ANODIC BEHAVIOUR OF POLYCRYSTALLINE SILVER ELECTRODES IN ACIDIC AND ALKALINE SOLUTIONS

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The anodic behaviour of polycrystalline silver electrode in sodium hydroxide and perchloric acid media were investigated by cyclic voltammetric and single pulse potentiostatic current-time transient studies. The monolayer formation was noticed in both NaOH and $HClO_4$ media. The monolayer region shows two, peaks in NaOH and only one in $HClO_4$ acid solution. Cyclic voltammetric studies revealed that all the monolayer peaks were found to arise mainly by adsorption-desorption kinetics. Potentiostatic current-time studies also confirm the above observations with an additional information that instantaneous nucleation-growth kinetic processes also contribute to a limited extent.

The anodic film reaction occurring on silver in strongly alkaline solution have been studied extensively owing to their high degree of reversibility and constant promise for energy storage application [1,4]. Droog et al [5] observed for the first time, the existance of a potential dependent coverage of Ag_2O in the range 300-380 mV (nhe). The apparent anomalies in the rates of reduction of O_2 and H_2O_2 at silver electrode in 0.1 M KOH was attributed to the presence of oxidised monolayer at potentials $\backsim$ 700 mV more negative than $Ag\text{-}Ag_2O$ reversible potential [6]. Further, the occurrence of two distinguishable types of monolayer formation in potential ranges (-440 ± 50 mV & 70 ± 50 mV) was noticed by Brustein et al [7,8] during their characterisation of current transients recorded by adopting scratching technique. The nature of kinetic processes involved during the monolayer and multilayer formation of silver sulphide [9] and silver chloride [10] were evaluated by utilizing cyclic voltammetric and single potential step experiments. The present paper reports the study of kinetic processes occuring during anodic film formation on polycrystalline silver electrode in NaOH and $HClO_4$ solutions.

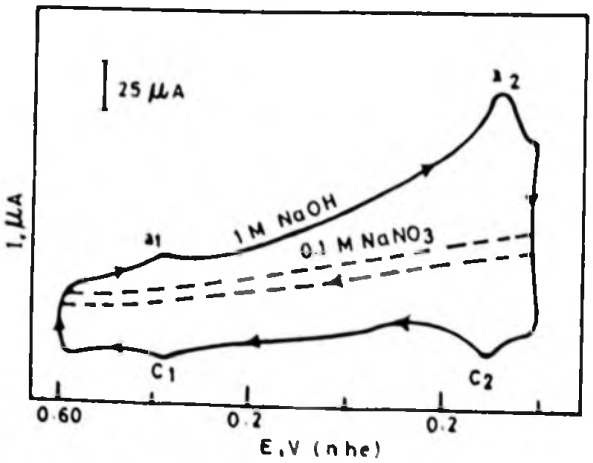
EXPERIMENTAL METHOD

Silver electrodes (Johnson Methey, 99.999% purity) in the form of mechanically polished and degreased discs of 7 mm dia were pressure fitted in teflon holder and set in with araldite. Deaeration was achieved by bubbling pure N_2 through the electrolyte. A luggin probe was positioned $\backsim$ 1 mm from the working electrode surface. Under these conditions, the maximum deviation from the programmed potential due to electrolyte resistance was < 50 mV. The potentials were measured relative to normal calomel electrode (1 N). The potential of the working electrode was controlled by a wenking potentiostat with a response time of $\backsim$ 1 μs fed by a voltage scan generator (Model VSG 72), supplying current to a platinum counter electrodes of area $\backsim$ 6 cm^2. Electrolytes were prepared by using analytical grade reagents and triple distilled water (distilled from all quartz triple distillation unit). A Ricadenki xy/t recorder (with pen speeds better than 120 cm/s) was used for recording I-E or I-t profiles in cyclic voltammetric and potential step experiments. Experiments were conducted at 300°K.

RESULTS AND DISCUSSION

Fig. 1 shows a cyclic voltammogram (cv) obtained with silver electrode in a 1 M sodium hydroxide solution in the potential range -600 to 400 mV vs NHE. Two peaks a_1 and a_2 precade the steep current rise beyond 400 mV (Fig. 2) during anodic scan. Corresponding to peaks a_1 and $a_2$in the anodic branch, peaks $c_1$and c_2 are seen in the cathodic branch. The peaks a_1 and c_1 are more clearly distinguishable when cv is drawn at more sensitive current and potential scales. The approximate locations of the peaks a_1, a_2, c_1 and c_2 are -0.40, 0.280, -0.480 and 0.260 V respectively. All these peaks occur at potentials much below the theoretical $Ag\text{-}Ag_2O$ reversible potential [7,11] for the reaction

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Cyclic voltammograms obtained with polycrystalline silver electrode in the potential scan range -0.60 to 0.40 V vs NHE at a sweep rate of 100 mV/s.

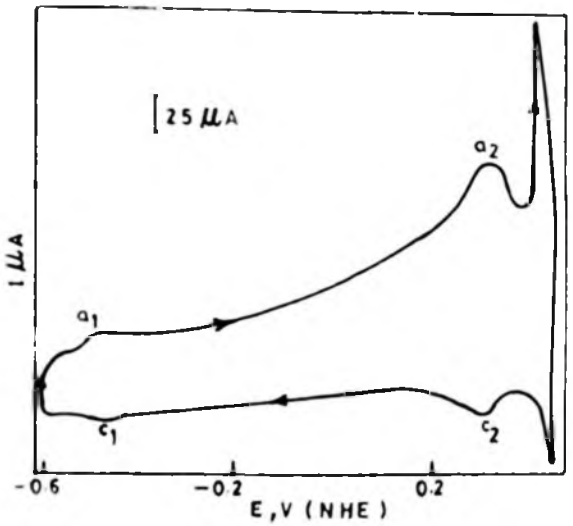


Fig. 2 Cyclic voltammogram obtained with polycrystalline silver electrode in 1 M NaOH in the potential scan range -0.60 to -0.45 V vs NHE at a sweep rate of 100 mV/s.

$$2\,Ag + H_2O \rightleftharpoons Ag_2O + 2\,H^+ + 2\,e$$

(E_o = 347 mV vs NHE at pH 14)

When the potential scan is extended to more positive potentials compared to Fig. 1, there is a sharp current rise of 2-3 orders of magnitude at a potential of ~ 0.39 V (Fig. 2). This potential is clearly associated with that at which thick Ag_2O films are formed on the electrode and this should be represented by E_o of Ag/Ag_2O electrode in the chosen medium as described elsewhere [7]. Thus, the charge density passed during the anodic sweep upto 300 mV is less than ~ 300 μc/cm^2 confirming that anodic reactions are occurring in addition to doubls layer charging below the Ag/Ag_2O reversible potential.

The size and shape of a_1, a_2, c_1 and c_2 were found to be stable and unaffected by repeated cycling. Different stirring rates also did not alter the above response characteristics. These observations clearly rule out the possibility of the peaks a_1, a_2, c_1, c_2 arising due to the impurities present in solution and their mass transport. On the other hand, the plot of peak current and sweep rate gave a linear relationship for peaks a_1 (curves A Fig. 3) and a_2 (not shown in Fig) and not with (sweep rate)$^{1/2}$. This fact coupled with occurrence of these peaks below the Ag/Ag_2O reversible potential confirms that the peaks a_1 and a_2 arise due to monolayer formation of anodic film in sodium hydroxide solutions. Further, the location of these peaks at -0.40 and 0.28 V confirms the observations of Brustein et al [7,8] who attributed these to the formation of AgOH and Ag_2O according to

$$Ag^+ + OH^- \rightleftharpoons AgOH\ (ads.) + e$$

$$Ag + AgOH\ (ads.) \rightleftharpoons Ag_2O + H^+ + e$$

Cyclic voltammetric studies were carried out at various sweep rates to understand the nature of anodic film formation in monolayer region resulting in peaks a_1 and a_2. Fig. 4 shows the changes in peak potential (E_p) and peak width at half height ($\Delta E_{1/2}$) with change in sweep rate. Thus, for peak a_2, E_p remains unaltered on change of sweep rate from 11 to 180 mV/s indicating that the anodic film formation is reversible and becomes irreversible on further increase of sweep rate [12]. The $\Delta E_{1/2}$ value besides being 90 mV remains unaltered upto sweep rates $\leq$ 180 mV/s expected for a reversible adsorption of monolayer species [13]. Similarly, the anodic film formation reactions resulting in peak a_1 were found to be reversible in the sweep rate range 11-180 mV/s as E_p remains constant. The charge transfer coefficients (α_a) were calculated by equating $\Delta E_{1/2}$ at higher sweep rates to $\frac{62.5}{\alpha_a n}$, to be 0.4 and 0.5 for peaks a_1 and a_2 respectively.

Single potential step experiments were carried out as they are expected to give considerable information on the kinetics and mechanism of electrochemical phase formation. Typical current-time transients obtained with a poly-

crystalline silver surface for a series of growth potentials scanning before, through and beyond the region of monlayer peak a_1 (Fig. 5) and a_2 (Fig. 6) of cyclic voltammogram. These potentiostatic current-time transients were analysed by the theoretical model suggested by Bosco and Rangarajan [14] who take into account the coupled nucleation-growth and adsorption-desorption processes during monolayer formation. Thus, by utilizing parametric plots, it is found that the monolayer formation of AgOH and Ag_2O occur mainly by adsorption -desorption coupled with a small contribution from nucleation-growth controlled processes. Further, the plot of I (e^T) vs T (e^T) is linear with an intercept indicating that nucleation-growth processes are instantaneous in nature (not progressive as I (e^T) vs T^2 (e^T) is non-linear). The symbol I and T are non-dimensional quantities of current (i) and time (t) respectively and is given by

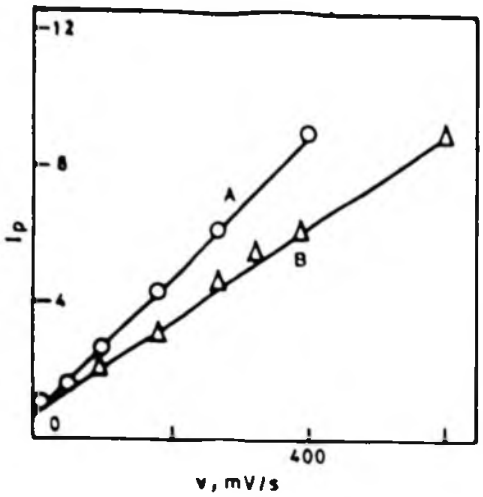


Fig. 3 Plot of peak current of monolayer peak of a_1 in NaOH (curve A) and that in $HClO_4$ (curve B) with sweep rate.

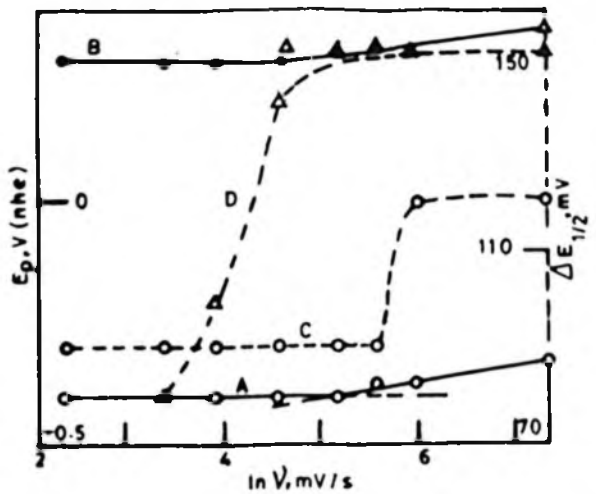


Fig. 4 Plot of E_p (curves A and B) and $\Delta E_{1/2}$ (curves C and D) Vs ln v. Curves A and C are of peak a_1 and curves B and D are of peak a_2 .

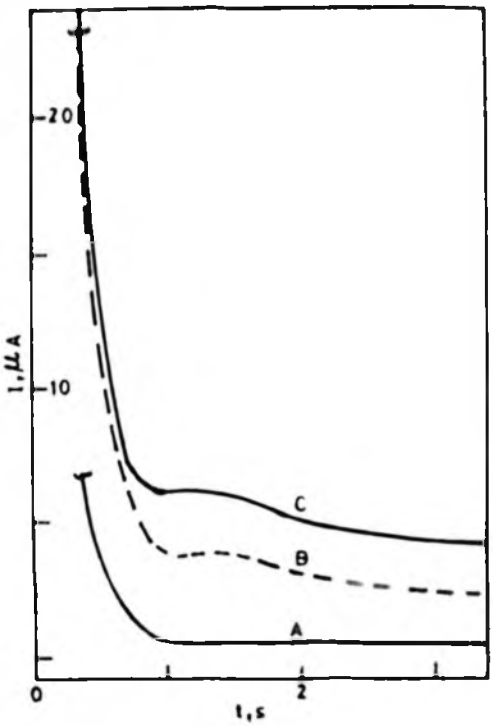


Fig. 5 Potentiostatic current-time transients obtained by holding the potential at -0.515, -0.415 and -0.315 V vs NHE (curves A, B and D respectively).

$$I = i/q_m \,.\; T = \mu t$$

where

q_m = monolayer charge

$\mu = \vec{k} + \vec{k'}$

$\vec{k}$ = adsorption rate constant

k' = desorption rate constant

The instantaneous nucleation-growth constants (D_1) (non-dimensional) were calculated to be 0.08 and 0.34 for peaks a_1 and a_2 respectively. The adsorption constants (non-dimensional) were calculated from the intercepts of I (e^T) vs T (e^T) as 6 and 2.6 respectively.

In contrast to studies in 1 M NaOH solutions, the cyclic voltammogram obtained in 1 M $HClO_4$ solutions shows only single anodic peak at 0.265 V (nhe) (Fig. 7). When anodic limit of triangular scan is extended to potentials beyond 450 mV (nhe), the anodic current rises rapidly. This potential corresponds to the onset of apreciable steady state anodic dissolution of silver from the entire electrode surface [8]. The peak occurring at 0.265 V can be thought of as due to the monolayer formation of AgOH as discussed elsewhere [8]. This assumption is further confirmed by the linear plot obtained for i_p vs $\sqrt{\nu}$ (curve B Fig. 3) and following data.

On change of sweep rate, the peak width at half-height ($\Delta E_{1/2}$) change from 90-120 mV on increase of sweep rate from 100 to 1100 mV/s indicating that monolayer formation occur by adsorption process. Fig. 8 shows the plot of peak potential (E_p) and $\Delta E_{1/2}$ as a function of sweep rate. The E_p and $\Delta E_{1/2}$(90 mV) values remain constant on change of sweep rate from 100-180 mV/s indicating that the monolayer formation process is reversible. However, at higher sweep rates the monolayer formation becomes irreversible[12,13]. The anodic charge transfer coefficient was calculated to be 0.5.

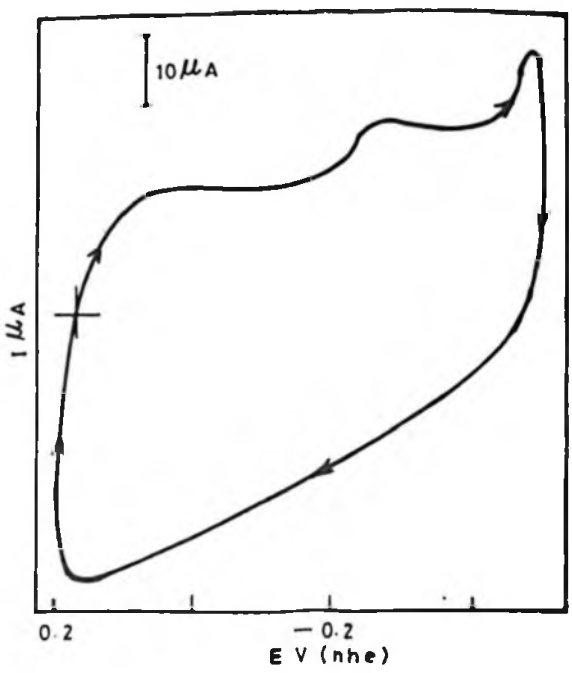


Fig. 7 Cyclic voltammogram obtained with polycrystalline silver electrode in 1 M $HClO_4$ in the potential scan range -0.2 to 0.5 V vs NHE.

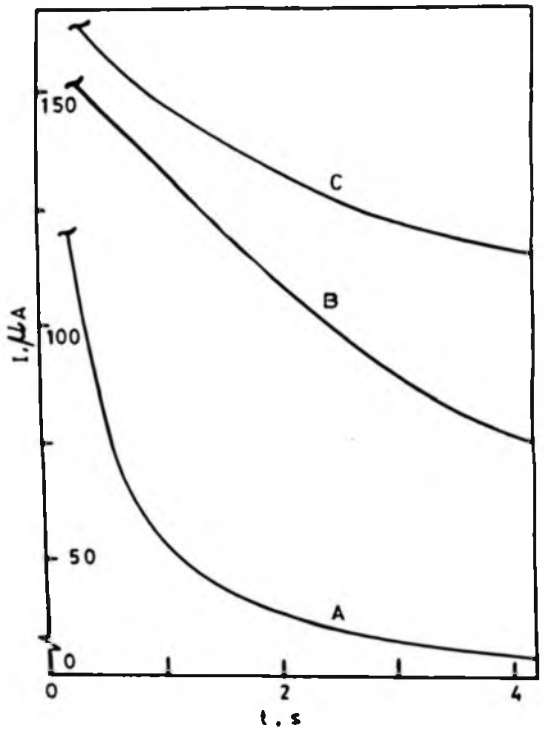


Fig. 6 Potentiostati ccurrent-time transients obtained by holding the potential at 0.185, 0.235 and 0.285 V vs NHE (curves A, B and C respectively).

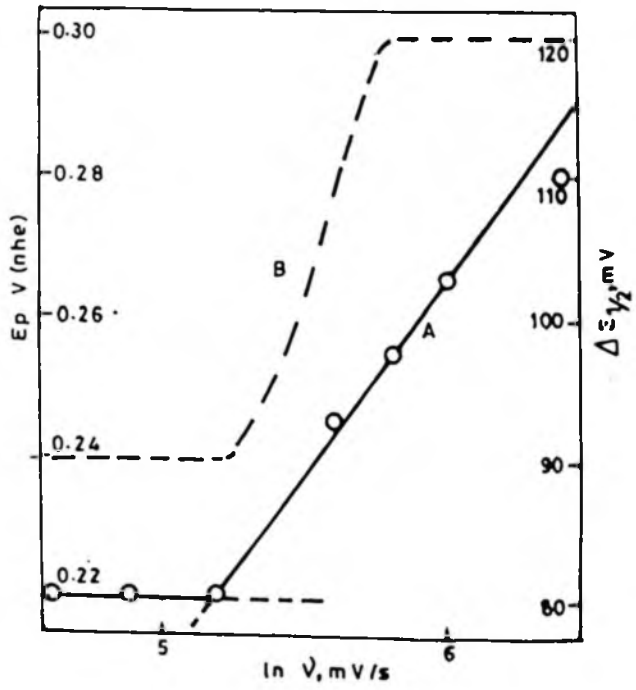


Fig. 8 Plot of E_p and $\Delta E_{1/2}$ vs ln ν (curve A and B respectively).

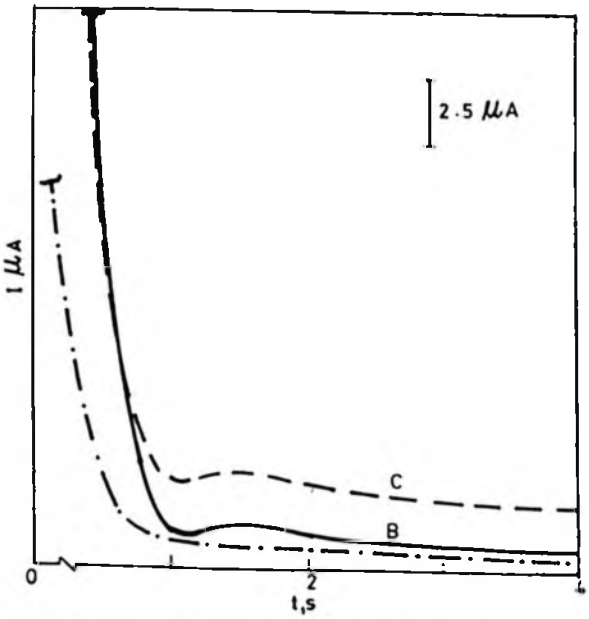


Fig. 9 Potentiostatic current-time transient obtained by holding the potential at 0.085, 0.285 and 0.385 V vs NHE.

Fig.9 shows a few examples of i-t transients obtained by stepping the potential from -0.2 V to +0.085 (curve A), 0.285 (curve B) and 0.385 V (curve C) and then potentiostating the polycrystalline silver electrode in $HClO_4$ 1 M solution. Curves B and C show a distinct feature, viz. initial rapid fall and a maximum and minimum, qualitatively suggesting the presence of adsorption and nucleation-growth processes respectively. These i-t transients were analysed as described earlier to those obtained in 1 M NaOH solution. The plot of I (e^T) vs T (e^T) gives a linear relationship with an intercept (not I (e^T) vs T^2 (e^T) indicating that nucleation-growth processes are instantaneous in nature and are in combination with adsorption-desorption processes. The non-dimensional adsorption-desorption (G) and instantaneous nucleation-growth rate constant (D_1) were calculated to be 0.24 and 0.056 from the intercept and slope respectively.

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