

## Chaotic, mixed-mode and periodic oscillations during the electro-oxidation of copper in trichloroacetic acid

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**Abstract:** The current oscillations of a copper electrode in trichloroacetic acid solutions were studied in this paper. The Cu/CCl<sub>3</sub>COOH system is a new electrochemical oscillator, showing rich dynamic behaviour on two controllable parameters: the trichloroacetic acid concentration ( $c_{\text{CCl}_3\text{COOH}}$ ) and the imposed potential ( $E$ ). Phase trajectories were reconstructed from time series using time delay methods in order that the complex oscillations could be analyzed. Five kinds of oscillations, periodic and quasiperiodic, mixed-mode, aperiodic, small amplitude and chaotic current oscillations, were observed. The EDS (energy dispersive spectroscopy) technique was used to analyze the elemental composition of the film formed on the surface of the copper electrode after the current oscillations.

**Keywords:** current oscillations, copper, trichloroacetic acid.

### INTRODUCTION

Since the time that nonlinear dynamics methods, such as time delays, were used for the analysis of electrochemical oscillations, interest in the investigation of the oscillations has been renewed.<sup>1,2</sup> Hudson and Tsotsis have reviewed the status of research on the dynamics of electrochemical reactions.<sup>3</sup> Dewald *et al.*<sup>1,2</sup> used nonlinear dynamical methods to analyze the different oscillatory modes of copper in acetate buffer and proposed that the oscillations arose from an intricate process involving surface reactions, film formation and dissolution, and mass transfer, but the nature of the surface film and its composition remained unclear.<sup>4</sup> Glarum and Marshall<sup>5,6</sup> also used nonlinear dynamical methods to analyze the electrochemical behavior of the anodic dissolution of copper in phosphoric acid solutions. They suggested that the film might be a highly viscous, dehydrated surface layer. However, whether the film was a true solid phase with distinct boundaries or a highly viscous layer maintained by water depletion has not been proved. Oscillations in copper/acidic chloride solutions have always been the main topic in discussing the electro-dissolution of copper in acidic solutions. Qualitative explanations for the oscillatory be-

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behaviour of copper in these systems have been suggested by several authors.<sup>7-14</sup> It is unlikely that a single model can explain all the oscillatory phenomena that have been observed, because the nature of the electrode surface and covering film depend strongly on the conditions under which the experiments were performed.<sup>15</sup> Thus, the origin of the oscillatory behaviour in the copper/acidic chloride system is not well understood. Surface films are believed essential for polishing, but the nature of the surface remains uncertain. Further investigations are needed in which the electrochemical oscillations of copper in other electrolytes are studied.

The purpose of this paper is to summarize the results of an experimental investigation of the anodic dissolution of copper in  $\text{CCl}_3\text{COOH}$  solutions. It was hoped that a better understanding of the dependence of the oscillatory behavior on the nature of the surface film would be gained.

#### EXPERIMENTAL

A three-electrode system was used in all experiments. A stationary working electrode, 6.0 mm in diameter, made of pure copper (99.9 % Cu) was used. The pure copper rod was embedded in resin, and only the end of the rod was exposed to the solution. The specimen was polished with #600 and #1200 emery papers to a mirror-like surface, then washed with alcohol and then two times with distilled water in an ultrasonic bath before each experiment. The counter electrode was a platinum sheet (surface area 5.0 cm<sup>2</sup>), and a saturated calomel electrode (SCE) was used as the reference, with its Luggin capillary probe located 2 mm below the working electrode (all potential values are reported with respect to the SCE). The electrolyte was prepared with analytical grade  $\text{CCl}_3\text{COOH}$  and two times distilled water. The electrochemical measurements were carried out using a PAR potentiostat/galvanostat Model 283 incorporated with M352 corrosion software. All measurements were performed at  $25 \pm 1$  °C.

The samples of Cu were prepared after oscillations of the Cu electrode had occurred in  $\text{CCl}_3\text{COOH}$  solution. Then the Cu electrode was rinsed three times with anhydrous ethanol and then two times with distilled water. The EDS technique (energy dispersive spectroscopy, AMRAY 1840) was applied to evaluate the elemental composition of the film formed on the surface of the Cu electrode after the current oscillations. The base pressure was  $2 \times 10^{-9}$  mbar, and the high voltage was 25 kV.

#### RESULTS

##### *Polarization phenomena*

The polarization curves of copper in solutions of different concentrations of trichloroacetic acid ( $c_{\text{CCl}_3\text{COOH}}$ ) at a scan rate of 10 mV/s are shown in Fig. 1, from which it can be seen that the current-potential ( $I$ - $E$ ) curves show two different types of current oscillations. The first type which occur in low concentrations of trichloroacetic acid ( $c_{\text{CCl}_3\text{COOH}} \leq 1.0 \text{ mol dm}^{-3}$ ), is when current oscillations are observed in both the forward (positive) and backward (negative) potential scans. In 0.50 mol dm<sup>-3</sup>  $\text{CCl}_3\text{COOH}$  solution (Fig. 1a), in the forward potential scan, the anodic dissolution current increases almost linearly as the potential is swept from 0 to about 0.80 V, then current oscillations are observed until the potential reaches about 1.10 V when the current decreases to a low value. The polarization behavior in the backward sweep resembles that in the forward one. As the  $c_{\text{CCl}_3\text{COOH}}$  increases to 1.0 mol dm<sup>-3</sup> (Fig. 1b), the amplitudes of the current oscillations obviously increase. The second type is when current oscillations are observed only in backward poten-

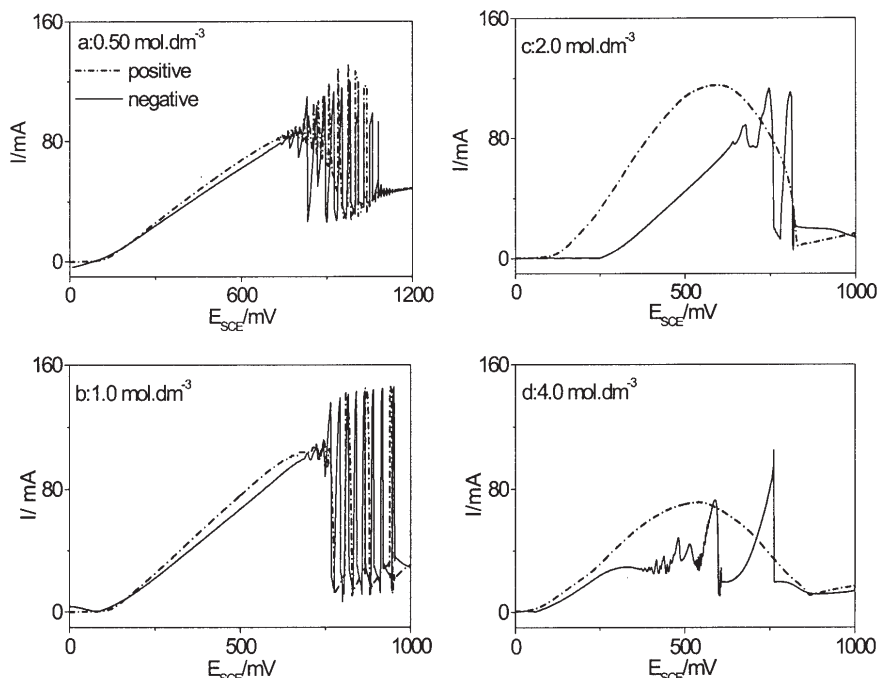


Fig. 1. Effect of  $\text{CCl}_3\text{COOH}$  concentration on the polarization behavior of the  $\text{Cu}/\text{CCl}_3\text{COOH}$  system. Scan rate: 10 mV/s.

tial scan in  $2.0 \text{ mol dm}^{-3} \leq c_{\text{CCl}_3\text{COOH}} \leq 4.0 \text{ mol dm}^{-3}$  solutions. In  $2.0 \text{ mol dm}^{-3}$   $\text{CCl}_3\text{COOH}$  solution (Fig. 1c), the current increases as the potential is swept to positive values and a maximum value of the current ( $I_{\text{max}}$ ) appears at about 0.60 V, then the current decreases until the electrode enters a passive region, and no current oscillations are observed. Current oscillations are observed only in the backward potential scan. The polarization curves in  $4.0 \text{ mol dm}^{-3}$  (Fig. 1d) resemble those in  $2.0 \text{ mol dm}^{-3}$   $\text{CCl}_3\text{COOH}$  solution. The maximum value of the current decreases as the  $c_{\text{CCl}_3\text{COOH}}$  increases.

#### Current oscillations

Current oscillations are observed with a stationary copper electrode from 0.50 to 4.0  $\text{mol dm}^{-3}$   $\text{CCl}_3\text{COOH}$  solutions. The upper and lower  $E$ -boundaries of the oscillatory region under potentiostatic condition of copper in different concentrations of  $\text{CCl}_3\text{COOH}$  solutions are shown in Table I. The oscillatory region shifts negatively as the  $c_{\text{CCl}_3\text{COOH}}$  increases. The current oscillations are found to depend strongly on two parameters, namely the  $c_{\text{CCl}_3\text{COOH}}$  and the imposed potential. Five main types of oscillations, namely periodic and quasiperiodic oscillations (ROs), mix-mode oscillations (MMOs), aperiodic oscillations (AOs), small amplitude oscillations (SMOs) and chaos, are observed for a copper electrode in different concentrations of  $\text{CCl}_3\text{COOH}$  solution.

In high concentrations, AOs and ROs are mainly observed. Typical current oscillations in  $4.0 \text{ mol dm}^{-3}$   $\text{CCl}_3\text{COOH}$  solution at  $E_{\text{SCE}} = 0.60 \text{ V}$  together with the corresponding

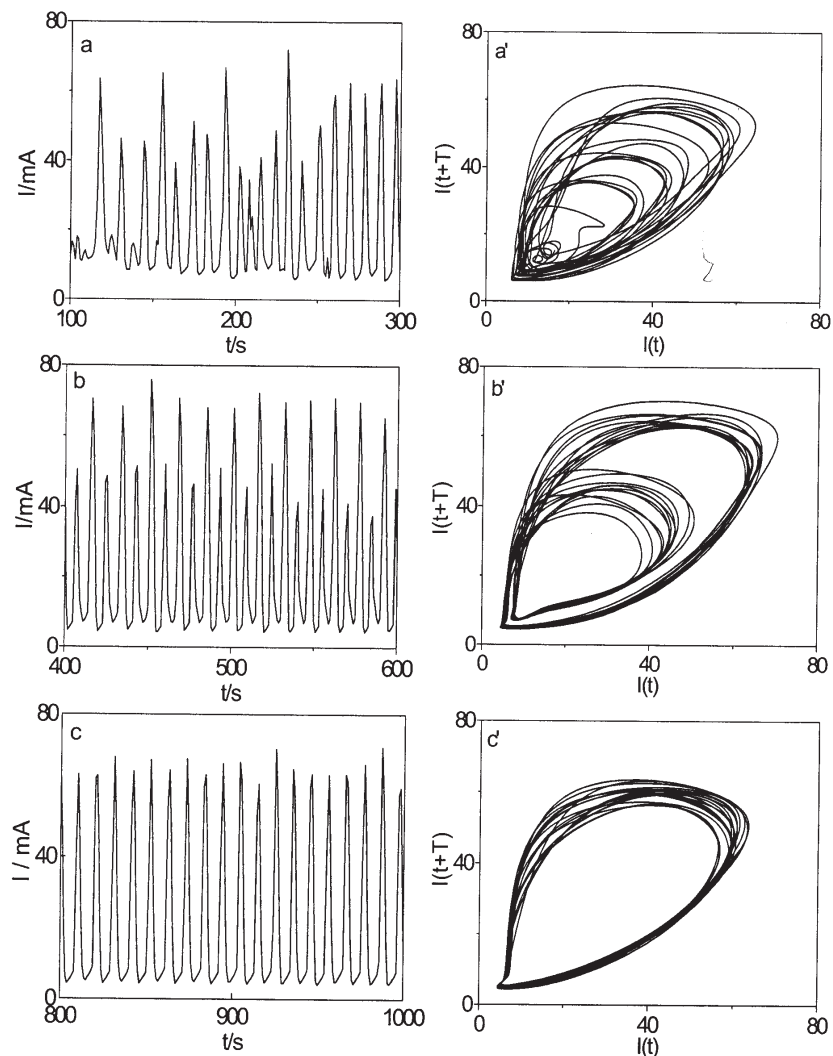


Fig. 2. Different oscillatory behavior of Cu at  $E_{\text{SCE}} = 0.60$  V in a  $4.0 \text{ mol dm}^{-3}$   $\text{CCl}_3\text{COOH}$  solution and the corresponding phase trajectories. ( $T = 1$  s).

phase trajectories are shown in Fig. 2. The current behavior goes through a series of transitions. The two dimension phase trajectories, projected into the  $[I(t), I(t+T)]$  ( $T = 1$  s) plane, have been constructed by time delay methods,<sup>11–15</sup> in order to analyze the character of the oscillations. (The phase trajectory was made by plotting every current measurement of the time series with that current as one coordinate, the current at time  $T$  after that as the second coordinate.) The shape of the phase trajectories has a one-to-one correspondence with the time series from which they were constructed. Fig. 2a shows the initial period and a multi-period state which occurs 100 s after the potential had been stepped from the open circuit potential to  $E_{\text{SCE}} = 0.60$  V. The phase trajectory (Fig. 2a') shows that the current oscillations are

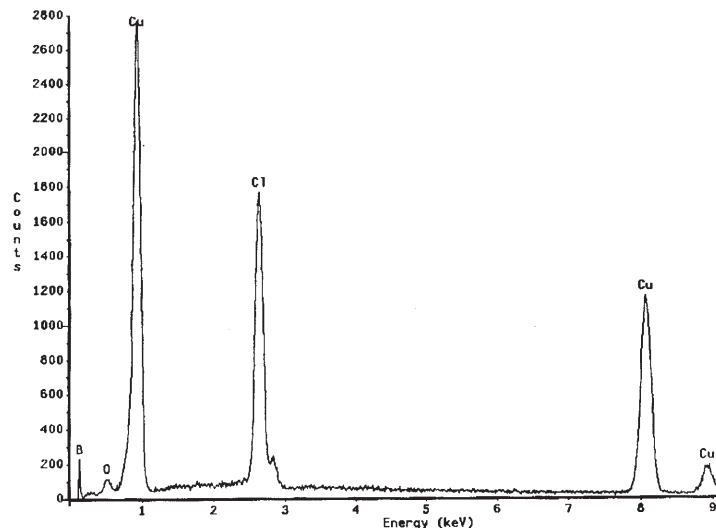


Fig. 3. EDS analysis of the film.

AOs. Beginning an experiment with the system in the aperiod state corresponding to a waveform, a critical value is reached at which point the period decreases, signalling the transition to a different oscillatory state, a period-two state.<sup>13</sup> The measured time series for the period-two state consists of alternating peaks of two different amplitudes. A time series of a portion of the 2-peak behavior and the phase trajectory can be seen in Figs. 2b and 2b', respectively. The trajectory on the attractor lies in two distinct loops and the flow on the attractor alternates between these two loops. The small loops correspond to the small amplitude oscillations whereas the large loops correspond to the large amplitude oscillations in the time series in Fig. 2b. Increasing the time further leads to a bifurcation in which the system makes a transition to another oscillatory state, a period-one state. A time series of a portion of the 1-peak behavior and the phase trajectory can be seen in Figs. 2c and 2c', respectively. This 1-peak behavior does not change. The limit cycle attractors are closed lines with a number of loops. Since the oscillation amplitude changes slightly in each cycle of oscillations, the radius of the loop changes slightly. At the beginning, the oscillations are AOs, and this behavior subsequently becomes less complicated, giving rise to two-peak oscillations, and finally one-peak oscillations (ROs). It is assumed that the composition and the structure of the film

TABLE I. The relationship between the oscillatory potential region ( $\Delta E_{OSC}$ ) and the  $CCl_3COOH$  concentration ( $c_{CCl_3COOH}$ )

$c_{CCl_3COOH}/\text{mol dm}^{-3}$	$\Delta E_{OSC}/V_{SCE}$
0.10	No current oscillations
0.50	0.80 – 1.10
1.0	0.74 – 0.92
2.0	0.50 – 0.80
4.0	0.45 – 0.75

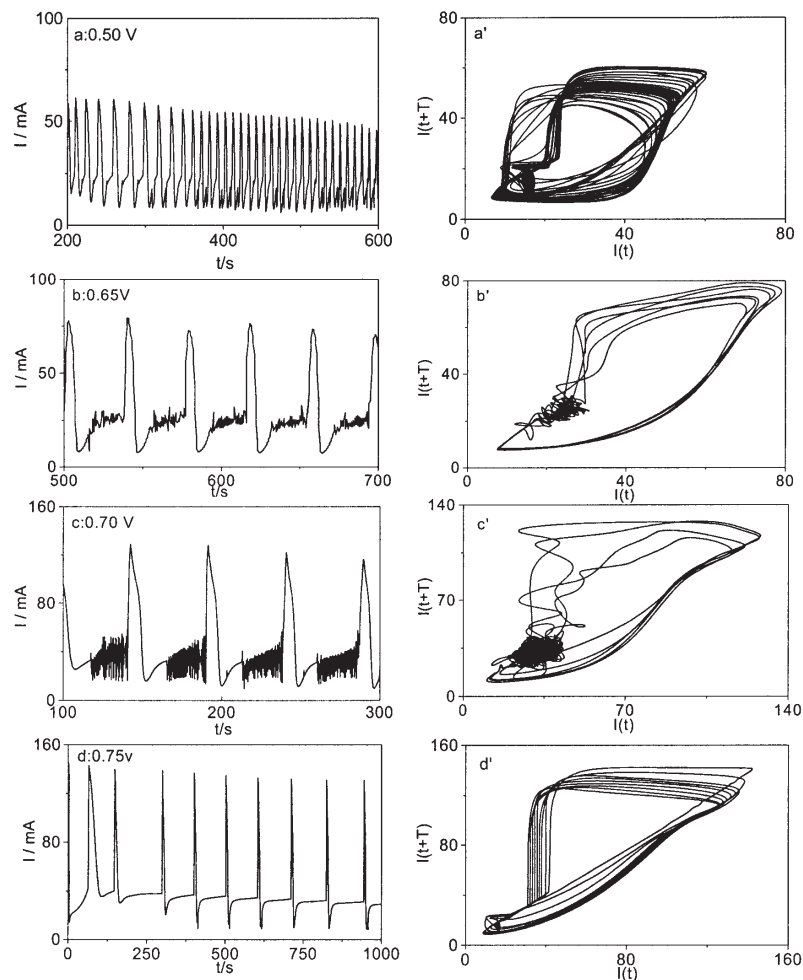


Fig. 4. The sequence of current oscillations of Cu in  $2.0 \text{ mol dm}^{-3} \text{ CCl}_3\text{COOH}$  solution and the corresponding phase trajectories as a function of potential ( $T = 1 \text{ s}$ ).

may change with time at the beginning of the experiment and may not change after a period of time. After the experiment, elemental EDS analysis of the corrosion product on the surface of the copper electrode shows an enrichment of the element Cl (Fig. 3). A salt film may be formed on the surface of copper electrode.

A sequence of  $i-t$  curves and the corresponding phase trajectories is illustrated in Fig. 4 when the Cu was electrodissoled in  $2.0 \text{ mol dm}^{-3} \text{ CCl}_3\text{COOH}$  solution. A sequence of oscillatory modes is observed on changing the potential in the Cu/ $2.0 \text{ mol dm}^{-3} \text{ CCl}_3\text{COOH}$  system. Analysis of this oscillatory sequence may lead to valuable information about the type of the dynamical equations governing the behavior of the system.<sup>16-18</sup> As shown in Fig. 4a', it is chaotic oscillation when the potential is held at  $0.50 \text{ V}_{\text{SCE}}$ . When the potential is increased to  $0.65$  and  $0.70 \text{ V}_{\text{SCE}}$ , the oscillatory

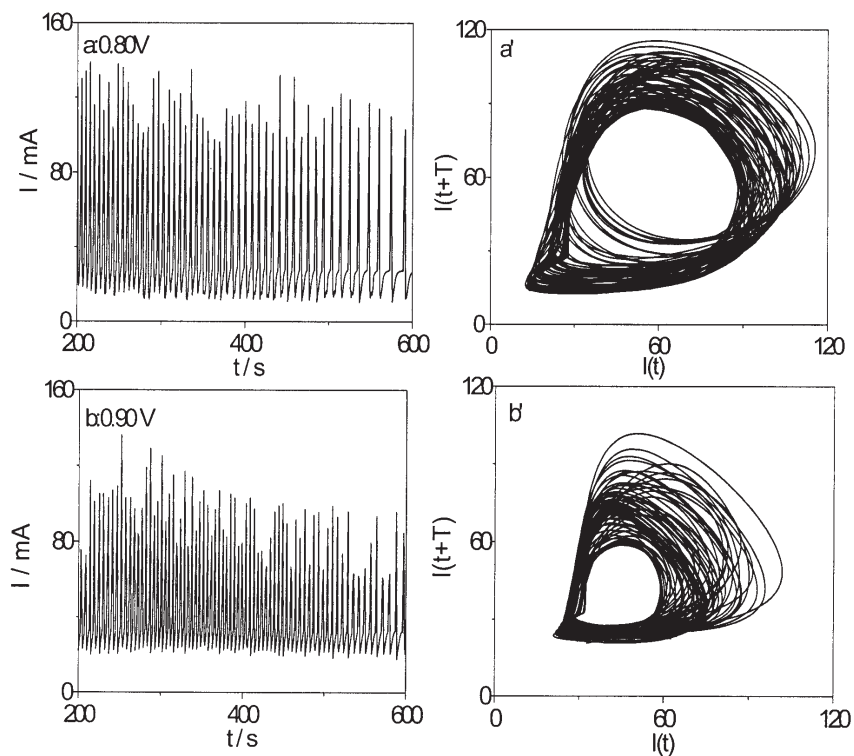


Fig. 5. Typical current oscillations of Cu in  $1.0 \text{ mol dm}^{-3} \text{ CCl}_3\text{COOH}$  solution and the corresponding phase trajectories. ( $T = 1 \text{ s}$ ).

curves (Figs. 4b and 4c, respectively) and the corresponding phase trajectories (Figs. 4b' and 4c', respectively) show that these oscillations are MMOs. These kinds of MMOs belong to a periodic-chaotic sequence in which intervals of periodicity are separated by intervals of a chaotic state, which resembles random mixing of adjacent periodic patterns.<sup>1</sup> For  $0.75 \text{ V}$  (Fig. 4d), the trajectory is a simple closed curve (Fig. 4d'), so the current oscillations are ROs. If the potential is held at  $0.80 \text{ V}$  (not shown), the current oscillations end after three cycles of oscillation.

At low concentrations of trichloroacetic acid ( $c_{\text{CCl}_3\text{COOH}} \leq 1.0 \text{ dm}^{-3}$ ), chaos and SMOs are observed. The oscillations occur at more positive potentials. A typical time series of copper in  $1.0 \text{ mol dm}^{-3} \text{ CCl}_3\text{COOH}$  solutions and the corresponding phase trajectories are shown in Fig. 5. The trajectories (Figs. 5a' and 5b') show that the oscillations are chaotic. In  $0.50 \text{ mol dm}^{-3} \text{ CCl}_3\text{COOH}$  solution (Fig. 6), SMOs are observed. A strange phase trajectory is observed (Fig. 6a'), so the oscillations are chaotic, too.

#### DISCUSSION

Although the origin of the oscillatory behavior of metals in acidic electrolyte is not well understood, there are at least two points that can be proposed. The first point is that the oscil-

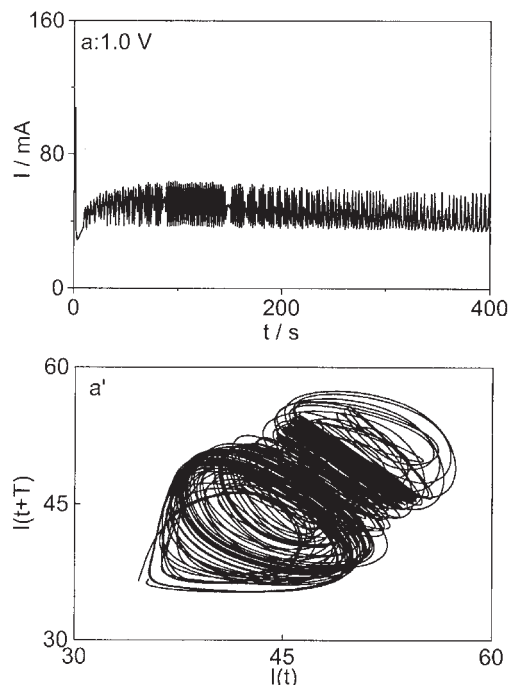


Fig. 6. SMOs observed in  $0.50 \text{ mol dm}^{-3} \text{ CCl}_3\text{COOH}$  solution and the corresponding phase trajectory. ( $T=1 \text{ s}$ ).

lations are caused by periodic film formation-dissolution. This was verified by the fact that current oscillations could be generated when the chemical environment near the surface of an iron electrode was changed artificially.<sup>19,20</sup> The second one is that the film formed on the surface of a copper electrode may contain more than one material.<sup>2,15</sup> The result of EDS analysis (Fig. 3) indicates that the surface film on the surface of a copper electrode in  $\text{CCl}_3\text{COOH}$  solutions is rich in chloride. Chloroacetic acid always contains some amount of  $\text{Cl}^-$  and it is known that insoluble  $\text{CuCl}$ <sup>15,21</sup> may be formed. Under potentiostatic conditions, the behavior of the current in the experiment with copper in  $4.0 \text{ mol dm}^{-3} \text{ CCl}_3\text{COOH}$  solution at  $0.60 \text{ V}$  (Fig. 2) changes slowly. This is because the film and the conditions on the surface of the copper electrode change slowly, which give rise to a change in the current.<sup>2</sup> It was found that the electrode surface was never in the same state during the oscillatory response.<sup>22</sup> There is a strong correlation between the film/surface properties and the type of the oscillation obtained.<sup>13</sup> Due to the slowly changing nature of the electrode surface, the current behavior is in fact transitory. However, the time scale of the surface change is much slower than that of the oscillations so that large enough sections of data can be extracted and analysed and be considered stable for the time period.

It was shown experimentally<sup>2</sup> and theoretically<sup>23</sup> that different films adsorbed on the copper electrode surface coexist when the system exhibits chaotic behavior.<sup>1</sup> A sequence of chaos and MMOs preceding ROs is observed for copper in a  $2.0 \text{ mol dm}^{-3} \text{ CCl}_3\text{COOH}$  solution under potentiostatic conditions. It may be assumed that the small and large ampli-



tude oscillations are related to different types of surface films formed on the surface of the copper electrode during its electrodisolution.

Sazou *et al.*<sup>24</sup> proposed that the complex periodic and chaotic oscillations observed during the corrosion of iron in chloride containing sulphuric acid solutions are related to different states of localized corrosion. It has been proposed that the various dynamic behaviours are caused by the different composition or structure of the films formed on the surface of the copper electrode. In low  $\text{CCl}_3\text{COOH}$  concentrations ( $c_{\text{CCl}_3\text{COOH}} \leq 1.0 \text{ mol dm}^{-3}$ ) solution, different types of films may be formed during the electrodisolution processes, so different types of current oscillations are observed.

Itagaki *et al.*<sup>25</sup> used a channel flow double electrode for studying the oscillatory electrodisolution of copper in acidic chloride solutions. They found that the oscillations originated from the dissolution of cupric ions and an adsorbed intermediate, which was composed of cupric species. The rich dynamical behavior observed with a stationary copper electrode in  $\text{CCl}_3\text{COOH}$  solutions may be explained by cupric ions and an adsorbed intermediate being easily formed on the electrode surface and, thus, a surface film is formed easily which induces current oscillations.

#### CONCLUSIONS

Current oscillations occur during the electrodisolution of copper in  $\text{CCl}_3\text{COOH}$  solutions. The new  $\text{Cu}/\text{CCl}_3\text{COOH}$  oscillatory system shows a rich dynamical behavior. The results of nonlinear-dynamic-analysis confirm the existence of different types of oscillations in the  $\text{Cu}/\text{CCl}_3\text{COOH}$  system. The different types of current oscillations may be caused by different types of films formed on the surface of the copper electrode during the processes of its electrodisolution.

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#### ИЗВОД

#### ХАОТИЧНЕ МЕШОВИТЕ И ПЕРИОДИЧНЕ ОСЦИЛАЦИЈЕ ТОКОМ ЕЛЕКТРООКСИДАЦИЈЕ БАКРА У ТРИХЛОРСИРЋЕТНОЈ КИСЕЛИНИ

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У овом раду су проучаване струјне осцилације на бакарној електроди у раствору трихлорсирћетне киселине. Систем  $\text{Cu}/\text{CCl}_3\text{COOH}$  је нови електрохемијски осцилатор који поседује широко динамичко понашање зависно од два параметра којим се оно може контролисати, концентрације трихлорсирћетне киселине и наметнутог електродног потенцијала. На основу временских низова осцилација користећи методу временских кашњења конструисане су фазне трајекторије како би се могле анализирати ове комплексне осцилације. Опажено је пет врста струјних осцилација: периодичне, квази-периодичне, мешовите, аперидичне и хаотичне. ЕДС техником анализиран је елементални састав филма који се стварао на бакарној електроди током струјних осцилација.

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