Experiments and bifurcation modelling of the oscillatory oxidation of HCHO on Pt

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The electrocatalytic oxidation of formaldehyde on platinum exhibits an intruiging dynamical response under certain conditions. More specifically a variety of spatial and temporal patterns have been observed under potentiostatic or galvanostatic conditions, such as bistability, periodic and chaotic oscillations, synchrony and intermittency [1]. In order to interpret the observed dynamical phenomena a dual path mechanism has been proposed. According to this mechanism, adsorbed HCHO molecules are oxidized to CO_2 via a direct and an indirect path [2].

In the present work an attempt is made to interpret the bifurcations that take place under galvanostatic conditions by considering the applied current as a bifurcation parameter. Thus, the oscillatory electrocatalytic oxidation of HCHO on Pt is studied experimentally and a bifurcation diagram is constructed, where the regions of steady state and oscillatory behavior can be observed . Also one can observe the presence of bistability between a stable limit cycle and a steady state for certain values of current as well as a hysteresis in the reappearance of oscillatory behavior as the applied current decreases.

Subsequently, the dual path mechanism is modified by considering the desorption of adsorbed CO and the formation of higher valent oxides at high potentials. Based on this new mechanism a mathematical model is proposed, in which Frumkin kinetics is presumed for all adsorbed species. The proposed model is studied numerically and a theoretical bifurcation diagram is obtained. In this diagram one can notice the existence of a Hopf bifurcation as well as two saddle - node bifurcations which provide sufficient information about the observed experimental dynamical response [3].

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