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General Character of Electrochaemically Adsorbed Cobalt on Smooth Platinum in Solutions of Various pH

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The adsorption of cobalt adatoms on to a smooth platinum electrode at different potentials was studied by voltammetric methods. The amount of cobalt coverage was determined from the hydrogen region of the platinum electrode. The number of electrons per adatom species was calculated. The experiments were carried out in the pH interval between 0-3 in H_2SO_4-containing solutions.

Introduction

It is well known that platinum adatom systems may indicate an activity higher than that of polycristalline platinum for various electrochemical oxidation reactions. There are different models for the mechanisms of the catalysis effects of adatoms. Enhancement of the activity of polycrystalline platinum by adsorbed bismuth, tin and lead in the electrooxidation of methanol, etylene-glycol and formic acid has been described in several papers[1–8]. There have also been studies conducted on Pt-Co adatom systems. The Pt-Co system is one of those platinum bimetallic systems that have been examined in view of both ctalytic and magnetic properties, Pt and Co form substitutional alloys and ordered compounds, although so far only random substitutuonal plases have been observed as the surface structure[9]. It has been observed that bimetallic Pt-Co catalysts are very effective and selective in the reduction of aldehyde[10]. However, adsorption of the Co atoms on the platinum electrode has yet to be studied. The present study deals with the electrochemical adsorption and catalytic behaviour of cobalt atoms on a smooth platinum surface.

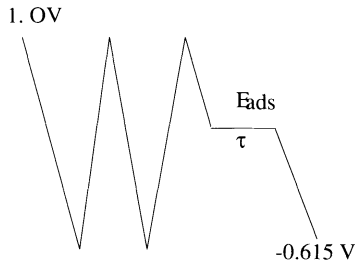
Experimental

All electrochemical measurements were conducted at 25 °C. The working electrode was a microsphere made of 0.5 mm diameter wire of a high purity platinum metal (Johnson Matthey) which has an active surface of about 0.25 cm^2. The counter electrode was a platinum wire with cylindrical geometry. A $Hg/HgSO_4$ (sat.) mercurous sulphate electrode (MSE) was used as a reference electrode. The electrolytic solutions were prepared with ultrapure water obtained from a Millipore Milli-Q system, and from chemical materials such as $CoSO_4.7H_2O$ (Merck pro-analysis).

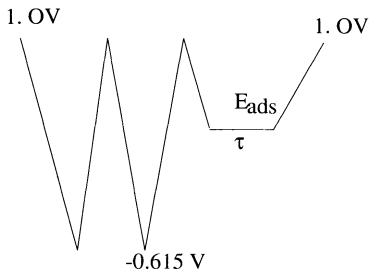
Linear cyclic and programmed potential voltammetry were used throughout this work. The electronic appparatus consisted of a Wenking Potentiostat, a GSTP Tacussel function generator, a Nicolet 400 Storage Oscilloscope and a Kipp-Zonen X-Y analog recorder.

Before the experiments, the working electrode was activated for 30 minutes between -615 mV and 1000 mV (MSE) in 0.5 M H_2SO_4 solution.

Two different potential-time programs were used in the experiments. Adsorption kinetics and adsorption isotherms were calculated using the first of these programs. The number of electrons per occupied site was calculated using the second program to avoid the effect of adsorbed hydrogen on Co atoms.



Program 1



Program 2

Results

Figure 1 shows voltammograms taken using the platinum electrode in the presence and absence of adsorbed cobalt at -215 mV (MSE) in 0.5 M H_2SO_4 solution. It can be seen that cobalt atoms were adsorbed on the electrode during application of potential program 1. Adsorption time and adsorption potential were 15 minutes and -215 mV, respectively. The chosen adsorption potential is more positive than the reversible potential of Co deposition, and hence a multilayer deposition of Co was not layer region of platinum.

As can be seen from Figures 1 and 2, the degree of hydrogen displacement depends on cobalt coverage. The positions of hydrogen adsorption peaks on Pt are invariant in the presence of various values of surface coverage. This may be introduced as evidence that a Co adatom covering one or more Pt atoms does not affect the neighbouring Pt atom. On that atom, hydrogen adsorption occurs as on a cobalt-free platinum surface. A suppression of hydrogen adsorption on Pt by smaller atoms occurs at the ratio 1:1 [11]. The formation of oxide on platinum also appears to be affected by the adsorbed cobalt atoms. Adsorbed cobalt atoms were oxidised during the positive sweeps between the potentials of 0.38 and 0.75 V to give a broad peak at 0.7 V. In order to observe the effect of the adsorption potentials, the first cycle of the anodic voltammograms were taken at different adsorption potentials (Figure 2). The amount of adsorbed cobalt increases at more cathodic adsorption potentials than -215 mV vs. MSE. This may be observed with increasing Q_{anodic}. The surface of the electrode becomes completely clean at the end of one cycle. This means that adatoms have completely oxidised and reducted during positive and reverse sweep, respectively. The reduction peak

observed is greater than that in the case without adatom mediums throughout the cathodic sweep. This increase of the quantity of electricity may be associated with the reduction of oxidised Co atoms.

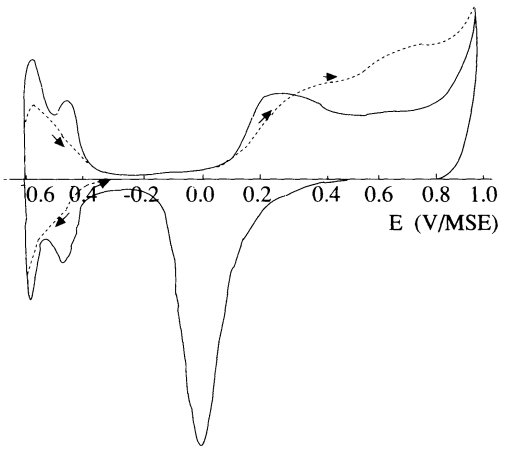


Figure 1. —— Standard voltammogram of smooth Pt in 0.5 M H_2SO_4 – – – – – – After deposition of cobalt for 15 minutes at -215 mV (10^{-4} M Co^{2+})

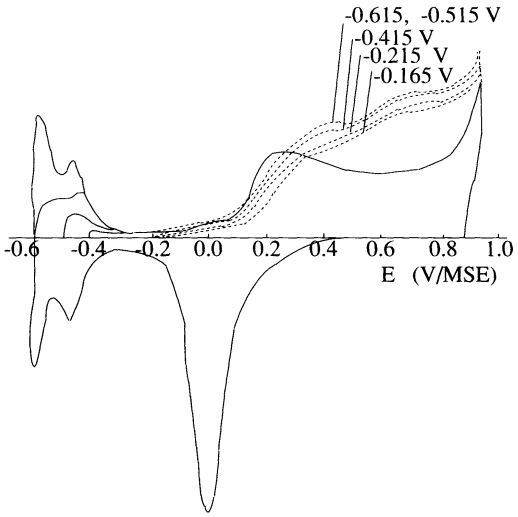


Figure 2. —— Standard voltammogram of smooth Pt in 0.5 M H_2SO_4 – – – – – – After deposition of cobalt for 15 minutes at different potentials (10^{-3} M Co^{2+})

The kinetics of cobalt adsorption

The coverage of surface (θ) has been calculated from the hydrogen region of platinum according to the following equation:

$$\theta = (Q_H^0 - Q_H^{Co})/Q_H^0$$

where θ is the amount of coverage, Q_H^0 is the load in the hydrogen region at the support media, and Q_H^{Co} is the load in the hydrogen region after adsorption of cobalt.

The kinetics of cobalt adsorption have been studied at -215 mV as a function of adsorption time in a solution containing 10^{-3} M Co^{2+} (Figure 3). A linear relation has been found between the coverages and the logarithm of time (Figure 4). This plot can be explained using the Roginsky- Zeldowich Epuation:[12]

$$\theta = B + (1/\alpha f)\ln t$$

where α is the transfer coefficient, and f is the inhomogenity factor.

The coverage of cobalt attained a constant value of (0.45) after 20 minutes. θ was also calculated as a function of Co concentration after a 15 minute adsorption time at -215 mV. The coverage attained equilibrium when the concentration of cobalt was equal to or greater that 10^{-4} M (Figure 5). All the θ values were calculated using the first cycle of the voltammogram.

The effect of the adsorption potential on the surface coverage degree was also studied, and θ=0.5 was obtained for E_{ads}=-615 mV (Figure 6).

It is possible to calculate the number of electrons per occupied site (n_e):

$$n_e = \Delta Q_0/\Delta Q_H$$

where

$$\Delta Q_0 = Q_0^{Co} - Q_0^0 \text{ and } \Delta Q_H = Q_H^0 - Q_H^{Co}$$

Here, Q_0^0 and Q_0^{Co} are anodic oxidation charges obtained in the presence and in the absence of adsorbed Co, respectively. Q_H^0 and Q_H^{Co} are the charges corresponding to the hydrogen desorption in the absence and presence of Co atoms, respectively.

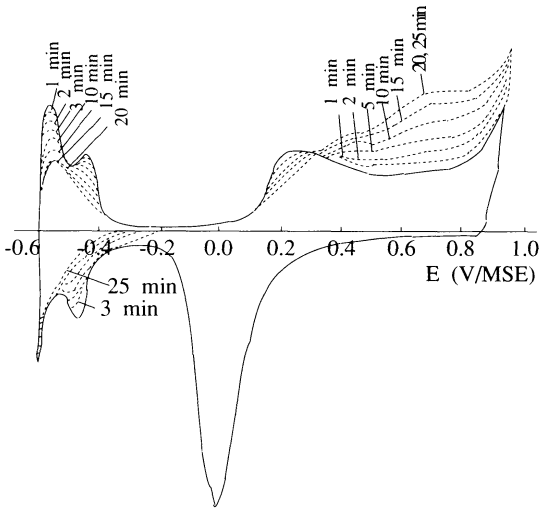


Figure 3. —— Standard voltammogram of smooth Pt in 0.5 M H_2SO_4 – – – – – – After deposition of cobalt for different adsorption times at -215 mV

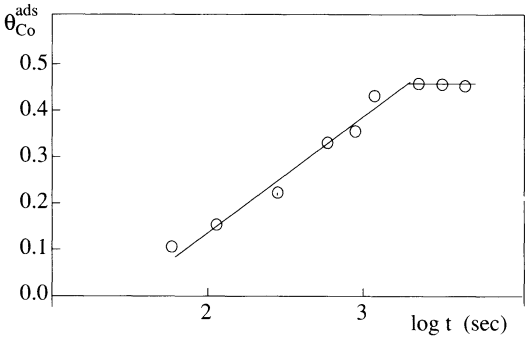


Figure 4. Relationship between the surface coverage and logarithm of adsorption time (E_{ads} =-215 mV/MSE (10^{-3} M Co^{2+})

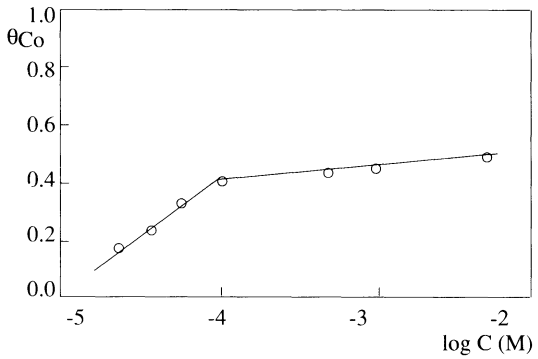


Figure 5. Plot of the θ_{Co} as a function of logarithm of cobalt concentration

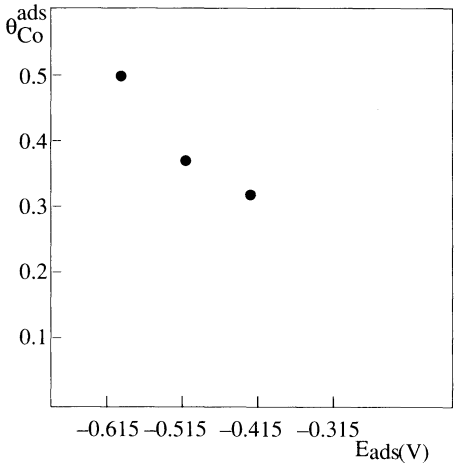


Figure 6. Plot of the ratio of the number of electrons to the amount of general adsorption sites as a function of adsorption potentials

Figure 7 shows the variation of the number of electrons per site with the logarithm of adsorption time. The value of n_e is 3 for shortened adsorption times. This value increases up to 4.5 with increasing time. An n_e value of greater than 3 may indicate the formation of Co clusters or a multilayer Co deposition. Initially, cobalt atoms would be adsorbed on the surface of the platinum electrode to form a monolayer; subsequent adsorption of cobalt would occur on this covered surface.

Figure 8 shows the plot of number of electrons per site for 10^{-3} M Co^{2+} as a function of the adsorptio potential values at different pH. n_e values were found to be pH dependent: When pH increases, dependenc of the adsorption potential of n_e decreases.

It is possible to determine the adsorption rate constant according to the following equation:

$$K_{ads} = [V_{ads}/C](S^{-1})$$

where

$$V_{ads} = d\theta/dt(mol1^{-1}S^{-1}),\ \text{C: concentration (M)}$$

The adsorption rate constant was calculated at a constant θ value ($\theta = 0.1$) for each pH (Table 1).

Table 1. Some properties of Pt-Co system at different pH (E_{ads} =-215 mV (MSE) and $C_{Co}^{2+} = 10^{-3}$ M)

pH	$t_{limit}(min)$	n_e	k_{ads} (at $\theta = 0.1$)
0	20	1.95	1.45 S^{-1}
1	10	2.10	3.73 S^{-1}
2	8	1.98	5.01 S^{-1}
3	6	2.20	180.9 S^{-1}

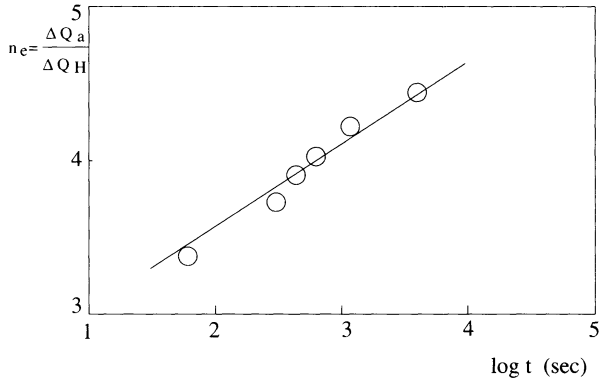


Figure 7. Plot of the number of electrons changed per site as a function of logarithm of time (E_{ads}=-215 MV/MSE, 10^{-3} M Co^{2+} in 0.5 M H_2SO_4)

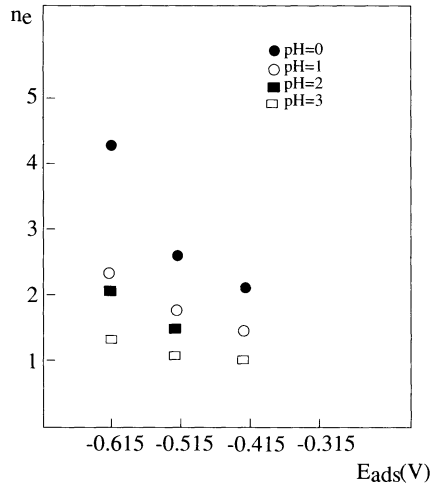


Figure 8. Plot of the number of electrons per site with different adsorption potentials in solutions

It was observed that the n_e values are close to those needed to obtain a coverage of $\theta = 0.1$. However, limit adsorption times to attain this coverage were different at each pH and decreased with increasing pH. The adsorption rate constant of Pt-Co system also increased with pH.

Conclusion

Co adatoms do not affect the properties of neighbouring bare platinum atoms. This is proven by the fact that for varying coverage of Co on Pt, the positions of hyrogen adsorption peaks do not change with the amount of adsorbed hydrogen.

The results indicate that the rates of adsorption of cobalt on platinum electrode increase with increasing pH at the same potentials. This shows that fractional coverage is affected by OH^- ions. The values of n_e do not depend on the pH (pH= 0-3) for the same concentration of cobalt and the same adsorption potential (Table 1).

The adsorbed adatom layers are oxidised completely until 950 mV vs. MSE at lower concentrations of cobalt.

Depending on the experimental conditions, cobalt adatoms may form an adsorption centre (site) or clusters on the platinum electrode surface at the values of $\theta \leq 1$.

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