

OSCILLATORY INTERFACIAL SYSTEMS

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Oscillatory reaction has been investigated in homogeneous as well as heterogeneous systems. Oscillatory phenomenon could involve a solid /gas (Pt/CO) or an electrode/electrolyte interface. Electro-dissolution of metal, electro-deposition and electrocatalytic reactions are three major categories of electrochemical oscillators. The iron/electrolyte interfacial system is characterized by rich dynamic behaviour under self oscillatory conditions as well as under the influence of an external EMF. The oscillations are found to sustain over a period of several hours in a medium containing the optimum concentration of the oxidant (Potassium bromate) and sulphuric acid. The behaviour of the self oscillatory iron/bromate system under such experimental conditions is of importance for the generation of A.C. power and is presented here.

Key Words : Oscillatory Reaction; Interfacial System; A.C. Power

Introduction

Oscillatory systems are significant from many points of view. A reaction mixture that is kept well stirred at room temperature changing its colour periodically every few seconds between red and blue or between colourless and dark blue is quite fascinating. The reaction is as much appealing to a young student as is absorbing to a researcher. Oscillatory phenomenon interests scientists in various disciplines. It is overwhelmingly significant in biological and biochemical investigations. Unravelling the chemical oscillator may provide the key to the understanding of oscillations in complex living systems. They lend themselves for experimental demonstration in view of the exotic periodic colour change of the oscillating solution.

Interestingly a very early report¹ of oscillations is in electrochemical systems by Fechner in 1828. During the decades that followed there have been several significant reports²⁻¹² connected with oscillatory phenomena. There are important landmarks leading to the present status of oscillatory reaction as a prominent area of research. Oscillatory interfacial system involves a solid/gas interface or solid/solution interface, can be spontaneous or can occur under the influence of an applied potential. This is represented in Scheme 1. It can be seen from the scheme that any oscillatory interfacial system would be of one of the following categories, namely, solid catalyzed gas phase reaction, electroless plating, self oscillatory interfacial system (Spontaneous) or electro-dissolution, electro-deposition or electrocatalytic reaction (Forced).

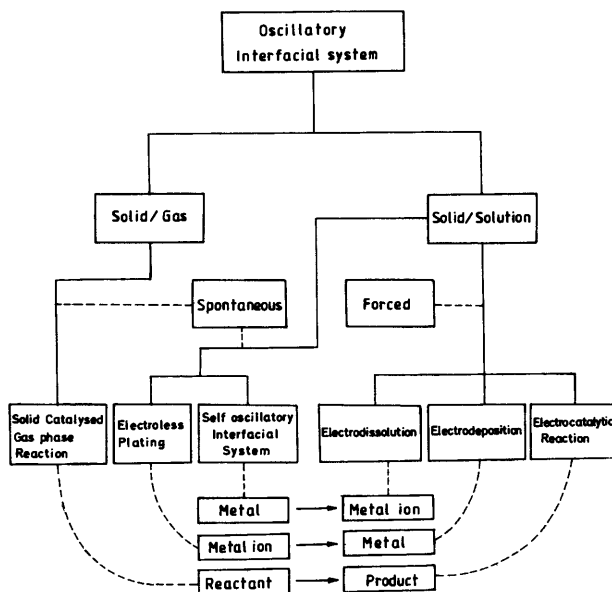
Solid Catalysed Gas Phase Reactions

Decomposition of N_2O

Experimental investigation in solid catalyst was first reported^{13,14} by Hugo. He observed periodic fluctuation in the exothermic decomposition of N_2O on CuO catalyst.

Oxidation of CO

Undamped oscillations in the oxidation of CO on platinum under isothermal conditions were studied¹⁵ by Hugo. Beusch *et al.* reported¹⁶ oscillations in the concentration of CO_2 . Ekert *et al.*¹⁷ investigated oscillations of the catalyst bed temperature and



Scheme 1

concentration of CO. The mechanism of the oxidation of CO on platinum has been elucidated with single crystal studies at low pressures and found to involve structural changes of the catalyst surface. These experiments are usually carried out under ultra-high vacuum (UHV) conditions to keep the impurity concentrations low. The first such study was made¹⁸ in the oxidation of CO on Pt (110). The system was found to exhibit¹⁹⁻²² dissipative structure, bistability, target patterns, spirals and stationary waves as well as a variety of oscillatory behaviour²³⁻³⁶. Quasiperiodicity in the oxidation of ethanol on zeolite supported Pd has been reported³⁷. The oxidation of NH₃ on Pt has been investigated³⁸. Other investigations include the oxidation of hydrogen, ethylene and NO on platinum, hydrogen and methanol on Pd and ethylene on Ni-Al₂O₃⁸.

Electrocatalytic Reaction

The galvanostatic oxidation of formaldehyde and formic acid/formate in acid solutions on a platinum disc electrode^{39,40} has been carried out where periodic – chaotic sequence occurs. The oxidation of hydrogen has received much attention⁴¹. The reaction has been studied under galvanostatic conditions with the bubbling of hydrogen in the electrolyte containing Cu (II). Oscillations are mainly caused by the deposition and dissolution of copper. The dynamics have also been investigated^{42,43} on single crystal of Pt. A mathematical model has been developed⁴⁴ for the In (III) – thiocyanate system.

Electro Deposition

Oscillatory behaviour during the electrochemical growth of Zinc dendrites has been investigated^{45,46}.

Electroless Plating

The oscillatory phenomena of the plating rate and electrochemical potential have been investigated⁴⁷ in the electroless plating of Cu and Cu-Cd alloy in basic solutions containing formaldehyde.

Electro Dissolution⁴⁸

Oscillatory phenomenon during electrodisolution of metals including iron, copper, nickel and cobalt has received considerable attention. The electrodisolution of copper in phosphoric acid is characterized by Huson bifurcation, period doubling, simple chaos and a variety of periodic and chaotic oscillations. Potential oscillations in the copper system in chloride medium are related to the cycle growth and break down of anodic film. The effect of external magnetic field has been studied in chloride as well as buffered media.

Periodic and chaotic behaviour have been reported in other investigations in buffered medium. Spectral analysis of current oscillations in the electrochemical dissolution of copper in sulphuric acid has been carried out by Gabor transformation which accurately reflects oscillation changes in time^{48b}. The electrodisolution of nickel in chloride as well as sulphuric acid media is accompanied by oscillations, period doubling and chaotic behaviour. Cobalt electrodisolution in phosphoric acid has been studied by sinusoidal perturbation. Cobalt electrodes have been coupled during the anodic dissolution in HCl/Chromic acid medium. Resonant and nonresonant behaviour have been observed during the impedance study of silicon in fluoride. Current oscillations have been investigated by impedance measurements with GeAs semiconductor in acidified hydrogen peroxide^{49a}.

Extensive investigations have been carried out in the electrodisolution of iron by several researchers in a medium of sulphuric acid with or without the inclusion of Cl, benzotriazole or dichromate as the additive. The results establish that Cl ions accelerate electrodisolution by creating local active centres while the oxide film formation causing passivation retards the effect of Cl⁻^{49b}. The studies include the effect of parameters viz. electrode dimension, applied potential, frequency, inhibitive and corrosive effect of additives, coupling, photoeffects and employment of arrays of iron electrodes. The iron system in phosphoric acid medium is characterized by rich dynamic behaviour.

Self Oscillatory Metal/Solution System

Oscillatory phenomenon in the self oscillatory metal/solution interfacial system is of considerable importance. The electrolyte includes an oxidizing agent (bromate or dichromate) as an essential constituent to facilitate the reaction. The potential oscillations and structure formation in the acid, bromate system has been investigated. Current oscillations in the iron/bromate/platinum system⁵⁰ and iron/dichromate/graphite or zinc system⁵¹ have been studied. The versatility of the self oscillatory iron/electrolyte system has prompted further investigations currently under way. An important objective has been to explore the possibility of practical application of the system. The system has been studied by employing bromate or dichromate as the oxidant and a variety of addition agents⁵²⁻⁵⁴. An important outcome of the study has been a concerted effort to screen corrosion inhibitors by the oscillatory reaction⁵⁵.

Studies have been directed towards the generation of a.c. power from oscillatory systems, homogeneous as well as interfacial. The a.c. peak power obtained from the homogeneous system is of the order of 10^{-5} W. However, there is a decrease in the frequency of oscillation with the progress of the reaction due to depletion of the constituents⁵³. The oscillations are well sustained when the coupling is between two homogeneous oscillators under Continuously Stirred Tank Reactor (CSTR) conditions⁵⁶.

Iron/Electrolyte System

The potentiality of the iron/electrolyte interfacial system has been examined for possible application for generation of a.c. power. An important pre-requisite for this would be a sustained oscillatory behaviour of the system over a reasonable duration. The iron / electrolyte system has been studied by employing either potassium dichromate or bromate in acidic medium. However the iron/dichromate, sulphuric acid system exhibits a variety of oscillatory behaviour, namely, period doubling, periodic triple oscillations, double mode as well as mixed mode oscillations⁵³. In the iron/dichromate system, the ions H^+ , CrO_4^- and $Fe^{III} Cr^{IV} O_4^+$ have been identified as the species controlling the appearance

and maintenance of oscillations. A mathematical model has also been proposed⁵⁷.

On the other hand, oscillations in the iron/bromate sulphuric acid system are well sustained over a considerable duration. The design of electrochemical generators of pulsating and alternating current in the iron/bromate system has been discussed⁵⁸. Accordingly, this system has been examined to ascertain its suitability for the generation of a.c. power. The experimental procedure for the potentiometric follow up of the system has been described elsewhere⁵². Under resistance loaded condition, coupling of two iron electrodes generates a.c. power while the coupling of iron electrode with a platinum electrode results in pulsating d.c. The maximum a.c. power is of the order of a few milliwatts.

The study was also directed towards identifying conditions in which the system would oscillate with a small time per oscillation. The frequency of oscillation increases when chloride (0.03M) is included in the system (time per oscillation is 8.5 sec)⁵⁴. However, the iron electrode suffers pitting corrosion under these experimental conditions. The inclusion of a suitable addition agent (x) at a concentration of 0.04 M has resulted in a considerable decrease in the time per oscillation.

The effective role of the additive in bringing down the time per oscillation is obvious from the following experimental results. The oscillogram of the iron/electrolyte system at a concentration of 0.35M potassium bromate and 0.1M sulphuric acid at a temperature of 30°C is presented in Fig.1. The system is characterized by oscillations of amplitude 500 mV in the potential range 0.2 to 0.7 V (vs NHE) and the time per oscillation is 20 sec. The oscillogram resulting under the same experimental conditions but with the inclusion of the addition agent (x) at 0.04M results in a considerable decrease in the time per oscillation (6sec.) (Fig.2). Moreover the presence of the additive does not cause any pitting corrosion of the working electrode. The result is of considerable significance in a.c. power generation and forms the basis for on going investigation in this direction.

Conclusion

The iron/bromate, sulphuric acid system provides sustained oscillations over a long duration and holds promise for the generation of a.c. power.

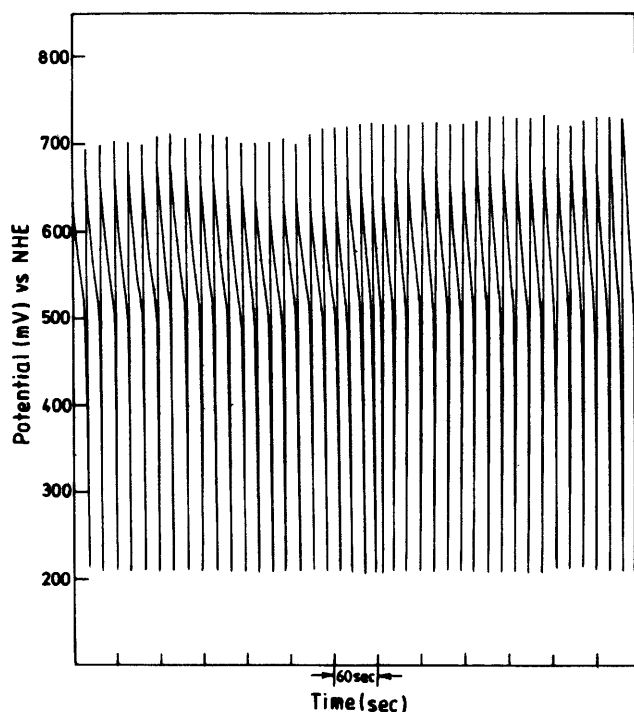


Fig. 1 Iron/electrolyte interfacial system Oscillogram with $[KBrO_3] = 0.35$ M; $[H_2SO_4] = 0.1$ M; $T = 30^\circ$ C

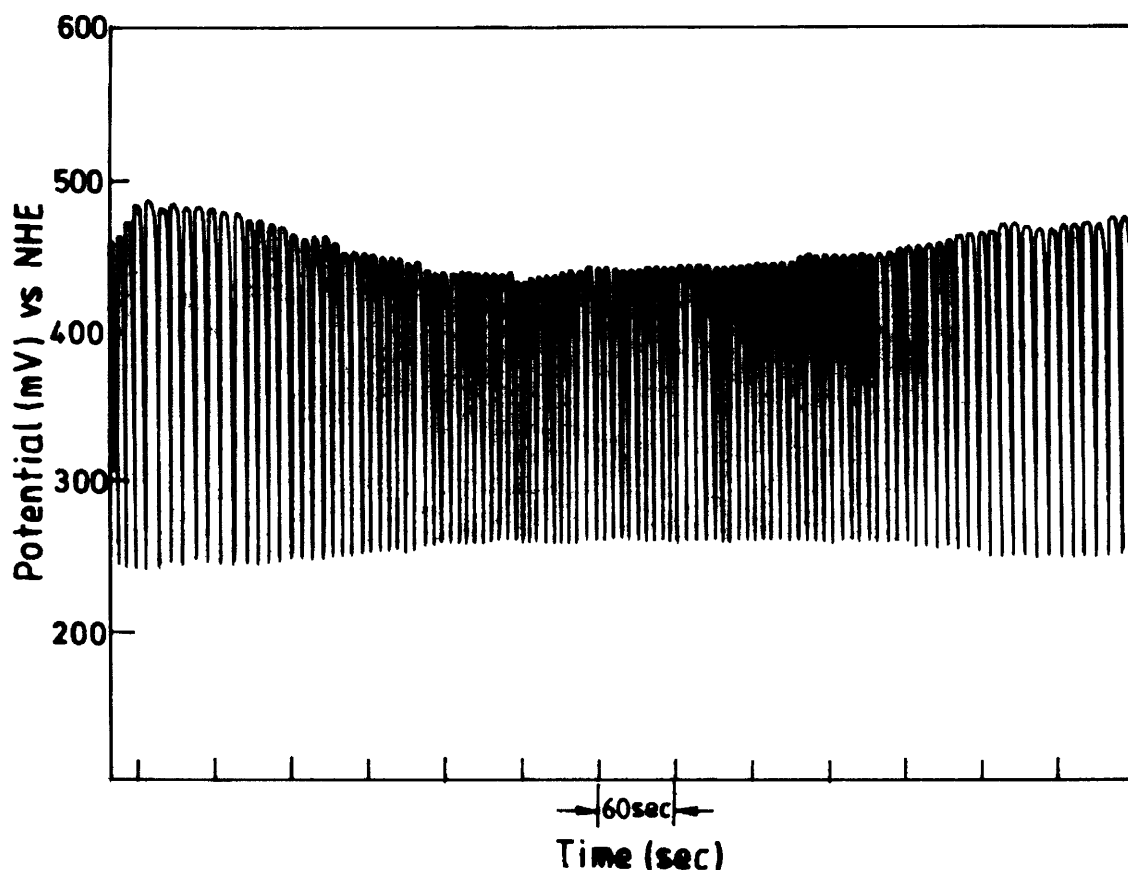


Fig. 2 Iron/electrolyte interfacial system Oscillogram with $[\text{KBrO}_3] = 0.35 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.1$ [Additive] = 0.04M ; $T = 30^\circ \text{C}$

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