

STUDY OF Bi, Re ADATOMES ON
POLYCRYSTALLINE RHODIUM
ELECTRODE IN PHOSPHATE MEDIUM.

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The underpotential deposition (UPD) of metal on foreign metal substrates has been studied with a wide variety of electrochemical and spectroscopic methods. In particular, the electrodeposition of Bi, Pb, Cd, on rhodium in the oxidation of formic acid has received a great deal of attention using technique IR "in situ" : Electrochemical Modulated Infrared Reflectance Spectroscopy (EMIRS) (1,2). This interest stems from a recognition of the influence fractional monolayer UPD may have on electrodes substrates in applications for electrocatalysis of electrosynthetic and fuel cell reactions, corrosion inhibition, etc. In this work, we report the effects of bismuth and rhenium adatoms on rhodium on hydrogen adsorption-desorption, formic acid and butane oxidation in solution of phosphoric acid.

The effect of UPD had been monitored by cyclic voltammetry using both, stationary and rotating disk electrode and potential step techniques.

Experimental: The blank solution was 0.5 M H_3PO_4 . Electrolytic solutions were prepared from ultrapure water (Millipore) and analytical grade $Bi(ClO_4)_3$ and $ReCl_3$ (Aldrich). A smooth Rh plate (0.25 cm^2) was used as a working electrode and the reference electrode was a RHE. The counter electrode was a Pt sheet.

Results and discussion : The Fig. 1 shows the effects of Bi and Re on the adsorption - desorption states of hydrogen on rhodium electrode at concentration of 10^{-3} M and 10^{-5} M respectively (optimal concentration for catalytic activity in electrooxidation of formic acid). It is very interesting remark the differences in the behaviour of these adatoms. Bi adatoms suppress the hydrogen adsorption / desorption charge at 10^{-3} M , the features of the cyclic voltammograms resemble that obtained in report ref 1. Re adatoms is more selectively, it suppresses the weak hydrogen (H_w) desorption and the others hydrogen adsorption - desorption charge to maintain a constant hydrogen coverage. These results were affected by the limits of cathodic potential and sweep rate program.

The number of rhodium sites $N_{Rh/X}$ occupied by Bi and Re was determined for the relation (3)

$$N_{Rh/X} = (Q_H^S - Q_H) / e$$

Q_H^S : charge Rh/X electrode, Q_H charge clean electrode, x : Bi, Re.

The approximate value for Bi is 3 in agreement with the ref 1,3. The approximate value for Re is 2.4.

The effects of these adatoms on the adsorption - desorption of hydrogen, formic acid and butane oxidation will be discussed.

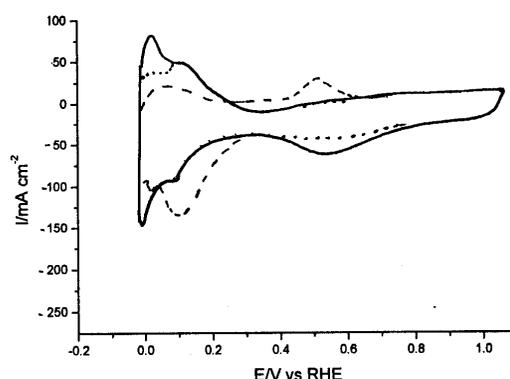


Fig. 1. Voltammograms of Rh electrode at a sweep rate of 50 mVs^{-1} in $0.5\text{ mM } H_3PO_4$ at $20\text{ }^\circ\text{C}$. a) Without adatoms, b) (----) 10^{-3} M Bi , c) (...) 10^{-5} M Re .

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References.

- 1.-M. Choy M., B. Beden, F. Hahn and C. Lamy, J. Electroanal. Chem., 1988, 249, 265.
- 2.-M. Choy M., Ph. D. Thesis, Université de Poitiers, Poitiers, France, 1989.
- 3.-S. Motoo and M. Shibata, J. Electroanal. Chem., 107 (1980) 159-164.