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Passivation of Silver and Current Oscillations During Anodic Dissolution of Silver in $H_2SO_4 + Ag^+$ Solutions

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We report the first observation of silver electrode passivation during anodic dissolution in sulphuric acid electrolytes. The passivation is of a salt type. Preliminary observations of nonlinear effects in this system: current oscillations and multiperiodic cyclic voltammograms are also presented. Microscopic inspection revealed, that during dissolution of the electrode, silver powder accumulates at the surface. Observed oscillations have a strong transient character, presumably resulting from the modification of diffusion conditions by powder accumulation.

Key words*:* silver passivation, current oscillations, anodic dissolutions, salt passivation, multiperiodic voltammograms

Passivation and current oscillations during anodic dissolution of Cu in sulphuric acid have been known for a long time [1–3]. The passivation is of a salt type and most probably consists in formation of $CuSO_4$ layer at the electrode. The oscillations occur as the electrode switches between passive and active states. Recently, in a series of works, the oscillations occurring in the system under potentiostatic conditions have been studied in detail [4–6]. Periodic (up to period eight) and chaotic oscillations were observed and analysed. It was found that during copper dissolution, Cu powder precipitation takes place. This changes diffusion conditions at the electrode surface and causes long lasting transients, which makes the oscillations change from one mode to another and complicates quantitative analysis of the results. The most probable mechanism of powder formation is by Cu^+ dismutation: $2Cu^+ \rightarrow Cu^{2+} + Cu^\circ$. Working on a rotating disc electrode reduces powder accumulation by removing both Cu^+ and the powder from the vicinity of the electrode, however, it does not completely solve the problem. Even at a rotation rate of 1000 rpm at some potential regions transients occur and powder accumulation can be observed at the electrode surface [6].

In the search for a simpler system, where powder formation would not interfere with the temporal structures, we have chosen the system of silver in sulphuric acid solutions. The only soluble silver species in this system not far from Ag/Ag^+ equilibrium are Ag^+ ions, and, therefore, the mechanism of powder formation by disproportionation should not come into play.

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While electrochemical behaviour of silver in a number of aqueous electrolytes including halides, NO_3^-, ClO_4^-, CN^-, NH_3, $S_2O_3^{2-}$, as well as in nonaqueous solutions and fused salts has been studied in detail [7] and the oscillations during anodic dissolution of silver have been reported in Cl^-, CN^-, ClO_4^- solutions [3], very little is known about this process in sulphuric acid. However, the solubility of silver sulphate being moderate (~26 mM in a water at ambient temperature), one could expect that as in the case of Cu, salt layer will be formed during Ag dissolution and the salt type passivation will take place. Negative differential resistance, appearing on a falling part of the current-potential curve in such a system, is a common cause of oscillatory behaviour [8].

EXPERIMENTAL

Measurements were carried out at 22 ± 1°C in a two-compartment electrochemical cell. The working electrode was a cross section of a 5 mm diameter rod made of 99.999% silver. The lateral surface of the rod was isolated with PTFE thermoshrinkable tubing and the working surface was positioned horizontally, face down. A large (10 cm^2) initially Pt foil that served as a counterelectrode soon became silver plated. An Ag/Ag^+ reference electrode placed in the working solution, but in a separate compartment, was connected to the main compartment by a capillary. All potentials in the present work are referred to this electrode.

Voltammetric measurements were performed using an EG-20 linear sweep generator and an EP-20 potentiostat from ELPAN. The same setup was used for oscillations measurements, with the difference that a variable resistor was connected in series with the working electrode. The data were recorded with a PC computer using an LC-011 data acquisition board from Ambex.

The ohmic drop between the tip of the Lugin capillary and the working electrode was estimated from impedance data at high frequency. This solution resistance was between 13 and 14 Ω and has neither been corrected for in the plots, nor added to resistor values in figures descriptions. The impedance measurements were carried out using Autolab FRA from ECO CHIMIE.

X-ray electron microprobe CAMECA SEMPROBE Su30 equipped with a WDS/EDS (wavelength/energy dispersive spectrometry) was employed in order to analyse local chemical composition of electrode surface. The microprobe had lateral resolution of 1 μm and provided composition information from the depth of 1 μm.

All the solutions were prepared from analytical grade H_2SO_4 (Merck), Ag_2SO_4 (p.a., Roth) and milipore water (Milipore Elix water 15 MΩcm). The concentration of H_2SO_4 was between 0.1 M and 0.05 M, and this of Ag_2SO_4 between 5 mM and 26 mM.

RESULTS AND DISCUSSION

Passivation of silver. Cyclic voltammograms (CV-s) obtained at 0.02 mVs^{-1} on the silver electrode in 0.1 M sulphuric acid for different concentration of Ag_2SO_4 are shown in Fig. 1. Such a low scan rate was employed in order to obtain CV curves possibly close to stationary (time independent) once. In order to prevent the electrode from being silver plated during a reverse scan, all the scans started about 10 mV anodic with respect to equilibrium potential in a given solution. As the first cycle always differed considerably from the asymptotic one, all presented curves are the second scans.

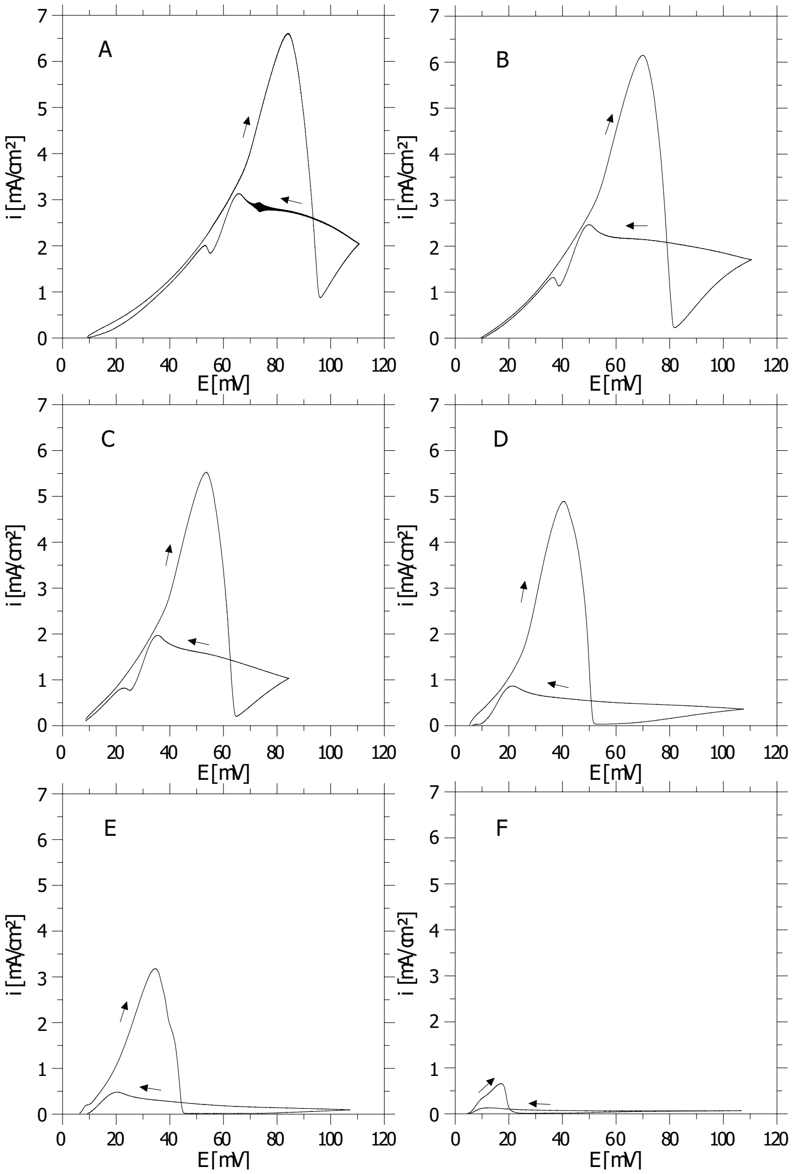

Figure 1. Voltammetric curves for silver electrode in 0.1 M H_2SO_4 at different concentrations of Ag_2SO_4: A – 5 mM; B – 10 mM; C – 15 mM; D – 20 mM; E – 23 mM; F – 25 mM. Scan rate 0.02 mV/s.

The observed CV-s are complex. On the forward scan, after initial increase, the silver dissolution current goes through maximum and rapidly decreases, due to the passivation of the electrode, and then slowly increases. The increase continues during a reverse scan; however, current values are considerably lower than those in the maximum. Near the point when the final part of the reverse scan merges with the forward trace, a small wavelet is observed. Additionally, an inflection point is well visible on the ascending part of each curve at about 45 mV, suggesting an unknown change in the mechanism of silver dissolution.

Passivation of the electrode takes place for all concentrations of Ag_2SO_4. Both the peak current and the potential at which it is observed on the forward scan decrease with increasing Ag_2SO_4 concentration. CV for the saturated Ag_2SO_4 solution is not presented here, because current densities are below 1 μAcm^{-2}. In this solution the electrode is in the passive state in the whole potential range. This result and the results presented in Fig. 1 clearly show that the passivation observed in the system is of the salt type. During the dissolution, the Ag^+ concentration at the electrode surface increases, and, when the sum of the concentration of dissolved Ag^+ and that initially present in the solution exceeds critical value, a salt, presumably Ag_2SO_4, precipitates, blocking further reaction.

Observed current – potential curves are N-shaped. The negative differential resistance on the falling part of the curve is the direct cause of instability and gives birth to oscillations. The N-shaped curve is characteristic of a system, where current oscillations in the potentiostatic conditions (with an additional resistor connected in series with the working electrode) are to be expected [8].

In principle, experiments with a series resistor are not carried out in true potentiostatic conditions. The potential difference between working and reference electrodes (E) differs from that imposed with a potentiostat (U) by a voltage drop on the external series resistor. It should be noted that even without an external resistor, some voltage drop always exists between the working and reference electrodes, due to solution resistance. Often, the solution resistance itself is sufficient for the oscillations to appear.

There are numerous examples, where authors reported the existence of current oscillations on voltammograms measured without any external resistor [10,11]. Fig. 2 shows an example of current oscillations on a voltammogram in the present system, observed when a diluted supporting electrolyte was used. Small amplitude current oscillations are also visible on the reverse scan in Fig. 1A.

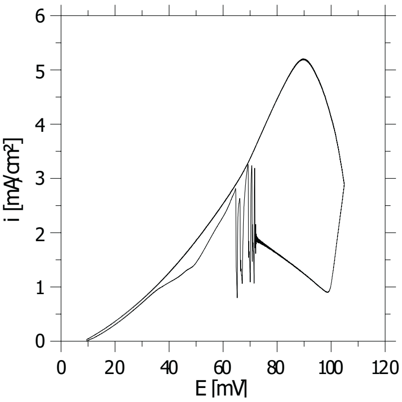

Figure 2. Voltammetric curve for silver electrode in 0.05 M H_2SO_4+ 7.5 mM Ag_2SO_4. Scan rate 0.02 mV/s.

It was noticed that during all the scans a gray “powder” accumulates at the electrode surface. Microscopic inspection of the electrode revealed that the powder particles have a size in the micrometer range. This grey powder is non soluble in the working solutions and has a relatively poor adhesion to the electrode surfaces: it can be easily removed from the electrode surface with a stream of water. Fig. 3 shows an X-ray microprobe spectrum of the powder particles. Only Ag peaks are visible on the spectrum. Neither sulfur nor oxygen peaks are observed, which proves that the powder consists of elmental silver.

Current oscillation at potentiostatic conditions with a series resistor. Before each run, the series resistor was set to zero and the electrode was passivated at the potential of 90 mV. Next, both the resistor (R) and the voltage (U) were adjusted to the desired values. Current oscillations were observed in the system for numerous combinations of voltage and series resistor values. Voltages in the range from 40 to 56 mV and resistors between 20 and 30 Ω were examined. Usually, it took between 15 and 30 minutes for the oscillations to begin.

A typical evolution of the current is shown in Fig. 4. As the electrode becomes less passivated, oscillations of gradually increasing amplitude appear on the current-time plot. After an initial transient a well-defined temporal pattern develops. The resulting oscillations, observed in this run, are virtually monoperiodic and relatively stable. Unfortunately, this was not the case for the majority of other runs. As a rule, transients were observed, with mode switching and oscillations decay. Fig. 5 shows an example of such a transient, where period two oscillations change to monoperiodic and then die away.

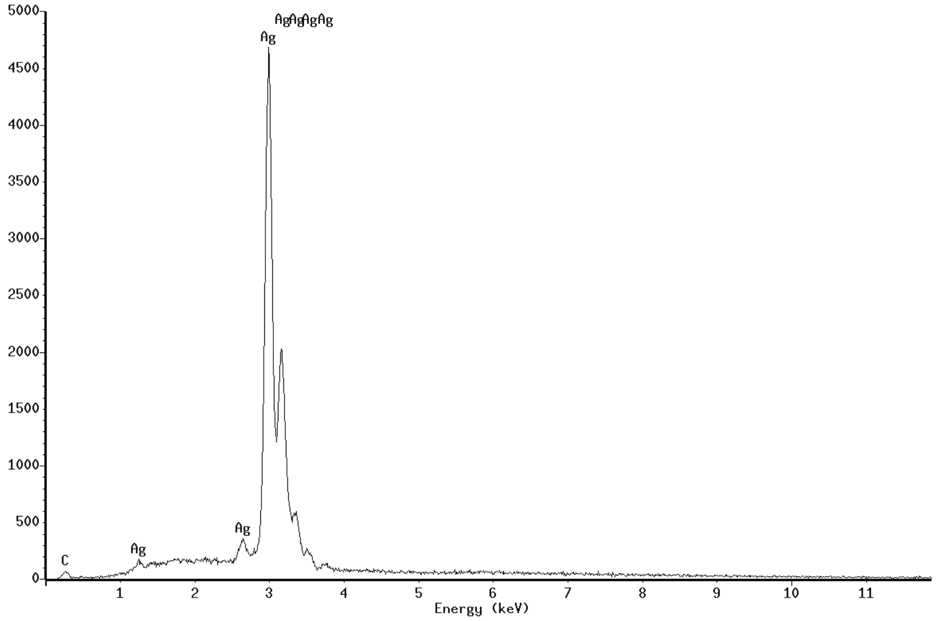

Figure 3. X-ray microprobe spectrum of powder particles.

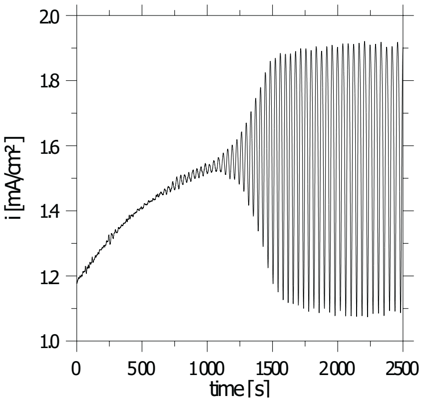

Figure 4. Current evolution after passivation: current increase due to partial depassivation; start of oscillations and monoperiodic asymptotic state at the silver electrode in 0.1 M H_2SO_4 + 15 mM Ag_2SO_4, U = 44 mV, R = 20 Ω.

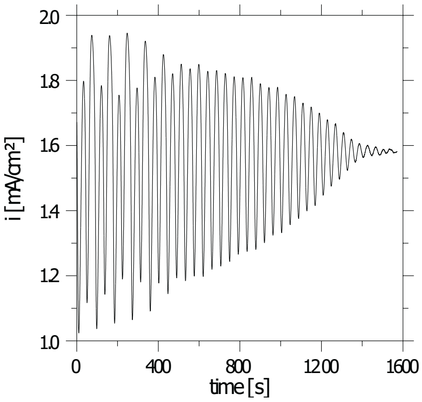

Figure 5. Decay of transient oscillations through period two and monoperiodic patterns at the silver electrode in 0.1 M H_2SO_4 + 15 mM Ag_2SO_4. U = 44 mV, R = 20 Ω.

The problem of the modification of diffusion conditions at the electrode surface by powder accumulation is in this system even more severe than for Cu electrodes. While at Cu oscillation periods are in the range of seconds and time scale for powder accumulation is by two orders higher, in the present system the time scales of the two processes are close to each other. In certain parameter ranges the time constant of periodic current changes is as long as 200 s (Fig. 6). The strong transient character of oscillations dynamics prevents, in fact, any quantitative analysis of the observed data. As a result, we will only give several examples of observed behaviour.

As it has been demonstrated in [6], a nonlinear system of the type described in the present work responds to cyclic voltammetry perturbation with multiperiodic patterns, when scan rate and scan limits are properly chosen. An example of such a behaviour for Ag in H_2SO_4 is given in Fig. 7. The response of the system to a cyclic (triangle

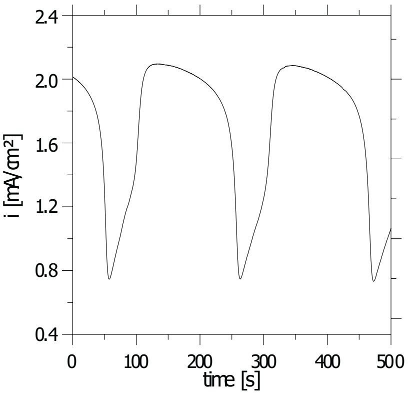

Figure 6. Long period current oscillations at the silver electrode in 0.1 M H_2SO_4 + 15 mM Ag_2SO_4. U = 50 mV, R = 27 Ω.

wave) voltammetric potential programme is two-periodic. Two closed loops form the voltammogram: these two loops are periodically visited during subsequent cycles. Two triangle wave periods are then necessary to complete such a voltammogram.

During anodic dissolution in an H_2SO_4 solution containing Ag^+ ions, the silver electrode undergoes passivation. The sequence of voltammograms, obtained in the series of solutions with increasing Ag^+ concentration, demonstrates clearly that the passivation is of the salt type and consists in isolating, presumably an Ag_2SO_4, layer built up at the electrode surface. Further in-situ characterization of the passive layer does not seem possible, because the electrode becomes very rough and standard methods of thin film analysis, such as ellipsometry cannot be employed. Ex-situ microprobe spectrum of the passivated electrode does not show any other peaks than these of elemental silver.

In spite of the apparent simplicity of the system (only univalent silver ions are expected in the examined potential range), during electrode dissolution powder

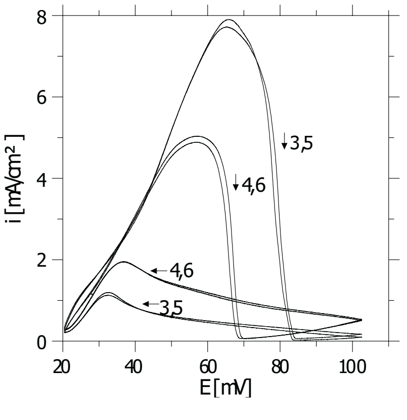

Figure 7. Period two cyclic woltammogram at the silver electrode in 0.1 M H_2SO_4 + 15 mM Ag_2SO_4. Scan rate 0.09 mV/s. The subsequent cycle numbers are marked on the plot.

accumulation at the electrode surface is observed, as in a Cu–H_2SO_4 system [4]. The fact, that silver powder particles are spheroidal in shape and loosely bound to the electrode surface, suggests that they are formed in the solution in direct vicinity of the electrode, rather than by etching of the electrode surface. While in the case of Cu, the mechanism of the powder formation is well understood: namely, it proceeds by disproportionation of unstable univalent copper species produced during Cu dissolution [12], for Ag any species of valence between 0 and +1 have never been observed. Nevertheless, production of the powder indicates, that mechanism of Ag dissolution is more complex than just single electron transfer and deserves further studies.

Negative differential resistance, appearing on the falling part of the current-potential curve, causes that nonlinear current oscillations can be observed. Moreover, multiperiodic voltammograms are also observed in the present system. On the stationary electrode employed in this work, powder accumulation creates additional parameter changes and introduces long lasting transients during oscillation measurements. We expect that, as in the case of a Cu–H_2SO_4 system [5], application of a rotating disc electrode should limit the effect of powder accumulation and allow a quantitative analysis of the oscillations.

Some of the observed oscillations have long periods, which makes the system a good candidate for possible observations of 2D spatio-temporal structures on the electrode surface. There are numerous reports on such structures, where current (or sometimes potential) changes both in time and in space [9]. Usually, experiments are carried out in one space dimension: either on a wire or on a rotating ring. In order to observe 2D patterns, a fast "photograph" of the current distribution should be taken at least several times during one cycle of oscillations. If the oscillations are too fast, the problem arises of how to disentangle the space and time changes.

Acknowledgments

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