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Comparative voltammetric behaviour of the silver/silver oxide electrode prepared on vitreous carbon and silver substrates

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The voltammetric behaviour of vitreous carbon/chemically precipitated silver hydroxide layer and silver/electrochemically formed silver oxide layer electrodes are compared. As the former type of electrode is free from silver substrate contributions during the oxidation–reduction cycles (ORC) the voltammetric data indicate the occurrence of soluble Ag(I) species in the gel-like silver hydroxide matrix. Soluble species can be formed during the ORC as a consequence of AgOH formation at the early stages of the oxidation and reduction processes. Nucleation and growth of new phases produce a non-homogeneous layer structure and a decrease in the amount of active material participating in the ORC under preset conditions.

1. Introduction

The behaviour of silver/silver oxide electrodes in alkaline solutions has been extensively studied under a wide variety of experimental conditions [1–55] and the probable structure of the composite anodic layer investigated by means of different optical *in situ* techniques [27, 28, 32, 33, 36, 46, 47, 54]. A review of the present knowledge of silver/silver oxide electrodes in alkaline solutions is given in the references [46, 51, 56–59]. Despite the amount of relevant work done, there are still basic questions relating to this important electrochemical system which deserve further investigation. Among these problems one can consider the role played by OH^- ion adsorption on the formation of OH-containing species on silver at the early stages of metal electrooxidation and soluble Ag(I) electroformation; the influence of the silver oxide layer preparation on the subsequent electrochemical reactions and the nature of the conducting substrate on the electrochemical behaviour of the silver oxide layer. The knowledge of these aspects of the reaction is important for attempting a correlation between the electrochemical behaviour and structure of silver oxide layers, particularly in relation to the higher oxidation stages of the silver/silver oxide electrode.

The present paper is devoted to a comparative voltammetric study in alkaline solution of silver/silver oxide electrodes prepared either by conventional electrooxidation–electroreduction cycles (ORC) or by chemical precipitation on vitreous carbon. The purpose of the second type of electrode is to have a well-defined amount of active material participating in the redox reaction and to avoid the proper electrooxidation of base silver.

2. Experimental details

The experimental set-up has already been described in previous publications [41, 46]. Two types of working electrodes were used, high purity silver discs ("Specpure", Johnson Matthey Chemicals Ltd., $0.063\,cm^2$ apparent area) and chemically precipitated hydrous silver oxide on a vitreous carbon disc (Union Carbide, low density, $0.070\,cm^2$ apparent area) supported on PTFE holders.

Silver electrodes were successively polished with 400 and 600 grade emery papers and $1.0\,\mu m$, $0.3\,\mu m$, and $0.05\,\mu m$ alumina-acetone suspensions on polishing cloths (Microcloth), then thoroughly rinsed with triply distilled water, and finally, held for 2 min at $E = -1.35\,V$, that is in the potential range of net hydrogen evolution to attain a reproducible electroreduced metal surface [47, 51]. The hydrous silver oxide electrodes were prepared through alternate immersions of a vitreous carbon substrate in x M NaOH solution ($0.01 \leqq x \leqq 0.1$) and in y M Ag_2SO_4 solution ($0.001 \leqq y \leqq 0.01$). The immersion time in each solution was set at 5 s and the number of alter-

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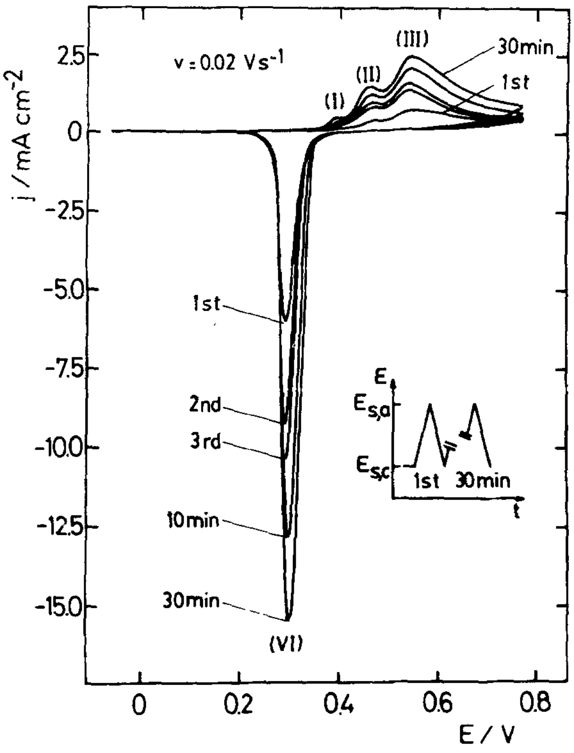

Fig. 1. RTPS voltammograms at $v = 0.02\,\mathrm{V\,s^{-1}}$. Silver/0.1 M NaOH. The first, second and third scans, and those obtained after potential cycling for different times between $E_{s,c} = -0.06\,\mathrm{V}$ and $E_{s,a} = 0.76\,\mathrm{V}$ are shown.

nate immersions (n) was varied from 1 up to 50. The vitreous carbon substrate was previously cleaned by immersion in a 1 : 10 $HNO_3 + H_2O$ mixture for 2 min, later repeatedly rinsed in triply distilled water, and finally subjected to potential cycling in 0.1 M NaOH at $0.02\,\mathrm{V\,s^{-1}}$ between $-0.05\,\mathrm{V}$ and 0.70 V for 10 min.

Potentials were measured in a conventional way against either a SCE or a Hg/HgO electrode in the same NaOH solution employed in the cell. Potentials in the text are referred to the NHE scale. The counter-electrode was a large area Pt sheet placed in a separate cell compartment.

Runs were made at 25°C in the following solutions: 1 M NaOH (solution A); 0.1 M NaOH (solution B); 0.1 M NaOH + Ag_2O (saturation) (solution C); 0.01 M NaOH (solution D). For solution C the correction due to liquid junction potential was neglected. All electrolyte solutions were prepared from analytical grade (p.a. Merck) reagents and triply distilled water. Voltammetric measurements were made by employing the following perturbing potentials: (i) Conventional triangular potential sweeps either single (STPS) or repetitive (RTPS) between cathodic ($E_{s,c}$) and anodic ($E_{s,a}$) switching potentials at different scan rates (v) in the $0.002\,\mathrm{V\,s^{-1}} \leqq v \leqq 2\,\mathrm{V\,s^{-1}}$ range; (ii) Combined RTPS with STPS; and (iii) triangularly modulated triangular potential sweeps (TMTPS) with a guide rampe at $1\,\mathrm{V\,s^{-1}} \leqq v_g \leqq 5\,\mathrm{V\,s^{-1}}$, and a modulating RTPS of amplitude $0.1\,\mathrm{V} \leqq A_m \leqq 0.15\,\mathrm{V}$, and sweep rate $20\,\mathrm{V\,s^{-1}} \leqq v_m \leqq 150\,\mathrm{V\,s^{-1}}$. Blank voltammograms of the vitreous carbon substrates were systematically obtained for each series of runs. The voltammetric charges resulting from the blanks were always negligible as compared to that related to redox processes involving the hydrous silver oxide layer.

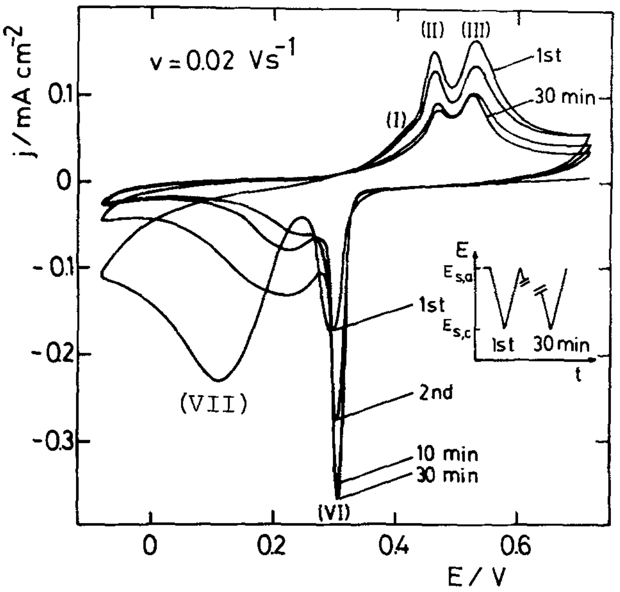

Fig. 2. RTPS voltammograms at $v = 0.02\,\mathrm{V\,s^{-1}}$. Vitreous carbon/precipitated hydrous Ag_2O/0.1 M NaOH + Ag_2O (saturated), $x = 0.1$, $y = 0.001$, and $n = 50$. The first and second scans and those obtained after potential cycling for different times (t) between $E_{s,a} = 0.72\,\mathrm{V}$ and $E_{s,c} = -0.08\,\mathrm{V}$ are depicted.

3. Results

The voltammetric response of polycrystalline Ag/0.1 M NaOH electrode at $v = 0.02\,\mathrm{V s^{-1}}$ in the potential region of the Ag/Ag_2O redox couples (Fig. 1) exhibits the previously described [41, 44, 46] anodic peaks (peaks I, II, and III) and a cathodic peak (peak VI). These voltammograms are practically the same for RTPS started either from $E_{s,c}$ or $E_{s,a}$. Peak I was assigned to the simultaneous formation of a few monolayers of AgOH and soluble Ag(I) species, and peaks II and III were associated with Ag electrooxidation yielding an inner hydrous Ag(I) oxide layer and a relatively more compact outer Ag(I) oxide layer. Otherwise, peak VI was related to the electroreduction of the complex layer anodically formed [46, 47]. Peaks IV and V (not shown in the figure) were previously assigned to the Ag(I)/Ag(II) redox couple which appears for $E_{s,a}$ values more positive than those set in this work.

Repetitive voltammograms of a vitreous carbon/silver oxide/0.1 M NaOH + Ag_2O (saturation) electrode at $v = 0.02\,\mathrm{V s^{-1}}$ between $E_{s,a} = 0.72\,\mathrm{V}$ and $E_{s,c} = -0.09\,\mathrm{V}$ after holding the electrode during 5 s at $E_{s,a}$ (Fig. 2), show two cathodic contributions in the first electroreduction scan, that is peak VI at ca. 0.3 V, and a broad peak at ca. 0.1 V (peak VII). The subsequent reverse scan presents peaks I, II, and III as also seen in Fig. 1. However, after a prolonged potential cycling the voltammogram changes in the following way: (i) the contour of peak VI turns sharper, both the charge and the height of peak VI increase and its peak potential becomes slightly more positive; (ii) the charge of peak VII as well as the cathodic current

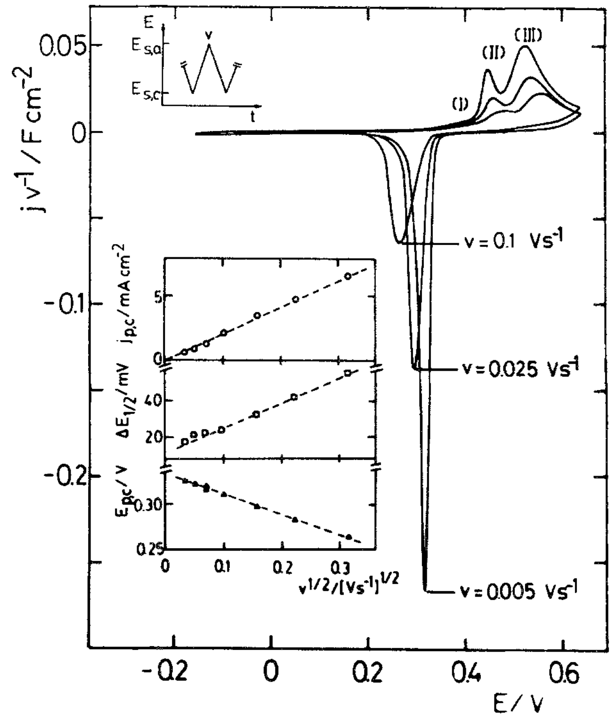

Fig. 3. Influence of v on the jv^{-1} against E plots. Vitreous carbon/precipitated hydrous Ag_2O/0.1 M NaOH + Ag_2O (saturated), $x = 0.1$, $y = 0.005$, and $n = 20$. The dependence of $j_{p,c}$, $\Delta E_{1/2}$, and $E_{p,c}$ on $v^{1/2}$ are inserted.

at the initial portion of the electrooxidation scan gradually decreases. This voltammetric behaviour is typical for a bulk diffusion controlled electrochemical reaction and it appears to be specific of vitreous carbon/precipitated silver oxide electrodes; and (iii) the overall anodic charge diminishes without an appreciable change in the relative distribution of peaks I, II, and III. These results are independent of the amount of active material precipitated on vitreous carbon, that is of the number of immersions in the precipitating solutions. It should be noticed, however, that the poorer the reproducibility of results the lower the value of n. This fact is presumably due to the incomplete coverage of the vitreous carbon substrate by the hydrous silver oxide layer.

The composition of the precipitating solution was also changed within limited values ($0.01 \leqslant x \leqslant 0.1$ for x M NaOH and $0.001 \leqslant y \leqslant 0.01$ for y M Ag_2SO_4) to determine its possible effects on the properties of the hydrous silver oxide layer as compared to that electroformed from silver electrodes, keeping in mind that, for the latter, the amount of silver oxide depended on the potential scan rate and switching potential limits.

The stabilized voltammograms in the form of jv^{-1} against E plots show that as v decreases the entire voltammetric charge increases, peak VI becomes sharper and its potential turns out to be more positive (Fig. 3). The height of the main cathodic peak VI ($j_{p,c}$), its half-peak width potential ($\Delta E_{1/2}$), and peak potential ($E_{p,c}$) change linearly with $v^{1/2}$ (Fig. 3). The stabilized voltammograms furnish an anodic to cathodic charge ratio, Q_a/Q_c, close to one. Both Q_a and Q_c depend linearly on $v^{-1/2}$, the charge value extrapolated to $v \to \infty$ is $Q_{a,\infty} = Q_{c,\infty} \cong 3\,\mathrm{mC\,cm^{-2}}$. Stabilized voltammograms for vitreous carbon/precipitated silver oxide electrodes are to a large extent comparable to those resulting from the early ORC for massive silver electrodes [46, 47, 51]. However, for the latter the $\Delta E_{1/2}$ value at a constant v [46] is practically one half of that found for vitreous carbon/precipitated silver oxide electrodes.

From these results two important conclusions are obtained. Firstly, the oxide layer electrochemically formed on massive silver behaves differently to that initially produced through chemical precipitation. The behaviour of the latter, however, approaches that of the former after a prolonged potential cycling, so that the characteristics of the anodic peaks are practically independent of the electrode preparation conditions, potential perturbation programme and pH. Secondly, for a constant amount of precipitated silver oxide the actual amount of electrochemically active material depends on v. Blanks for vitreous carbon immersed in 0.1 M NaOH revealed a negligible charge contribution due to reactions on the carbon substrate as compared to the charge involved in the precipitated active surface material during potential cycling.

The stabilized voltammetric charge, however, can be appreciably increased by preheating the vitreous carbon/silver oxide electrode at ca. 100° C for 60 min (Fig. 4). This confirms that the hydrous oxide layer structure is very sensitive to the preparation conditions and subsequent treatments. The decrease of $E_{s,a}$ stepwise (Fig. 4a) shifts $E_{p,c}$ to more positive values and for a $E_{s,a}$ value set in the potential range of peak II, the peak VI shows two clear contributions. Furthermore, a highly reversible response appears for $E_{s,a}$ set in the potential region of peak I (Fig. 4a). On the other hand, when $E_{s,c} < E_{p,c}$ the stepwise increase of $E_{s,c}$ (Fig. 4b) causes only little changes in the anodic profile, whereas when $E_{s,c} > E_{p,c}$ a reactivation of the cathodic process at potentials more positive than that of peak VI can be observed in the anodic potential scan. This is accompanied by the increase in the anodic current at potentials more negative than that of peak VI during the reverse scan. Consequently, the voltammetric stabilization is directly related to changes in either the structure or the composition of the silver oxide layer. For a system which still has not attained stabilized voltammogram the gradual decrease of $E_{s,a}$ stepwise shows that for $E_{s,a} < E_{p,II}$ peak VII is no longer observed (Fig. 5), although the cathodic limiting current extending from 0.4 V downwards remains the same.

The strong dependence of voltammograms on the perturbing potential is depicted in Fig. 6. Thus, the jump of v to a new v' ($v' > v$) changes the stabilized voltammogram at v into a voltammogram at v' which resembles closely that of massive silver (Fig. 1). On the other hand, when the jump in v is reversed ($v' < v$), then the stabilized voltammogram at v' shows the disappearance of the sharp peak VI and the simultaneous appearance of a new peak with current instabilities. In this case, the voltammogram approaches

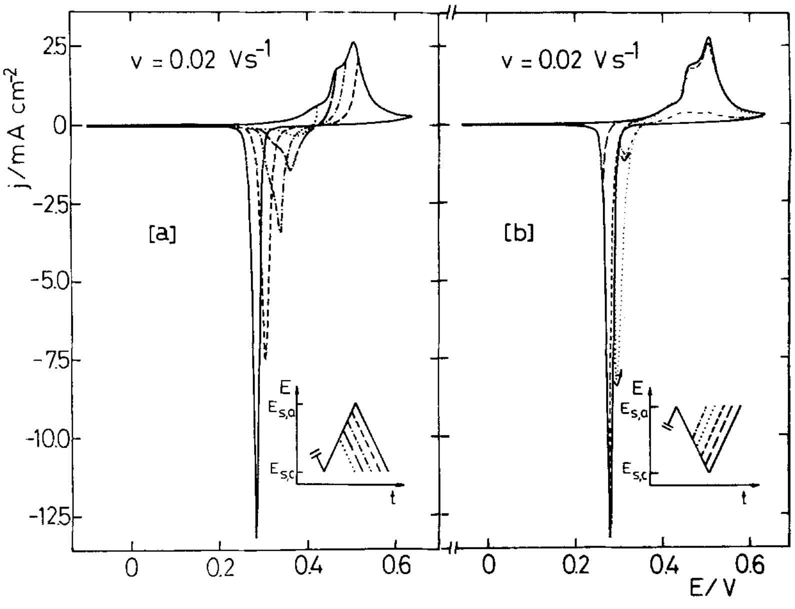

Fig. 4. Voltammograms with $E_{s,a}$ and $E_{s,c}$ stepwise changed at $v = 0.02\,V\,s^{-1}$ in 0.1 M NaOH + Ag_2O (saturated). Vitreous carbon/precipitated AgO electrode prepared from $x = 0.1$, $y = 0.005$, and $n = 20$ followed by heating to 100°C during 60 min. The stabilized voltammogram was attained after 120 min potential cycling between $E_{s,a} = 0.64\,V$ and $E_{s,c} = -0.10\,V$.

that depicted in Fig. 5b. In the first case, as v is increased from 0.02 to $0.2\,V\,s^{-1}$ (Fig. 6a) the overall charge increases, particularly that related to peaks III and VI. On the other hand, when the change in v operates reversely, that is from 0.2 to $0.002\,V\,s^{-1}$ the overall charge is hardly modified, but the characteristics of peak III are somewhat changed.

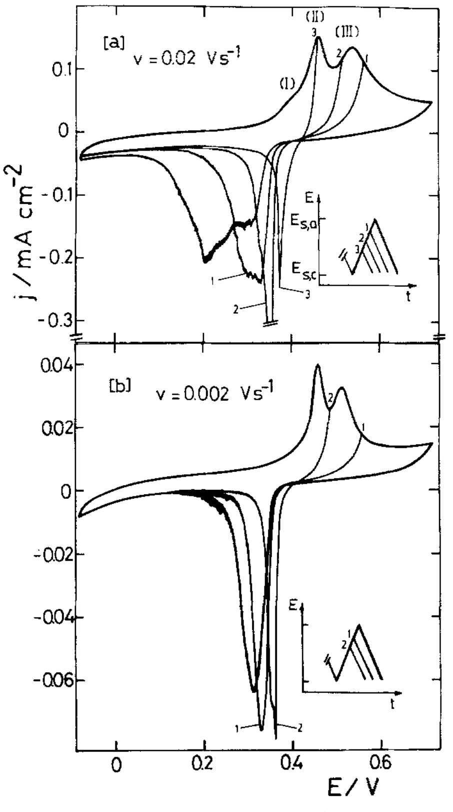

Fig. 5. Voltammograms at $v = 0.02\,V\,s^{-1}$ and $0.002\,V\,s^{-1}$ and $E_{s,a}$ stepwise changed. Each voltammogram is preceded by 10 ORC between $E_{s,a} = 0.72\,V$ and $E_{s,c} = -0.08\,V$ at the same v. Vitreous carbon/precipitated hydrous AgO/0.1 M NaOH + Ag_2O (saturated). The electrode was prepared from $x = 0.1$, $y = 0.01$, and $n = 20$ conditions.

Voltammograms preceded by a potential step at either $E_{s,a}$ or $E_{s,c}$ (Fig. 7), run at pH 12, with vitreous carbon electrodes involving a relatively large amount of active material show, in the first anodic scan, a cathodic current contribution appearing in the potential range of peak VI, which becomes more remarkable when the potential has been previously held at $E_{s,c}$, but it disappears on subsequent cycles. Under the experimental conditions of this work the presence of a cathodic contribution during the first positive going potential was observed only in voltammograms performed in 0.01 M NaOH independently of the starting potential (Fig. 7). Other changes in the rest of the voltammograms become largely comparable to those already described.

It should be noticed that electroreduction voltammograms comparable to those shown in Figs 5–7 also result for massive silver electrodes in 0.1 M NaOH subjected to combined RTPS and STPS perturbing potentials as indicated in Fig. 8. The envelope of the TMTPS voltammogram run at $v = 2\,V\,s^{-1}$ with a triangular potential modulation at $100\,V\,s^{-1}$ (Fig. 9b) exhibits a highly reversible redox couple in the vicinity of 0.05 V, which corresponds to the early stages of OH-electroadsorption/electrodesorption on silver. On the other hand, the comparison between RTPS (Fig. 9a) and TMTPS voltammograms confirm that soluble Ag(I) species are already formed at initial stages of surface film formation. These results agree with those recently obtained by using the rotating ring-disc technique and ellipsometry [51].

4. Discussion

The results obtained with silver hydroxide electrodes precipitated on vitreous carbon substrates offer the possibility of discussing the kinetics and mechanism of the overall electrochemical processes without inter-

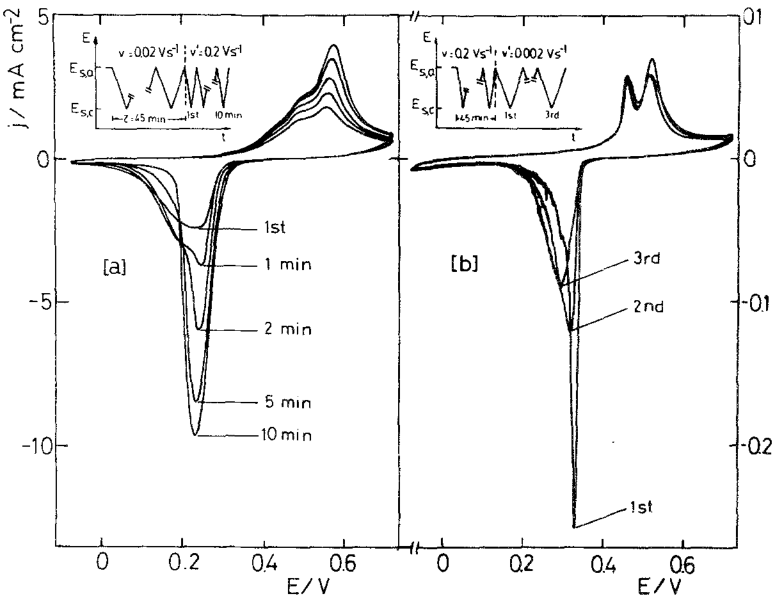

Fig. 6. (a) RTPS voltammograms run at $v' = 0.2\,\mathrm{V\,s^{-1}}$ between $E_{s,a} = 0.72\,\mathrm{V}$ and $E_{s,c} = -0.08\,\mathrm{V}$, preceded by ORC during $\tau = 45\,\mathrm{min}$ at $v = 0.02\,\mathrm{V\,s^{-1}}$. Same electrode as indicated in Fig. 5. The identification of the scan and voltammograms results from their comparison to the ORC indicated in the E/t programme. (b) RTPS voltammograms run at $v' = 0.2\,\mathrm{V\,s^{-1}}$ between $E_{s,a} = 0.72\,\mathrm{V}$ and $E_{s,c} = -0.08\,\mathrm{V}$ after $\tau = 45\,\mathrm{min}$ potential cycling at $v = 0.2\,\mathrm{V\,s^{-1}}$ for an electrode prepared also as indicated in Fig. 5. The first, second and third scans from the change of sweep rate are shown.

ference of additional faradaic reactions resulting from the use of a silver substrate.

In a system such as silver hydroxide/vitreous carbon, there are two questions which must be considered. One of them is related to the electrochemical contributions resulting from the vitreous carbon substrate itself, and the other one concerns with possible differences resulting from the hydrous silver oxide layer preparation either through chemical precipitation on the vitreous carbon substrate or from the anodic polarization on the vitreous carbon substrate or from the anodic polarization of silver in the base electrolyte. Concerning the first question the only reactions taking place on vitreous carbon in base sol-

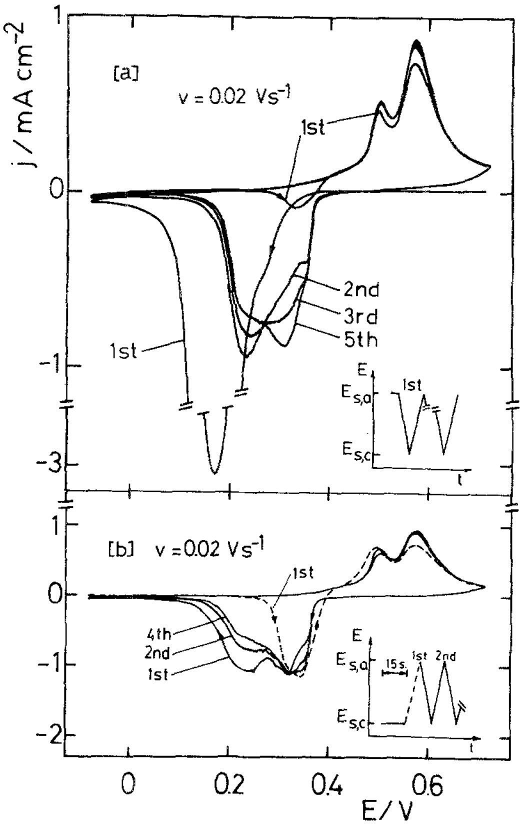

Fig. 7. RTPS voltammograms run at $v = 0.02\,\mathrm{V\,s^{-1}}$ between $E_{s,a} = 0.72\,\mathrm{V}$ and $E_{s,c} = -0.08\,\mathrm{V}$. Vitreous carbon/precipitated hydrous Ag_2O/0.01 M NaOH. The electrodes were prepared from $x = 0.01$, $y = 0.004$ and $n = 50$ precipitating conditions. (a) Potential cycling was starting from $E_{s,a}$ after 15 s potential holding at $E_{s,a}$. (b) Potential cycling was started from $E_{s,c}$ after 15 s potential holding at $E_{s,c}$.

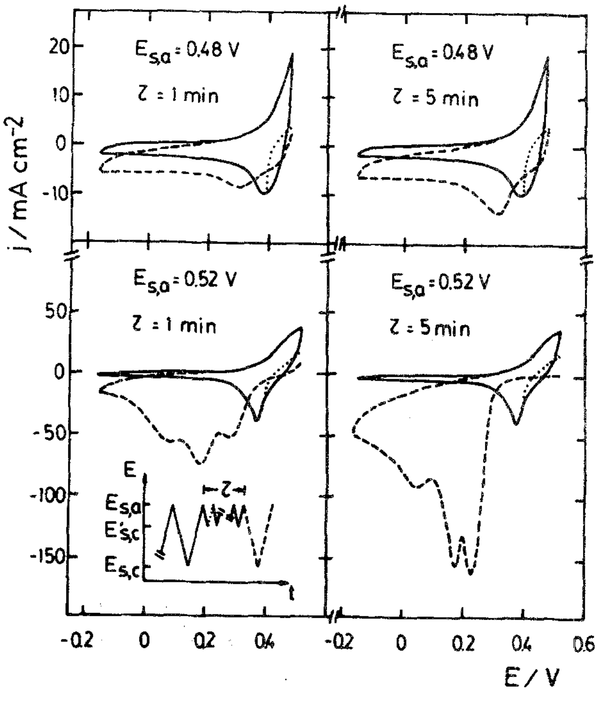

Fig. 8. Voltammograms obtained at $v = 2\,\mathrm{V\,s^{-1}}$ in the Ag/0.1 M NaOH with the combined E/t programme indicated in the figure. The full traces correspond to the stabilized voltammograms between $E_{s,c} = -0.16\,\mathrm{V}$, $E_{s,a}$ either 0.48 V or 0.52 V, and the dashed traces correspond to previous ORC between $E'_{s,c} = 0.40\,\mathrm{V}$ and $E_{s,a}$ during the time τ.

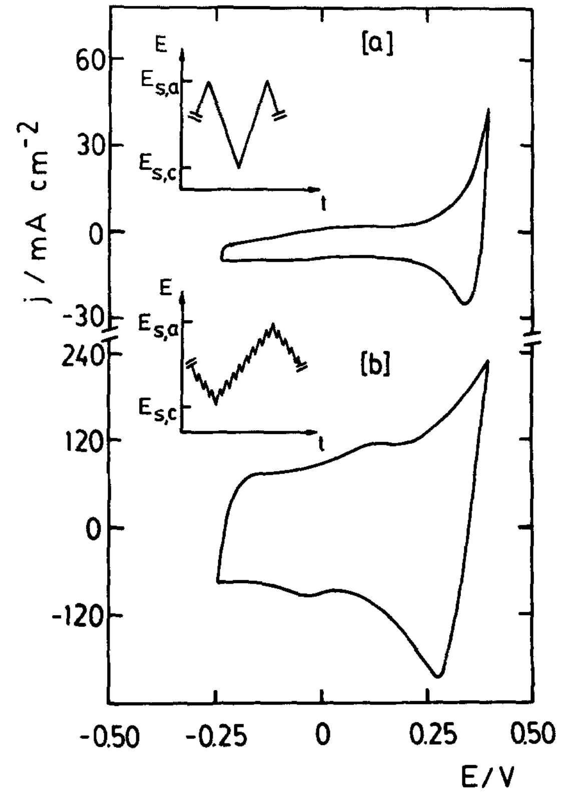

Fig. 9. Comparison between RTPS voltammogram (a) and TMTPS contours (b) resulting for a silver electrode in 0.1 M NaOH solution. (a) $v = 2\,\mathrm{V\,s^{-1}}$; (b) $v_g = 2\,\mathrm{V\,s^{-1}}$, $v_m = 100\,\mathrm{V\,s^{-1}}$, $A_m = 0.1\,\mathrm{V}$.

utions in the potential range of bulk water stability are surface processes such as redox chemical adsorption of oxygen and the irreversible redox reactions of existing surface groups. The charge contribution of these processes is negligible as compared to the overall charge involved in the redox processes of the hydrous silver oxide layer. Nevertheless, the surface reactions on vitreous carbon presumably play a determining role in the adhesion of the active layer to the substrate, probably through H-bonding of adsorbed OH-species on the substrate [60–66].

Concerning the second question, voltammetric results indicate that the electroreduction of the starting hydrous silver hydroxide layer behaves substantially differently as compared to an electrochemically formed anodic layer (Figs 1 and 2). This difference, however, disappears on subsequent potential cycling. Therefore, the fresh chemically precipitated silver hydroxide on vitreous carbon, in contrast to the oxide layer produced by silver anodization in base solution, appears to be formed of a gel-like hydroxide matrix containing soluble Ag(I) species, probably as anionic species. This explains that for the vitreous carbon/chemically precipitated silver hydroxide electrode during the first potential cycles the soluble Ag(I) species gradually disappear yielding Ag on the substrate. This electroreduction process which is related to peak VII, involves diffusion kinetics in the hydrous silver oxide layer. As the contribution of peak VII decreases and that of peak VI increases, the entire voltammogram approaches the conventional one, as during the ORC the structure of the interface progressively changes from that of vitreous carbon/hydrous silver (I) oxide + soluble Ag(I) species to that of vitreous carbon/silver/hydrous silver (I) oxide. Accordingly, the voltammogram moves to that of a conventional Ag/silver hydroxide electrode in base; the overall voltammetric charge decreases to about half that resulting in the first triangular potential scan. This provides a first indication that during the repetitive cycling other processes are taking place simultaneously which gradually transform a relatively large proportion of the initial material into an electrochemically inactive material at least under the conditions of the voltammetric experiment. From the stabilized voltammograms it is evident (Fig. 3) that the larger the amount of active material the lower the potential sweep rate. Correspondingly, peaks I and VI become sharper and their peak potential difference smaller. These facts indicate that the anodic layer undergoes ageing effects, that is structure modifications including change in the water content and nucleation and growth of new phases. This is consistent with the fact that the characteristics of peak VI, which is by far the most clearly defined peak, fit $E_{p,c}$, $\Delta E_{1/2}$, and $j_{p,c}$ against $v^{1/2}$ relationships. As discussed earlier [46], these results can be taken as an indication that nucleation and growth processes are probably coupled to the electrochemical reactions. The evidence of nucleation and growth processes also emerges from the experiments depicted in Figs 4 and 5. Thus, when $v = 0.02\,\mathrm{V\,s^{-1}}$ and $E_{s,a}$ is increased stepwise, the greatest $E_{s,a}$ (that is the longer potential sweep times), the more marked the sharpness in peak VI. Furthermore, when $E_{s,a}$ is decreased stepwise, a clear hysteresis can be seen for the most positive values of $E_{s,a}$, as expected for chemical changes at the hydrous silver hydroxide-oxide layers involving nucleation and growth of new phases. The modified anodic layer structure becomes more difficult to electroreduce so that, for anodic layers similarly prepared but with different histories, the amount of active material participating in each ORC increases as the potential sweep rate decreases, that is when longer electroreduction times are involved.

Results also show that under constant $E_{s,a}$ and $E_{s,c}$, the contribution of nucleation and growth competes with the formation of soluble Ag(I) species at the layer matrix. The relative contribution of the latter becomes more relevant as v increases. The formation of soluble Ag(I) species can occur in each ORC, as the Ag(OH) intermediate is formed. During the electrooxidation half-cycle the Ag(OH) intermediate can undergo either stabilization, as a hydrous silver hydroxide layer and subsequently start to form a new phase, or dissolution, as Ag(I) species, and later precipitation to increase the layer growth. Apparently, the rate of the former process is smaller than that of the second process, a fact which explains that for each ORC the greater v, the larger the amount of soluble Ag(I) produced.

The increase in the amount of Ag(I) soluble species can be observed in combined RTPS with STPS experiments where there is a remarkable increase in the cathodic charge after the potentiodynamic ageing treatment (Fig. 7). Similarly, TMTPS runs show the reversibility of early stages of ORC involving Ag(OH) species (Fig. 8). The appearance of soluble Ag(I) species on applying an anodic potential sweep to a silver electrode in base has been conclusively demonstrated by means of the rotating ring-disc electrode technique and ellipsometry [51]. Furthermore, the amount of soluble Ag(I) species increases as $E_{s,a}$ is made more positive. This means that by changing either $E_{s,a}$ under constant v, or v under constant $E_{s,a}$, the relative contribution of soluble Ag(I) formation and that of nucleation and growth processes can be changed. Consequently, the structure produced for the oxide layer during the ORC treatment can be rather inhomogeneous, containing a gel-like phase, a solid phase, and Ag(I) soluble species in the gel-like patches. Hence, under these circumstances one might expect that the electroreduction of Ag(I) soluble species be associated with current fluctuations (Fig. 5) caused by the inhomogeneity of the silver oxide-hydroxide layer.

5. Conclusion

According to the preparation procedure of the silver/silver oxide electrodes, different electrochemical behaviour can be observed, presumably related to the structure and properties of the silver oxide layer in contact with the conducting substrate.

The electrochemical behaviour of silver oxide electrodes prepared on a conducting support, which is stable in the potential range where the electrochemical processes are investigated, suggests that the first oxidation level can be interpreted in terms of the reversible formation of Ag(OH) surface species. Depending on the operation conditions one part of Ag(OH) can be dissolved yielding Ag(I) species in solution and another part can be further transformed into an inhomogeneous layer structure. The relative contribution of those two reactions depends on the ORC conditions.

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