAS 10 wt% and 1.4 g dm^{-3} Ni.

black colour (i.e. the suspension) disappeared progressively, giving place to a green colour corresponding to $Ni(OH)_2$.

In order to test the possibility of reactivation, an electrode activated according to the technique given in [27] was kept for 15 days in the supporting electrolyte and reused at the end of this period. As shown in Fig. 7, the voltammogram obtained (dotted curve) indicated significant electrode deactivation. However, if a new activation was undertaken, the current-potential sweep (continuous line of Fig. 7) again became similar to that of Fig. 1.

4. Conclusions

Among the possible nickel matrixes for the oxidation of diacetone-L-sorbose (DAS) to diacetone-2-keto-gulonic acid (DAG), nickel foam appears to be a satisfactory material. The reactive agent is the nickel peroxide. Its formation mechanism and its stability in an alkaline medium are well known from the field of Ni–Cd batteries, but no information existed on the influence of a high concentration of a dissolved organic compound, like DAS, which can react with the peroxide.

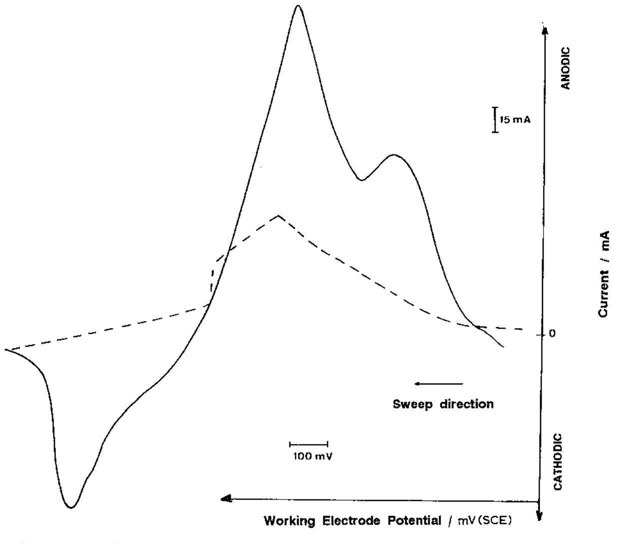

Fig. 7. Cyclic voltammograms obtained with a nickel foam electrode in 1 M KOH at 29° C: after deactivation (----); after new activation (———).

Experiments with the supporting electrolyte alone revealed the anodic potential range for peroxide formation on the nickel foam, and showed the influence of temperature; the results are in agreement with the literature.

By using a smooth rotating disc electrode, the poor adherence of the peroxide on the nickel matrix was established. In the presence of DAS, the reaction DAS/DAG appears to occur in a potential range which changes with the DAS concentration and which tends towards the oxygen evolution potential at sufficiently high DAS concentrations. Contrary to the literature, the peroxidation peak is less and less clear as the DAS concentration increases.

The experiments with the nickel foam matrix led to anodic current–potential sweeps in disagreement with [19] concerning the presence of a peak and of a 'camel back' in the curve. This is probably due to the different order of magnitude of the DAS concentrations used in the two studies. Finally, the stability and the reproducibility of the electrode activity has been demonstrated experimentally.

A further paper [33] will be concerned with the production of DAG from DAS.

Acknowledgements

F. Cœuret particularly thanks J. Nanzer and S. Langlois who made possible this contractual experimental work which received its financial support from the Direction des Études et Recherches d'Electricité de France.

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