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Electrochemical formation and characterization of Ag_2O

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Abstract: The process of Ag_2O formation has been investigated in 0.1 M, 0.3 M, 1.0 M and 2.0 M NaOH solutions on polycrystalline Ag electrodes by cyclic voltammetry, potentiostatic pulse and SEM techniques. The SEM micrographs of the chemically polished Ag surface and the surface after oxide formation revealed considerable roughening of the Ag surface after Ag_2O formation and reduction. The roughening was more pronounced at higher NaOH concentrations, indicating that only the first cycle or pulse applied on a freshly polished Ag electrode should be considered in mechanistic studies of Ag_2O formation. In the given range of NaOH concentrations, it was shown that the process is not controlled simply by the diffusion of the reacting species. A nucleation phenomenon was clearly detected in all the examined solutions. The SEM micrographs confirm that the two anodic peaks, present on the voltammograms of Ag_2O formation, correspond to two types of oxide film, *i.e.*, non-homogeneously and homogeneously distributed ones. Potentiostatic formation of the oxide at potentials corresponding to the first and second anodic peak yielded simple cubic Ag_2O but of very different grain size.

Keywords: Ag_2O formation, 3D nucleation and growth, morphology, surface roughening.

INTRODUCTION

In order to gain a better understanding of Ag_2O and AgO formation, which is necessary for the development of silver – zinc rechargeable batteries, the electrochemical behavior of silver in hydroxide containing solutions has been investigated primarily on polycrystalline Ag electrodes in the potential region of silver oxidation. A detailed review of the results obtained until 1988 has been given in the paper of Teijelo *et al.*[1] Most authors[2–6,9,11] agree that the first anodic peak (or shoulder) appearing between 0.1 V and 0.2 V *vs.* Hg/HgO corresponds to the formation of an AgOH (or Ag_2O) monolayer, while the next two peaks (between 0.2 V and 0.4 V *vs.* Hg/HgO) are associated with the formation of a compact and porous Ag_2O layer, respectively. At more anodic potentials, about 0.5 V *vs.* Hg/HgO, the sharp anodic peak corresponds to the formation of AgO on top of Ag_2O.

Potentiostatic investigations of Ag_2O formation[2–5,9] have shown that the first (compact) layer of Ag_2O deposits under diffusion control (linear j *vs.* $t^{-1/2}$), indicating that the solid state diffusion of Ag^+ through the oxide layer is the rate controlling process. The mechanism behind the formation of the second, porous layer of Ag_2O, was investigated by Alonso *et al.*[5] Using equations for 3D nucleation and growth under diffusion control (originally developed by Sharifker *et al.*[8]) for fitting the experimentally recorded j *vs.* t transients, they concluded that the porous Ag_2O layer grows as 3D islands on top of a compact (primary) oxide layer and that this process is also controlled by the diffusion of Ag^+ through the oxide layer. It is important to note that these conclusions wer reached after investigation of this process in 0.1 M NaOH solution only, and that the experimentally recorded j *vs.* t transients were found to fit the predicted model only after special preparation of the electrode surface, *i.e.*, after prolonged polarization at a potential of 0.19 V *vs.* SCE.[5]

According to the results of Hepel *et al.*,[7,10] at a higher concentration of hydroxide (1 M KOH solution), a slow nucleation phenomenon is observed at potentials corresponding to the first anodic peak. The steady-state oxidation currents measured on a polycrystalline silver rotating disc electrode (RDE) were found to follow the limiting Levich equation, despite the fact that the electrode was covered with a thin layer of Ag_2O film. The final value of these currents indicated that saturation of the solution with respect to Ag^+ species was maintained. Accordingly, a steady-state model of the metal/semiconductor electrode undergoing dissolution was proposed.

The process of Ag_2O formation on an Ag(111) surface in 1 M NaOH has been investigated by cyclic voltammetry and potentiostatic pulse techniques in combination with spectroscopic ellipsometry.[11] The authors showed that the thickness of the first (compact) Ag_2O layer was limited to a thickness of about 150 nm prior to nucleation of the second (porous) layer. The thickness of the first layer then dropped to zero, indicating that initially, the second layer grew at the expense of the oxide from the first layer. According to their results it seems that the process of Ag_2O formation is more complicated than the precipitation mechanism mostly accepted in the literature.[1]

Recently, combined surface enhanced Raman spectroscopy (SERS), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and cyclic voltammetry investigations of Ag(111) oxidation in the UPD region[12] of Ag_2O/Ag revealed the presence of oxygen-containing adsorbates, such as surface OH groups ($OH_{ads}{}^{\gamma-}$), surface oxide-like species ($O_{ads}{}^{\delta-}$) and OH groups incorporated in the bulk of the electrode (OH_{bulk}). The suggested mechanism of the Ag(111) sub-monolayer oxidation assumed adsorption of OH^- species as the first step

$$OH^- \Rightarrow OH_{ads}{}^{\gamma-} + (1-\gamma)e^- \tag{1}$$

and further transformation of the $OH_{ads}{}^{\gamma-}$ species *via* incorporation in the bulk of the Ag(111) after loss of charge by the reaction

$$OH_{ads}{}^{\gamma-} \Rightarrow OH_{bulk} + \gamma e^- \tag{2}$$

Alternatively, it was assumed that the $OH_{ads}{}^{\gamma-}$ species could be oxidized to give surface oxide-like species $O_{ads}{}^{\delta-}$ by the reaction

$$OH_{ads}^{\gamma-} + OH^- \Rightarrow O_{ads}^{\delta-} + H_2O + (1-\gamma-\delta)e^- \qquad (3)$$

with the $O_{ads}^{\delta-}$ species being the precursor for bulk Ag_2O formation, which occurs at more positive potentials[12] than 0.2 V *vs.* Hg/HgO.

Most recently, a STM investigation of the oxidation of Ag(111) in a solution of 0.5 mM NaF + 0.1 mM NaOH showed that this process starts at the steps and extends to the terraces as the electrode potential is positively scanned, but still in the UPD region of Ag_2O/Ag.[13] Potential reversal was found to restore the initial surface morphology in the investigated solution. At the same time, very small amounts of impurities (about 3 at. % of carbon and about 1.5 at. % of silicon) were found to behave, together with surface defects, as nucleation centers for the commencement of the oxidation process.[13]

In this study, the mechanism of formation and the structure of the electrochemically formed Ag_2O oxide on fresh mechanically and chemically polished polycrystalline silver electrodes in NaOH solutions of varying concentration (0.1 M, 0.3 M, 1.0 M and 2.0 M), were investigated in order to a better understanding of the process of oxide formation and the morphological structure of Ag_2O.

EXPERIMENTAL

All experiments were carried out in a standard electrochemical cell at (25 ± 1) ºC under an atmosphere of purified nitrogen. Electrochemical investigations were performed on a polycrystalline silver rod (d = 6.7 mm) sealed in an epoxy resin resistant to alkaline solutions (resin EPON 828 + hardener TETA) in such a way that only the disc surface (0.363 cm^2) was exposed to the solution. Glancing angle X-ray diffraction and SEM investigations were performed on a larger electrode (1.3 cm^2). The oxide layers were formed potentiostatically on a freshly prepared electrode surface.

The procedure of polycrystalline silver surface preparation was the same as that given in detail for single crystals in previous papers.[14-16] The counter electrode was a platinum sheet, while a mercury/mercury oxide (Hg/HgO) electrode in 0.1 M NaOH was used as the reference electrode. All solutions were made of 99.999 % NaOH (Aldrich) and EASY pure UV water (Barnstead).

The cyclic voltammetry and potentiostatic pulse experiments were performed using a potentiostat (PAR M-173) and a universal programmer (PAR M-175) in conjunction with a computer. The electrochemically formed silver oxides were examined by scanning electron microscopy (SEM) using a JOEL 840 instrument.

RESULTS

Several authors[17–19] have reported that the original silver electrode surface becomes destroyed after cycling or pulsing the electrode into the potential region of Ag_2O oxide formation/reduction. The influence of Ag_2O oxide formation on the electrode roughness, as well as on the shape of the silver oxidation voltammetry is reported in this paper.

The first (full line) and 10-th cycle (dotted line) recorded in 0.1 M NaOH and in 2.0 M NaOH at a sweep rate of 1 mV s^{-1} are shown in Figs. 1a and 1b, respectively. It is interesting to note that peak *a* is much better defined in 0.1 M NaOH solution than in 2.0 M NaOH and that this peak transforms into a shoulder with increasing number of cycles in 2.0 M NaOH solution (Fig. 1b). The potential of peak *b* had moved toward more negative values after 10 cycles. The shift is about 75 mV in 0.1 M NaOH and about 35 mV in 2.0 M

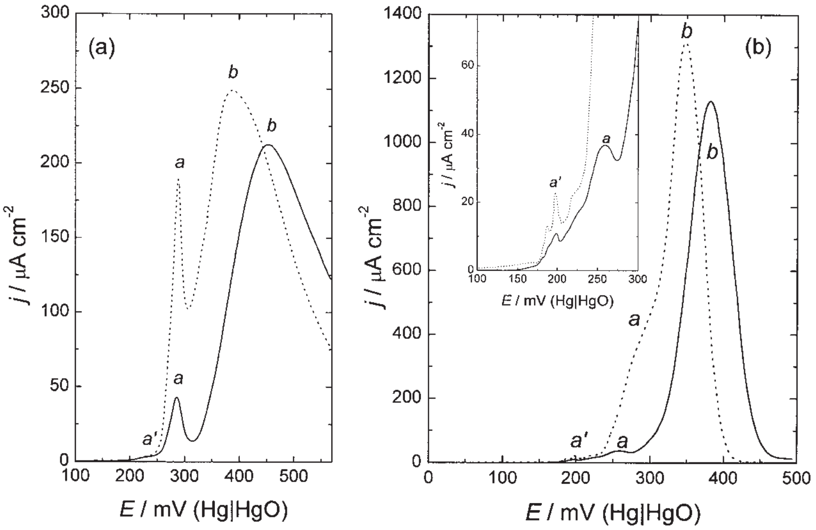

Fig 1. (a) First (full line) and 10-th cycle (dotted line) recorded on a freshly polished Ag electrode in a 0.1 M solution of NaOH at a sweep rate of 1 mV s^{-1} in the potential region of peaks *a'*, *a* and *b*. (b) First (full line) and 10-th cycle (dotted line) recorded on a freshly polished Ag electrode in a 2.0 M solution NaOH at a sweep rate of 1 mV s^{-1} in the potential region of peaks *a'* and *a* (inset of the figure) and in the region of peaks *a'*, *a* and *b*.

NaOH. By comparing the SEM micrographs of chemically polisehd Ag electrode (Fig. 2a) with the micrographs obtained after one cycle in the potential region of Ag_2O formation/reduction (recorded at a sweep rate of 1 mV s^{-1}) in both 0.1 M NaOH and 2.0 M NaOH solutions, Fig. 2b and c, respectively, it can be concluded that the roughening of the electrode surface is much more pronounced in the 2.0 M NaOH solution than in 0.1 M NaOH (Fig. 2c and b). It is obvious from this analysis that the original electrode surface significantly changes during the process of Ag_2O formation/reduction. Accordingly, all furhter results presented in this paper represent the first cycle, or the first pulse applied at a certain potential on a fresh mechanically and chemically polished electrode surface.

The first cycle of Ag_2O formation recorded on freshly polished Ag electrodes at a sweep rate of 1 mV s^{-1} in NaOH solutions of different concentration are shown in Fig. 3. As can be seen the shape of the voltammogram is more or less the same, characterized by the presence of peaks *a'*, *a* and *b*. The current density of peak *b* increases with increasing NaOH concentration and its potential shifts to more negative values. A plot of $E_p(b)$ *vs.* log c(NaOH) shows a linear dependence with a slope of about 40 mV dec^{-1}. The potential of peak *a* also shifts towards more negative values with increasing NaOH concentration, but a plot of $E_p(a)$ *vs.* log c(NaOH) shows a parabolic dependence, increasing from 0.1 M NaOH to 0.3 M NaOH and decreasing at higher concentrations of NaOH, indicating the complex nature of Ag_2O formation.

It is interesting to note that the shoulder *a'* in 0.1 M NaOH and 0.3 M NaOH, with a charge of about 150 μC cm^{-2}, becomes well-defined peak at the highest NaOH concentra-

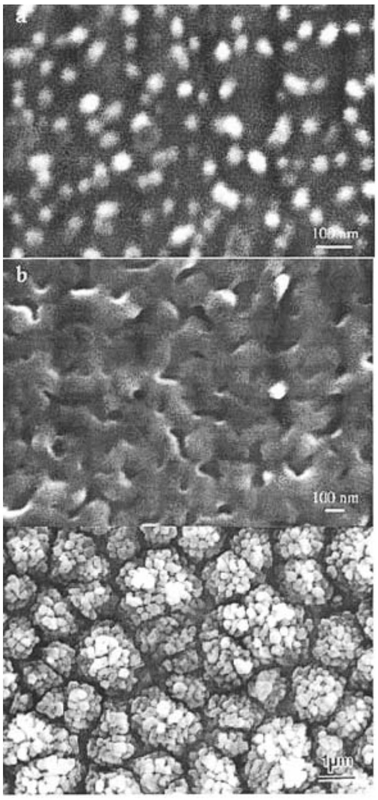

Fig. 2. (a) SEM of mechanically and chemically polished Ag surface. (b) SEM of mechanically and chemically polished Ag surface after the formation and reduction of Ag_2O oxide in a 0.1 M solution of NaOH at a sweep rate of 1 mV s^{-1}. (c) SEM of mechanically and chemically polished Ag surface after formation and reduction of Ag_2O oxide in a 2 M solution of NaOH at a sweep rate of 1 mV s^{-1}.

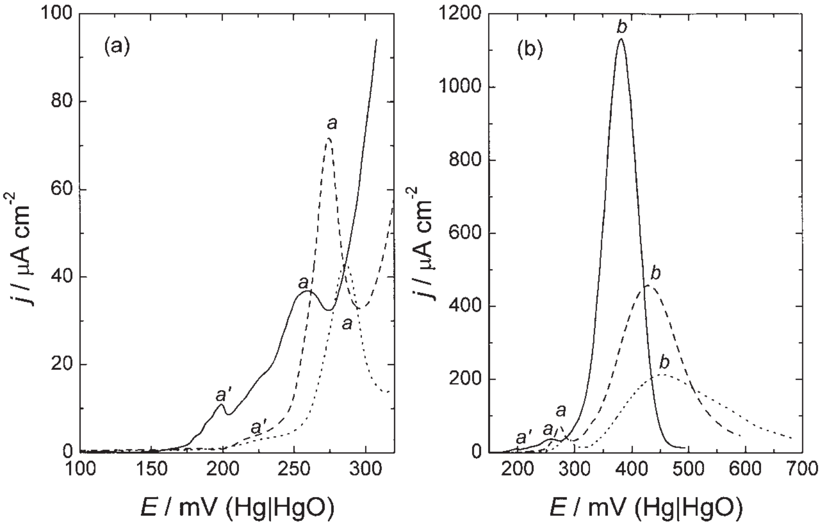

Fig. 3. First cycle recorded at a sweep rate of 1 mV s^{-1} on freshly polished Ag electrodes in solutions of different NaOH concentration in the potential region of peaks *a'* and *a* (a) and in the region of peaks *a'*, *a* and *b* (b): full line – 2.0 M NaOH; dashed line – 0.3 M NaOH; dotted line – 0.1 M NaOH.

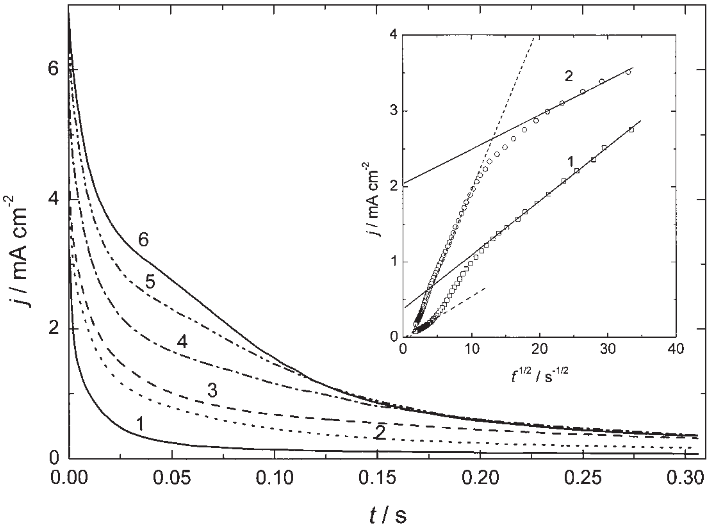

Fig. 4. First potentiostatic j *vs.* t transients recorded on a freshly polished Ag electrode in a 0.1 M solution of NaOH at different potentials (*vs.* Hg/HgO): 1. $E_p = 230$ mV; 2. $E_p = 300$ mV; 3. $E_p = 350$ mV; 4. $E_p = 400$ mV; 5. $E_p = 450$ mV; 6. $E_p = 500$ mV. Inset of this Figure: j *vs.* $t^{-1/2}$ dependences for pulses 1 and 2.

tion (Fig. 3a). Although the peak is better resolved, the charge associated with this peak (after deconvolution from peak *a*) increases only by about 6 % compared to that measured in 0.1 M NaOH.

The potentiostatic j *vs.* t transients recorded for the first pulse applied on freshly polished electrodes in 0.1 M NaOH solution are shown in Fig. 4. Pulse number 1 ($E_p = 230$ mV *vs.* Hg/HgO) corresponds to the potential of the shoulder *a'*, pulse number 2 ($E_p = 300$ mV *vs.* Hg/HgO) corresponds to the potential region of peak *a*, while pulses number 3–6 correspond to the potential region of the peak *b* shown in Fig. 3. Although the pulses number 1 to 4 in Fig. 4 look like monotonously falling transients, none of them follows a j *vs.* $t^{-1/2}$ linear dependence, indicating that this process is not diffusion controlled. Actually, all of them possess two linear regions (see inset of Fig. 4). It is interesting to note that j *vs.* $t^{-1/2}$ dependences for pulses number 1 and 2 are different, indicating that those two processes are different in nature. At the same time, the shape of the j *vs.* $t^{-1/2}$ dependences for pulses number 2 to 4 are identical, the only difference being the slopes of the linear parts. The shape of pulse number 5 and 6 (the presence of a shoulder on them) already indicates deviation from linearity for the j *vs.* $t^{-1/2}$ dependence.

SEM of Ag_2O formed in 0.1 M NaOH solution

For SEM investigations of Ag_2O oxide formed in the potential region of peak *a* in 0.1 M NaOH solution (Fig. 1), samples were held at a constant potential for about 2 h, although the anodic current density had dropped to a constant and small value after about 5 s. It was found that Ag_2O formation is very sensitive to the applied potential and that it is a time consuming process.

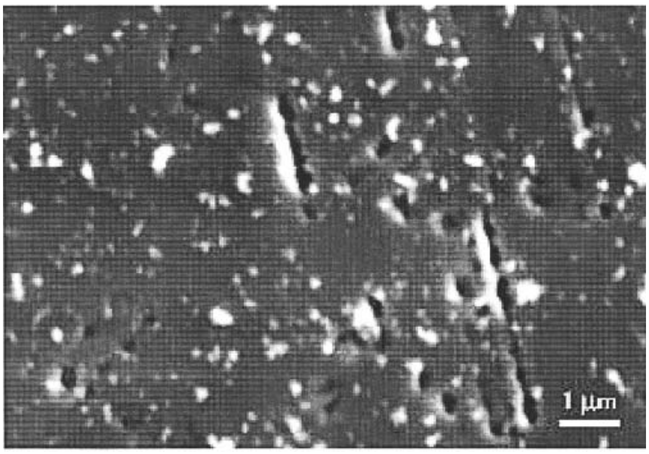

Fig. 5. SEM of the oxide formed at E = 285 mV *vs.* Hg/HgO in a 0.1 M solution of NaOH.

Figure 5 shows the surface following oxidation at a potential of 285 mV *vs.* Hg/HgO (close to the potential of peak *a*). A very small amount of Ag_2O had been formed as indicated by the white spots in the Figure. The particle size of the oxide species varied from about 0.01 µm to about 0.02 µm . The charge associated with the oxide formation was

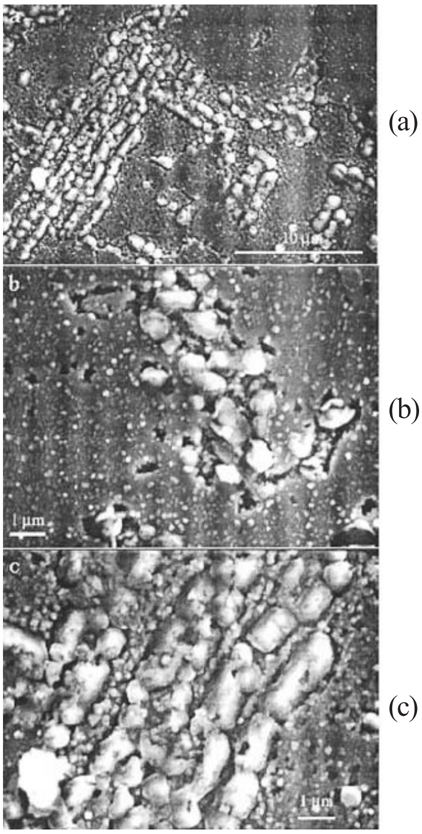

Fig. 6. SEMs of the oxide formed at E = 290 mV *vs.* Hg/HgO in a 0.1 M solution of NaOH: (a) a general view; (b) the region of low density of nuclei; (c) the region of high density of nuclei.

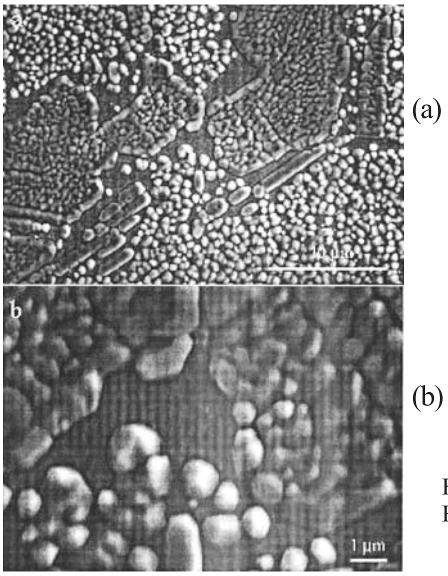

Fig. 7. SEMs of the oxide formed at E = 300 mV *vs.* Hg/HgO in a 0.1 M solution of NaOH: (a) lower magnification; (b) higher magnificartion.

about 10 mC cm^{-2}. Although the SEM suggests limited oxidation of the surface, visual inspection shows that the entire surface changed from specular to cloudy.

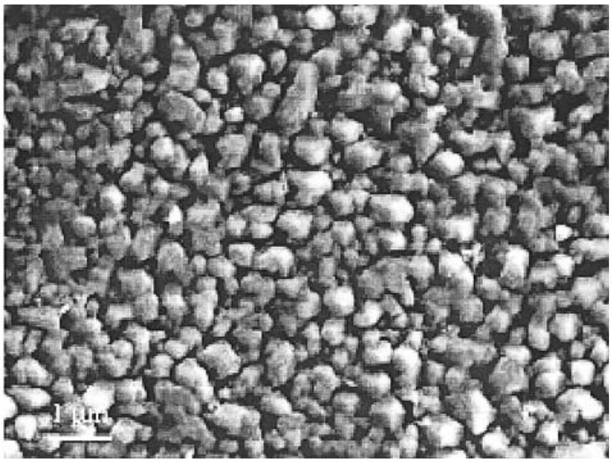

Fig. 8. SEM of the oxide formed at E = 480 mV *vs.* Hg/HgO in a 0.1 M solution of NaOH.

At the more positive potential of 290 mV *vs.* Hg/HgO, only a small portion of the electrode surface (about 1/3) was covered with a visible dark oxide layer (bright areas on the SEM), while the rest of the surface was covered with the same oxide morphology as seen previously. As can be seen in Fig. 6, the distribution of the oxide species is non-homogeneous (Fig. 6a) and some crystals in the dark oxide area are much larger, exceeding 2 µm, in one direction (Fig. 6c). The amount of charge recorded during the oxide formation was approximately 12 mC cm^{-2}.

At a potential of 300 mV *vs.* Hg/HgO, the entire surface was covered with a dark oxide layer and the diameter of the crystals varied between 0.5 µm to 1.5 µm, Fig. 7. The dis-

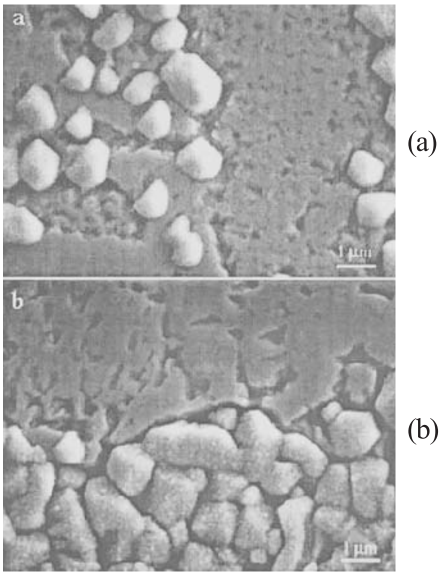

Fig. 9. SEMs of the oxide formed at E = 255 mV *vs.* Hg/HgO in a 2.0 M solution of NaOH: (a) the region of lower density of nuclei; (b) the edge of the region of higher density of nuclei.

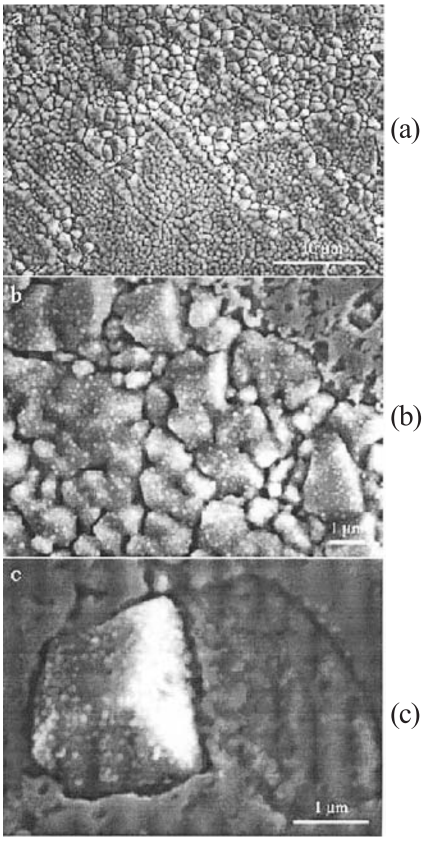

Fig. 10. SEMs of the oxide formed at E = 290 mV *vs.* Hg/HgO in a 2.0 M solution of NaOH: (a) a general view; (b) higher magnification; (c) a single (isolated) nucleus.

tribution of oxide species was also non-homogeneous, although at this potential two oxide regions, one dense and the other less dense, were observed on the electrode surface. The total amount of charge recorded during the oxide formation was much greater, about 38 mC cm^{-2} and the residual current density recorded after about 10 s was much higher than that of the two previous cases at more negative potentials.

In the potential region of peak *b*, 480 mV *vs*. Hg/HgO, a very dense and homogeneous oxide layer was formed after 500 s, Fig. 8. Although the anodic charge for oxide formation was approximately 51 mC cm^{-2}, the cyrstal size varied from 0.2 μm and 0.8 μm, significantly smaller than that observed at more negative potentials.

SEM of Ag_2O formed in 2 M NaOH solution

When the concentration of NaOH was increased to 2.0 M, well defined and large crystals of Ag_2O (0.5 μm to 1.5 μm) can be formed at the potential of peak *a* ($E = 255$ mV *vs.* Hg/HgO, see inset of Fig. 1b), Fig. 9. As in the case of dilute NaOH, the entire electrode surface was not covered with oxide after 2 h. On parts of the electrode surface the oxide was only partially dense (Fig. 9a). It is interesting to note that parts of the surface are oxide-free, there were no traces of small oxide crystals on the surface, as in the case of oxides formed at the potential of peak *a* in 0.1 M NaOH solution (Fig. 6). The total charge recorded during this pulse was only about 7 mC cm^{-2}.

At a potential of 290 mV *vs.* Hg/HgO (the beginning of peak *b*), a dense and homogeneous oxide layer was formed, as can be seen in Fig. 10a. Again, there was no oxide on a small portion of the surface, as can be seen in Fig. 10b (right upper corner). One isolated crystal, about 1 μm in size, was detected on the part of the surface that was not completely covered with oxide, Fig. 10c. The total amount of charge recorded during the oxide formation was high, amounting to about 100 mC cm^{-2}.

At a potential associated with peak *b* ($E = 320$ mV *vs.* Hg/HgO, see Fig. 1b), a homogeneous oxide layer, similar to that formed at the potential of peak *b* in 0.1 M NaOH (Fig. 8), was formed after a pulse of only 100 s, corresponding to a charge of about 71 mC cm^{-2}.

DISCUSSION

Roughening of the electrode surface during Ag_2O formation/reduction

By careful investigation of mechanically and chemically polished Ag electrode it was found that the voltammogram of Ag_2O formation/reduction changes with the number of applied cycles. This change was found to depend on the sweep rate. At sweep rates higher than 5 mV s^{-1}, only the peak currents were seen to increase with the number of cycles, while at lower sweep rates, peaks *a* and *b* (see Figs. 1a and b) became more pronounced (peak currents increase) and the potential of peak *b* shifted to more negative values. Depending on the applied sweep rate, a reproducible voltammogram could be obtained after a certain number of cycles. The number of cycles necessary to obtain a reproducible voltammogram decreased with increasing sweep rate. For example, in 0.1 M for $\nu = 100$

mV s^{-1} this number is about 5, for ν = 10 mV s^{-1} this number is about 20, while for ν = 1 mV s^{-1} it is practically impossible to obtain a reproducible voltammogram. At higher concentrations of NaOH solution these numbers are different for different concentrations and the difference between the first and second cycle increases with increasing NaOH concentration.

It was also found from the voltammetric analysis that after forming the oxide, not all of the charge was recovered in the reduction cycle. The difference between the anodic and cathodic charge recorded during the first cycle of Ag_2O formation and reduction in 0.1 M NaOH exponentially increases with decreasing sweep rate. This difference is negligible for a sweep rate of ν = 20 mV s^{-1} (less than 1 %), but is significant for a sweep rate of ν = 2 mV s^{-1} (higher than 8 %). This difference was also found to depend on the NaOH concentration, being more pronounced at higher concentrations of NaOH.

After considering Figs. 1 and 2, it can be concluded that the dependence of the peak currents and peak potentials on the number of cycles applied is different for solutions of different NaOH concentration and that such behavior is a consequence of the increase in the electrode roughness.[20] At lower concentrations this effect is less pronounced. As a consequence, only the first cycle or pulse, applied on a freshly polished Ag electrode should be considered when investigating the mechanism and kinetics of Ag_2O formation/reduction. It should be emphasized here that this is not in accordance with the results of an STM investigation using Ag(111) in a solution of 0.5 mM NaF + 0.1 mM NaOH.[13] This could be due to the fact that the concentration of NaOH in this STM investigation was very low (only 1 mM), or that the potential was not cycled in the region of bulk Ag_2O formation.[13]

Mechanism of Ag_2O formation

Some authors claim that the process of Ag_2O formation is controlled by the diffusion of Ag^+ ions through the compact oxide layer only,[3–6] or through a basal layer of oxide.[2,7,10] Alonso *et al.*[5] claim that this assumption is supported by the fact that the current density remains independent of both stirring and OH^- concentration in the solution, citing the paper of Hepel *et al.*[10] Such a statement seems to be incorrect since Hepel *et al.*[10] showed that the steady-state oxidation current in 1.0 M KOH solution depends linearly on the square root of the rotation speed in a limited potential region only (from 200 mV to 230 mV *vs.* Ag/AgCl), while this dependence deviates from linearity at more positive potential. Hence, the current density of Ag_2O formation does depend on the rotation speed. Unfortunately none of the authors compared results obtained in 0.1 M and 1.0 M hydroxide solution and, accordingly, the assumption that the OH^- concentration does not influence the formation of Ag_2O oxide was reasonable, since the voltammograms recorded in both solutions are very similar. Furthermore, all these results were obtained on a rough electrode surface already cycled in the potential region of Ag_2O formation/reduction, which was changing during the experiment. On the other hand, it was recently shown in an STM investigation of the oxidation of Ag(111)[13] that the nucleation of Ag_2O starts already in the UPD region of Ag_2O formation, *i.e.*, at potentials more negative than the reversible potential of Ag_2O/Ag. Hence, it is most likely that peaks *a'* and *a* correspond to the beginning of 3D nucleation and growth of Ag_2O.

The *j vs. t* transients, recorded after the application of the pulse to a freshly polished Ag electrode surface, shown in Fig. 4, clearly indicate that this process is more complex and the assumption that the process is controlled by the diffusion of Ag^+ ions through the oxide layer is not correct, since it is not possible to obtain a linear *j vs.* $t^{-1/2}$ dependence in the potential region of either peak *a'* or peak *a* (see the inset of Fig. 4). It should be emphasized here that none of the transients shown in Fig. 4 fit the equation for nucleation and 3-D growth under diffusion control given in the paper of Alonso *et al.* (Ref. 5, Eq. (2)). It is obvious that this model can fit experimentally recorded *j vs. t* transients only after special pretreatment of the electrode surface, *i.e.*, by applying two pulses, as given in the paper of these authors (Ref. 5, Fig. 2).

By considering Fig. 1 it can be seen that at higher concentrations of NaOH solution (2.0 M), the cyclic voltammogram of Ag_2O formation becomes more complex in the region of peaks *a'* and *a* (inset of Fig. 1b, both the first and the 10-th cycle) in comparison with the cyclic voltammograms recorded in 0.1 M NaOH (Fig. 1a), indicating the more complex nature of this process and, simultaneously, the importance of the solution concentration for the formation of Ag_2O.

The results presented in Figs. 5–10 clearly show that nucleation of Ag_2O has already started at the potential of peak *a* (Figs. 5 and 6) in all the investigated solution concentrations. It is interesting to note that in 0.1 M NaOH solution two types of oxide appear in the region of peak *a*. Bigger crystals start growing, most probably on active sites (defects) on the Ag surface, as found in Ref. 13, at 290 mV *vs.* Hg/HgO (Fig. 6) covering only 1/3 of the electrode surface, while the rest of the surface is covered by smaller crystals. At the somewhat less positive potential of 285 mV *vs.* Hg/HgO the entire electrode is covered by much smaller, homogeneously distributed crystals of Ag_2O (Fig. 5). In a solution of high NaOH concentration (2.0 M), the appearance of small crystals in the potential region of peak *a* was not detected. It should be emphasized here that the appearance of a compact oxide layer[2–5,9] in the potential region of peak a could only correspond to the Ag_2O oxide formed in 0.1 M NaOH at the more negative potential of 285 mV *vs.* Hg/HgO, while at more positive potentials in the same solution and in the solutions of higher concentrations of hydroxide, a non-homogeneously distributed oxide layer was formed in this potential region, as can be seen in Figs. 5–7 and 10. This finding is in accordance with the STM results presented in Ref. 13, *i.e.*, Ag_2O crystals are formed on active sites (defects) on a freshly polished Ag surface. On the other hand, a homogeneous oxide layer was formed in the potential region of peak *b* in both solutios, Fig. 8. Hence, it is obvious that the formation of oxide follows the expected behavior for 3-D nucleation and growth, *i.e.*, bigger crystals are formed at less positive potentials and nucleation starts at active sited (defects) on the original Ag surface.

Finally, it should be mentioned here that peak *a'* (with a charge of about 150 μC cm^{-2}) is most likely the consequence of the adsorption of OH^- species and the formation of OH_{bulk} or $O_{ads}{}^{\delta-}$ species, as postulated in Ref. 12 by the Eqs. (1), (2) and (3).

CONCLUSIONS

It is shown that considerable roughening of an Ag surface occurs after Ag_2O formation and reduction, the roughening being more pronounced at higher NaOH concentrations. Accordingly, only the first cycle or pulse applied on a freshly polished Ag electrode should be considered in investigations of the mechanism of Ag_2O formation. It is shown that the process is not controlled only by the diffusion of reacting species in the studied range of NaOH concentrations. A nucleation phenomenon was clearly detected in all the investigated solutions. It was found that two anodic peaks present on the voltammograms of Ag_2O formation correspond to two types of oxide films, non-homogeneously and homogeneously distributed ones. The same type (but different grain size) of Ag_2O crystals can be obtained at the potential of the first (*a*) and the second (*b*) anodic peak in all the investigated solutions.

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ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ФОРМИРАЊЕ И КАРАКТЕРИЗАЦИЈА Ag_2O

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Процес електрохемијског формирања Ag_2O на поликристалном сребру из раствора 0,1 M, 0,3 M, 1,0 M и 2,0 M NaOH испитиван је методама цикличне волтаметрије и потенциостатског пулса, док је морфологија насталих оксида испитивана скенирајућом електронском микроскопијом. Показано је да при формирању и редукцији оксида долази до храпављења оригиналне површине електроде и да је храпављење израженије у концентрованијим растворима хидроксида. Због тога су за испитивање нуклеације оксида коришћени само први циклични волтамограм или први пулс примењен на свеже припремљеном поликристалу сребра. Формирање оксида Ag_2O окарактерисано је појавом два струјна врха на цикличним волтамограмима у свим испитиваним растворима. На потенцијалима првог струјног врха формира се нехомогено распоређен оксид (нуклеација се одвија на активним местима – дефектима на површини сребра), док се на потенцијалима другог струјног врха формира хомогено распоређен, густо пакован оксид са кристалима знатно мање величине од оних који карактеришу оксид настао на потенцијалима првог струјног врха. Анализом струјних одговора на пулсеве констатног потенцијала показано је да процес није контролисан дифузијом Ag^+ јона кроз порозни (или компактни) оксидни филм,[2,5,7,10] да је механизам формирања оксидног филма знатно компликованији и да зависи од концентрације хидроксида. Такође је показано да формирање оксида следи основне законитости нуклеације и раста тро-димензионалних кристалних зрна, одн. да се при негативнијим потенцијалима формирају већи кристали (први струјни врх), док се при позитивнијим потенцијалима (други струјни врх) формирају мања кристална зрна Ag_2O.

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