

Cyclic voltammetry on Ag(111) and Ag(100) faces in sodium hydroxide solutions

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Received 14 April 1999; received in revised form 24 May 1999; accepted 26 May 1999

Abstract

The electrochemical behavior of silver (100) and (111) single crystal surfaces was examined by cyclic voltammetry in aqueous NaOH solution. In the 'double layer' region (between -1.2 and 0.1 V (SCE)) adsorption of OH^- ions followed by phase transformation into an Ag–OH monolayer was found to take place. The difference in peak potentials recorded in 0.1 and 0.01 mol dm^{-3} NaOH solutions of about 60 mV indicates that one electron is exchanged in the overall electrochemical reaction, implying a complete charge transfer between OH^- ions and the silver surface. The adsorption process has been modeled to a Frumkin adsorption isotherm. Further oxidation of silver into Ag_2O takes place at more positive potentials. The formation of bulk Ag_2O results in considerable change to the original single crystal surface. This is likely to be due to roughening of the silver surface as a consequence of the formation and reduction of the oxide. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Silver single crystals; Adsorption; Charge transfer; Phase transformation; Frumkin isotherm; Silver oxide

1. Introduction

The electrochemical behavior of silver in hydroxide-containing solutions has primarily been investigated on polycrystalline Ag electrodes in the potential region of silver oxidation [1–10]. The focus has been to gain a better understanding of the processes of Ag_2O and AgO formation, which are important for the application of silver in silver–zinc rechargeable batteries. In these investigations the negative potential limit was mainly between -0.2 and -0.4 V (versus SCE), except in the potentiostatic pulse investigations of Ag_2O [9] and AgO formation [10], where the electrode was precathodized at -1.3 V (versus SCE) before the application of pulses in the oxide formation region. According to Teijelo et al. [11], who presented a detailed review of the literature prior to 1988, most of the authors agree that the first anodic peak (or shoulder) appearing between 0.1 and 0.2 V (SCE) corresponds to the formation of an Ag–OH monolayer, while the next two peaks (between 0.2 and 0.4 V) are associated with the formation of a compact and a porous Ag_2O layer, respectively. At more positive potentials of about 0.5 V (SCE) a sharp anodic peak corresponds to the formation of an AgO layer on top of Ag_2O .

Recently, two papers were published [12,13] in which linear sweep voltammograms of an Ag electrode were recorded in the 'double layer' potential region between -1.4 and 0.0 V (SCE). In these investigations either $\text{NaCl} + \text{NaOH}$ or $\text{NaClO}_4 + \text{NaOH}$ solutions were used. Although the cyclic voltammograms showed no peaks for OH^- adsorption/desorption, the authors concluded from XPS measurements that OH^- ions are specifically adsorbed on Ag in the investigated alkaline solutions even at negative potentials [12,13]. The presence of adsorbed OH^- species on a polycrystalline [14] and Ag(111) surface [15] in pure NaOH solution at negative potentials (down to -0.8 V (SCE)) has also been confirmed by Raman spectroscopy investigations.

Stevenson et al. [16] investigated oxidative adsorption of 14 anions on the Ag(111) surface which had been prepared by thermal deposition of Ag onto mica, followed by extensive thermal annealing in vacuum in order to produce an atomically smooth (111) surface. Broad voltammetric peaks associated with OH^- adsorption were observed for Ag(111) in 0.1 mol dm^{-3} NaOH.

Most recently Marinkovic et al. [17] investigated ionic adsorption on the Ag(111) electrode surface in sulfate-containing solutions of different pH. It was concluded that the adsorption of sulfate in alkaline solutions is inhibited by more

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strongly adsorbed OH^- species. A cyclic voltammogram recorded on the Ag(111) in a pure NaOH solution (0.01 mol dm^{-3}) revealed a characteristic ‘butterfly’-shaped peak which was attributed to the early stages of OH^- adsorption.

This paper describes our investigation of the adsorption and desorption of OH^- ions on the (111) and (100) faces of silver in electrolytes containing only sodium hydroxide. The single crystal electrodes were examined in the ‘double layer’ potential region, i.e. between -1.2 and 0.0 V (SCE). Also, the formation of Ag-OH and Ag_2O was investigated and compared for both single crystals.

2. Experimental

All experiments were carried out in a two-compartment electrochemical cell at $25 \pm 1^\circ\text{C}$ in an atmosphere of purified nitrogen. A single crystal electrode was sealed in epoxy resin (resin EPON 828 + hardener TETA), which is resistant to alkaline solutions, in such a way that only the (111) or (100) disc surface was exposed to the solution. The surface area of the electrode exposed to electrolyte was 0.316 cm^2 . The single crystal surfaces were mechanically polished on fine emery papers (up to 4000 grit) with subsequent polishing on polishing cloths impregnated with alumina ($1, 0.3$ and $0.05 \mu\text{m}$). After mechanical polishing, the single crystal surfaces were chemically polished in a solution containing sodium cyanide and hydrogen peroxide. This procedure of single crystal surface preparation has been given in detail in previous papers [18–20]. The counter electrode was a platinum sheet and was placed in the same solution as the working electrode. The reference electrode was a saturated calomel electrode (SCE) which was placed in a separate compartment and connected to the working compartment by means of a Luggin capillary. Potential values are referenced to SCE. All solutions were made from 99% NaOH pellets (Mallinckrodt¹) and milli-Q water. The cyclic voltammetry (CV) was performed using a potentiostat (PAR M-173), universal programmer (PAR M-175) and an X-Y recorder (Houston Instruments 2000R).

3. Results and discussion

Cyclic voltammograms recorded on the (111) face of silver in solutions of 0.1 and 0.01 mol dm^{-3} NaOH at a sweep rate of 50 mV s^{-1} are shown in Fig. 1. Both voltammograms are characterized by two pairs of asymmetric anodic and cathodic peaks appearing between -0.7 and -0.5 V , and between -0.1 and 0.1 V . The first anodic peak, at more negative potentials, can be ascribed to the process of OH^- ion adsorption. As can be seen in Fig. 1 this peak is actually comprised of a sharp peak with a trailing broad shoulder. This

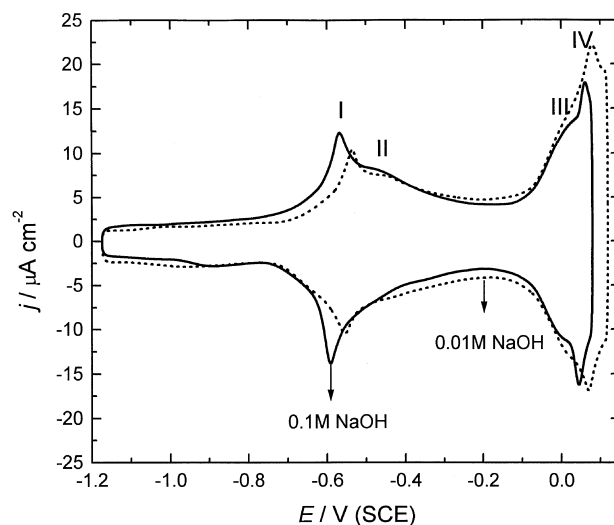


Fig. 1. Cyclic voltammograms recorded on the Ag(111) in solutions of different concentrations of NaOH at a sweep rate of 50 mV s^{-1} .

certainly indicates that OH^- ion adsorption is not a simple process and the appearance of the sharp peak further suggests that a phase transformation occurs at this stage of the adsorption [21,22]. The difference in peak potentials recorded in 0.1 and 0.01 mol dm^{-3} NaOH solutions of about 60 mV indicates that one electron is exchanged in the overall electrochemical reaction, implying that a complete charge transfer between OH^- ions and the silver surface occurs.

The second pair of anodic peaks, again characterized by the superposition of a broad and smaller sharp peak, indicates that a second phase transformation is associated with the adsorbed structure. It seems likely that this final transformation is that of the adsorbed structure into a monolayer of Ag-OH , as has been proposed by other authors [17]. Although the exact structure of the Ag-OH monolayer on Ag(111) has yet to be reported in the literature, several two-dimensional structures have been observed for halides adsorbed on Ag(111) [22–24]. These halides tend to form incommensurate phases which electrocompress as the potential is increased to more positive values. Surface coverages up to 0.442 , corresponding to a rotated-hexagonal structure, have been reported [23]. The charge associated with an Ag-OH monolayer, assuming complete charge transfer and $\theta = 0.442$, amounts to $98.5 \mu\text{C cm}^{-2}$.

By integrating the anodic portion of the voltammogram shown in Fig. 1 (0.1 mol dm^{-3} NaOH) one obtains a charge of about $135 \mu\text{C cm}^{-2}$. Assuming that the $1.8 \mu\text{A cm}^{-2}$ current density observed in the potential range of -1.15 to -1.0 V of Fig. 1 is associated with double layer charging, a correction of $45 \mu\text{C cm}^{-2}$ should be applied, which results in a net anodic charge of approximately $90 \mu\text{C cm}^{-2}$ for the adsorption of OH^- . This estimate of the charge is consistent with that one might expect, based on coverages reported for halide adsorption, and suggests that the four peaks associated with the transient represent no more than a monolayer coverage of OH^- . Consequently, the formation of an Ag-OH

¹ Certain tradenames are mentioned for experimental information only; in no case does it imply a recommendation or endorsement by NIST.

monolayer, as a first step of silver oxidation into Ag_2O and AgO oxides, takes place through two steps, i.e. adsorption of OH^- ions and phase transformation into a monolayer.

If the double layer charging current of $1.8 \mu\text{A cm}^{-2}$ is subtracted from the anodic portion of the Fig. 1 voltammetry, one obtains the voltammogram represented by the circle data points in Fig. 2(a). The best fit to the experimental results, represented by a solid line in Fig. 2(a), can be obtained with four peaks, presented in the same figure (b). Each of these peaks should represent the formation of some adsorbed structure and, accordingly, can be treated by a corresponding adsorption isotherm. All four peaks were transformed into θ – E relationships where θ was obtained from the integrated current of a particular peak, normalized to the total charge of that peak. It was found that the Frumkin isotherm, developed for a simple adsorption reaction with a linear dependence of the adsorption free energy on coverage, and assuming complete charge transfer between the adsorbed species and the substrate, can be used to fit the θ – E data [25]. The Frumkin isotherm is given by the following equation:

$$\left(\frac{\theta}{1-\theta}\right) \exp(f\theta) = K_{\text{ads}, \theta \rightarrow 0}^{\circ} c_o \exp\left(\frac{FE}{RT}\right) \quad (1)$$

where θ is the fractional surface coverage, f is a dimensionless interaction factor (r/RT) describing the rate of change of adsorption free energy (r) with coverage, $K_{\text{ads}, \theta \rightarrow 0}^{\circ}$ is the equilibrium constant for adsorption at low coverage, c_o is the bulk concentration of the species being adsorbed, E is the electrode potential, and the remaining terms have their usual meaning.

The θ – E data obtained from Fig. 2 were fitted to Eq. (1) using the interaction factor (f) and $K_{\text{ads}, \theta \rightarrow 0}^{\circ}$ as fitting parameters. The results are shown in Fig. 3. As can be seen, much better fitting was obtained for sharp peaks (peaks I and IV). The interaction parameters for all four isotherms (peaks) are different. The two sharp peaks at potentials of -0.567 V (peak I) and 0.063 V (peak IV) yield negative interaction factors of -0.66 ± 0.19 and -2.40 ± 0.04 , respectively, indicating lateral attraction interactions between the adsorbed species. The two broad peaks at -0.477 V (peak II) and 0.042 V (peak III) yield positive interaction factors indicating that surface inhomogeneity or lateral repulsion interactions between the adsorbed species characterize the adsorption process. Such a behavior can be expected, particularly for the second set of peaks where the adsorbed structure transforms into a monolayer of Ag-OH . Concerning peaks I and II (as well as III and IV) it seems that Gibbs energies of adsorption are almost identical, since the peak potentials are very close. However, the values of Gibbs energies of adsorption for peaks I and II obtained by the fitting procedure using the Frumkin adsorption isotherm are very different, being $\Delta G_{\text{ads}}^{\circ}(\text{I}) = -52.3 \text{ kJ mol}^{-1}$ and $\Delta G_{\text{ads}}^{\circ}(\text{II}) = -63.0 \text{ kJ mol}^{-1}$, since values of $\Delta G_{\text{ads}}^{\circ}$ are obtained for the Frumkin adsorption isotherm from the equilibrium constant ($K_{\text{ads}, \theta \rightarrow 0}^{\circ}$) for adsorption at low coverage. This can clearly be seen by considering deconvoluted peaks. It is obvious that

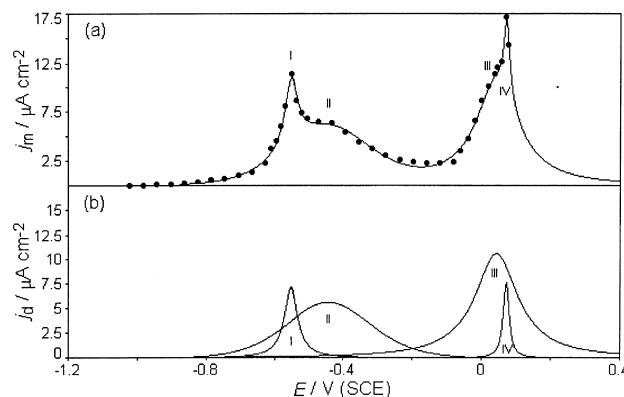


Fig. 2. Deconvolution of experimentally recorded anodic part of the voltammogram obtained in the solution of $0.1 \text{ mol dm}^{-3} \text{ NaOH}$ (presented in Fig. 1). (a) Experimental points are represented by circles, while the line represents the best fit. (b) Peaks obtained by deconvolution.

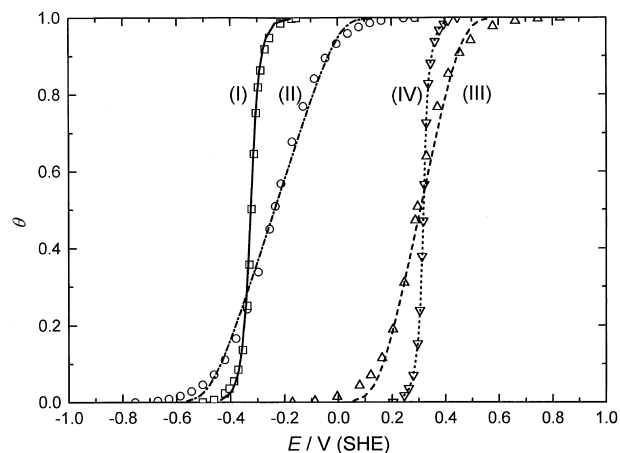


Fig. 3. θ – E data obtained by the analysis of peaks I, II, III and IV presented in Fig. 2(b). Corresponding f values, obtained by fitting θ – E data with the Frumkin adsorption isotherm (Eq. (1)) are: $f(\text{I}) = -0.66 \pm 0.19$; $f(\text{II}) = 17.55 \pm 0.83$; $f(\text{III}) = 13.69 \pm 1.30$ and $f(\text{IV}) = -2.40 \pm 0.04$.

the beginning of peak II appears at more negative potentials than the beginning of peak I, indicating a more negative value of $\Delta G_{\text{ads}}^{\circ}$.

There are subtle differences between our results and those reported by Stevenson et al. [16] and by Marinkovic et al. [17], particularly in the region of the first adsorption/desorption peak (between -0.7 and -0.5 V). According to Marinkovic et al. [17] the shoulder is shifted to more negative potentials and actually precedes the sharp peak. In contrast, the voltammogram presented by Stevenson et al. [16] shows two broad peaks in this potential region. These subtle differences could be due to the following: (i) different procedure of single crystal preparation (Stevenson et al. made $\text{Ag}(111)$ on mica by thermal deposition/annealing, while we used a commercial electrode — Metal Crystals and Oxides, Cambridge Ltd.); (ii) different procedure of single crystal chemical polishing (Marinkovic et al. used chromate, while we used cyanide solution); (iii) different technique of electrode immersion into solution (Marinkovic et al. used a ‘meniscus’ technique, while our electrode was sealed in

epoxy resin); (iv) purity of the system (Marinkovic et al. used milli-Q + UV water and 50% w/w solution of NaOH (Fisher), while we made solutions from milli-Q water and 99% NaOH pellets (Mallinkrodt)).

It can be seen in Fig. 4 that after the second set of adsorption peaks at 0.06 V, a much sharper set of anodic/cathodic peaks appears on the voltammogram. The charge associated with the oxidation peak amounts to about $180 \mu\text{C cm}^{-2}$, corresponding to the oxidation of less than one monolayer of silver. It is interesting to note that cycling the electrode in this potential region (up to 0.2 V (SCE)) does not produce any change in the shape of the voltammogram in the 'double layer' region, indicating reversibility of this process.

Further oxidation of silver into Ag_2O takes place at more positive potentials, between 0.2 and 0.5 V. The formation of Ag_2O in 0.1 mol dm^{-3} NaOH onto the (111) face of silver is characterized by two sharp peaks and one broad peak (see Fig. 5), which is different from that observed on polycrystalline silver electrodes [11], indicating that the substrate orientation influences the process of silver oxide formation. For reasons mentioned below, only the first voltammetric sweeps are shown in Fig. 5.

The irreversibility of bulk Ag_2O formation and reduction, and the influence of this process on the original single crystal surface are demonstrated by the voltammogram shown in Fig. 6. The voltammogram recorded before entering the oxide formation region (curve 1) is different from that obtained after the Ag_2O formation and reduction (curve 2). A much larger double layer current, and smaller anodic and cathodic peaks recorded after $\text{Ag}(111)$ oxidation (up to 0.5 V) indi-

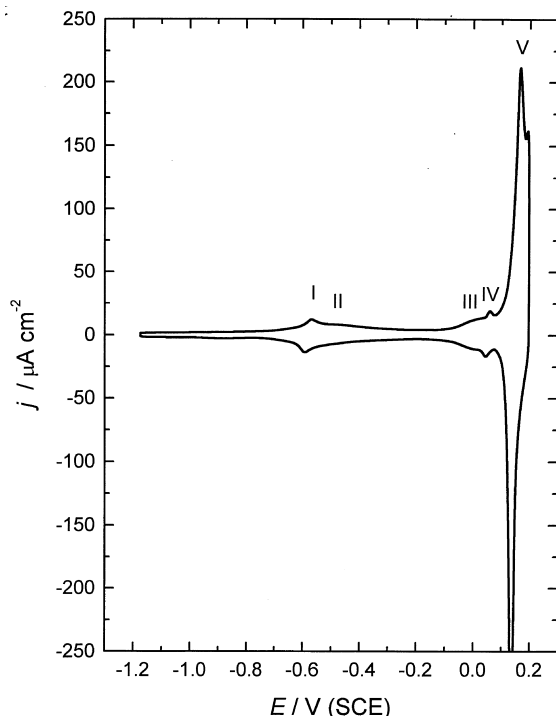


Fig. 4. Cyclic voltammogram recorded on the $\text{Ag}(111)$ in the solution of 0.1 mol dm^{-3} NaOH at a sweep rate of 50 mV s^{-1} .

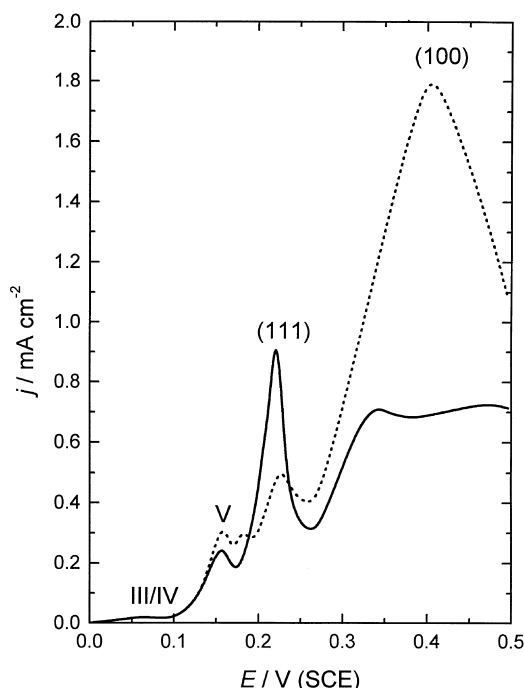


Fig. 5. First cycle of Ag_2O oxide formation recorded on the $\text{Ag}(111)$ and $\text{Ag}(100)$ in a solution of 0.1 mol dm^{-3} NaOH at a sweep rate of 50 mV s^{-1} .

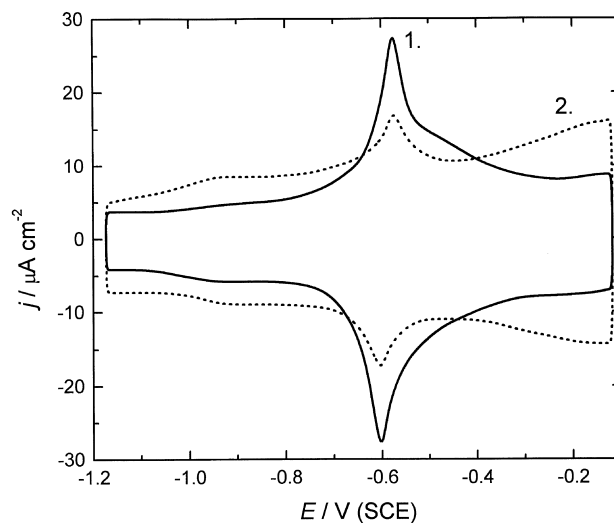


Fig. 6. Cyclic voltammograms recorded on the $\text{Ag}(111)$ in the solution of 0.1 mol dm^{-3} NaOH at a sweep rate of 100 mV s^{-1} : (1) before cycling in the potential region from 0.2 to 0.5 V; (2) after cycling in the potential region from 0.2 to 0.5 V.

cate considerable change of the original surface. This is likely to be due to significant roughening of the silver surface resulting from the formation and reduction of the oxide. The charge associated with the formation of Ag_2O was about 4 mC cm^{-2} , which corresponds to the dissolution of about 18 monolayers of silver under these experimental conditions ($v = 50 \text{ mV s}^{-1}$). Hence, it is important to note that only the first sweep, or pulse into the region where the porous layer of Ag_2O forms can be considered as relevant for the investigation of silver

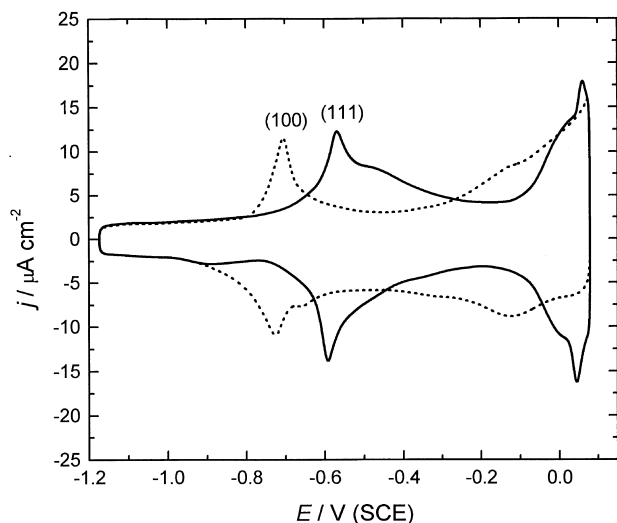


Fig. 7. Cyclic voltammograms recorded on the Ag(111) and Ag(100) in the solution of 0.1 mol dm^{-3} NaOH at a sweep rate of 50 mV s^{-1} .

oxidation processes onto single crystal surfaces. This is consistent with the findings of other authors for the polycrystalline surface [5,14].

The voltammograms recorded in 0.1 mol dm^{-3} NaOH solution at a sweep rate of 50 mV s^{-1} on the (111) and (100) faces of silver are compared in Fig. 7. The adsorption of OH^- ions on the (100) face of silver takes place at more negative potentials, as one would expect since the (100) face is more suitable for anion adsorption. It can be seen that the first set of adsorption peaks is essentially the same on both single crystals, although the broad shoulder appears to be somewhat suppressed on the (100) surface. The voltammetric response of the (100) face is also different from that of the (111) near 0.0 V where one would expect completion of the adsorbed structure into an Ag–OH monolayer. The sharp peak which we had attributed to a phase transformation on the (111) surface is absent; however, the total charge under the anodic part of the voltammogram (after subtraction of the charge for the double layer) is also very close to that required for the formation of an Ag–OH monolayer on the Ag(100). It is interesting to note that the broad set of peaks which appears at about -0.15 V on the (100) face becomes more pronounced at lower sweep rates ($\nu < 20 \text{ mV s}^{-1}$), and completely disappears at higher sweep rates ($\nu > 100 \text{ mV s}^{-1}$).

Finally, it should be emphasized that these are only preliminary results and that more detailed investigations of OH^- ion adsorption and corresponding monolayer formation are needed for a better understanding of the mechanism and kinetics of these processes.

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