Current Oscillations During CO Electro-oxidation on Smooth Platinum

D. C. Azevedo, A. L. N. Pinheiro and E. R. Gonzalez

Instituto de Quimica de Sao Carlos - USP, Cx.P. 780 -
Sao Carlos, SP; 13560-970; Brazil

INTRODUCTION

The occurrence of non-linear behavior such as multistability, kinetic oscillations, spatiotemporal structures and chaos, have been well documented in several electrochemical processes, like the electrodissolution of metals[1], the anodic oxidation of H_2 in the presence of Cu^+ and Cl^{-2} or CO[3,4], and in the oxidation of small organic molecules which have been tested for their potential use as fuels in low temperature fuel cells[5].

In this work, we report self-sustained oscillatory phenomena in the anodic oxidation of carbon monoxide under potentiostatic conditions. As far as we know, this is a new finding regarding the oscillatory regime of this system, because oscillations related to the oxidation of CO have been primarily reported in heterogeneous catalysis or in binary systems[3,4].

EXPERIMENTAL

Experiments were carried out at room temperature in a three-electrode electrochemical cell with a platinum counter electrode and a reversible hydrogen electrode (RHE) as reference. All potentials are given with respect to this reference. The working electrode consisted of a polycrystalline Pt cylinder (Degussa S.A.) of 6.5 mm in diameter embeded in PTFE. The measurements were made with the electrode stationary or rotating at 1000 rpm. The base electrolyte was 0.1 molL^{-1} $HClO_4$. The electrolytic solution was saturated with CO (AGA, 99.5%) by bubbling the gas for 30 min. and in the course of the measurements a small flux of CO was passed through the solution in order to maintain the bulk concentration. Electrochemical measurements were done with a Solartron Schlumberger 1286 electrochemical interface, a Nicolet 430 oscilloscope and a Kemo variable filter.

RESULTS AND DISCUSSION

Studies about the electro-oxidation of carbon monoxide have been carried out in this laboratory as part of the research on the anodic reaction in fuel cells. A remarkable behavior was observed during the chronoamperometric studies at a potential of 950 mV, where, for the rotating electrode (ω = 1000rpm) and after an induction time of around one minute, the current started oscillating as shown in Fig. 1. The oscillations could be observed for over 12 h (when the experiment was halted) and they were perfectly reproducible, in the sense that they were always observed under the conditions reported here. No current oscillations were observed at potentials either lower (900 mV) or higher (1000 mV), or for a stationary electrode.

During the course of oscillations, the oscillatory regime changes with time. In the beginning, the oscillations have a complex behavior that after some time changes to a periodic oscillation with period one. After about 8 hours the oscillations resemble mixed-mode oscillations.

In order to examine further the different behavior on stationary and rotating electrodes the system was also studied by voltammetric measurements with potential scans from 50 mV to either 1200 mV or 1500 mV after adsorption of CO during one minute at 300 mV.

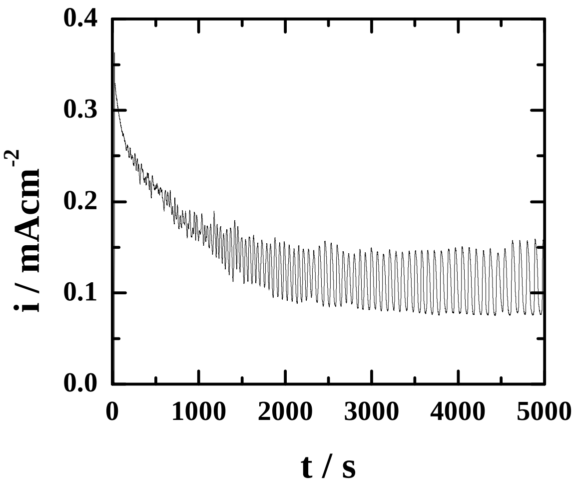

Figure 1. Chronoamperometric response of the platinum electrode, polarized at 950 mV and rotating at 1000 rpm, in CO saturated 0.1 molL^{-1} $HClO_4$ solution.

The main differences observed in the voltammograms when the electrode is rotating or stationary are related to the potentials were the peaks for CO oxidation are observed, i.e. they are displaced to more positive potentials for the rotating electrode, and to the behaviour when the electrode is cycled many times. In the last case, the voltammograms for the rotating electrode are quite repoducibles. For the stationary electrode the response is affected by a depletion of the CO on the electrode surface. According to the voltammetric results it seems reasonable to propose that the effect of the rotation is to maintain a high concentration of CO on the surface of the electrode, which makes possible the mutual influence of two adsorption processes (CO and OH adsorption). The absence of current oscillations when the electrode is stationary may be then related to the low solubility of CO in acid electrolytes (0.96x10^{-3} molL^{-1}), which slows the replenishment of the CO consumed at the surface. The maintenance of a high availability of CO on the surface, promoted by the rotation of the electrode, is essential to make the CO adsorption process interact with the formation of oxygenated species, leading to the oscillatory phenomenon.

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