Autoradiographic Studies on the Effect of Cathodic Prepolarization on Metallic Surfaces

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The effect of cathodic prepolarization of platinum, gold and silver electrodes has been studied. It has been found in all cases that the velocity of the spontaneous deposition of Po is greater on a prepolarized than on a non-polarized electrode. Studies of the histograms of the α -particles of Po showed a relative increase of the apparently shortened trajectories in case of the previously polarized electrodes.

The effect of prepolarization on the process of electro-deposition of radio-elements was noticed by Haissinsky¹ in a study of the cathodic deposition of ThC on a gold electrode. The curve representing the quantity deposited in function of time manifested a maximum which indicated the possibility of a change of the state of the cathodic surface during electrolysis. In fact he noticed moreover that if the electrolysis is carried out under the same conditions, using a fresh electrode in a solution exempt from the radio-element, and then the radio-element is added while continuing the electrolysis, the maximum disappears and the deposition curve has a normal form. Since then the same author and his collaborators studied different aspects of this interesting phenomenon. Danon and Haissinsky² have indicated that the Nernst law is not applicable to the deposit of RaE (10^{-16} M) on a gold cathode in nitric acid solution except after prepolarization of the electrode. Haissinsky and Coche³ have found, in the case of the cathodic deposition of Po on tantalum, a modification in the form of the deposition curve as well as a displacement of the critical deposition potential towards more positive values as a result of the prepolarization of the electrodes. Ferradini⁴ has observed a spontaneous deposit of Pa on platinised platinum which was prepolarized anodically. Finally our recent studies⁵ on Rd-Ru have shown that prepolarization of the cathode plays a decisive role on the electro-deposition of this radio-element. In all cases studied, except for platinised platinum, there is practically no

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deposit at ordinary temperature without prepolarization, while after prepolarization under favourable conditions practically quantitative deposits can be obtained.

The object of this study is to provide a direct evidence of the modification of the metallic surface produced by the cathodic prepolarization of metallic electrodes.

EXPERIMENTAL

In the present work we have used the autoradiographic method which has been previously utilized by Haissinsky *et al.*⁶ in their studies of the metallic surfaces.

In our experiments we have studied the spontaneous deposit of Po on prepolarized and non-polarized platinum, gold and silver electrodes. All the electrodes were pure and electro-polished thin metallic foils. They were further purified chemically. Platinum electrodes were ignited in an oxidising flame and then boiled with concentrated nitric acid while gold electrodes received the nitric acid treatment only. Silver electrodes were purified by introducing them rapidly for a few times in 50 % HNO_3 . The water used for washings and preparation of solutions was bidistilled and different reagents were of analytical purity.

Prepolarization was effected by electrolysing 10 ml of $\text{N H}_2\text{SO}_4$ using these electrodes as cathodes while separating the cathodic from the anodic compartments by an appropriate electrolytic bridge. The anode was a thin platinum wire. Concerning conditions of prepolarization, *cf.* Table 1.

Table 1. Conditions of prepolarization.

Metal	Current density (in mA/cm^2)	Time, h	Temperature, $^{\circ}\text{C}$	Approximate cathode potential, V
Pt	500	5	85	-2
Au	2.7-1.3	48	ordinary	-0.6
Ag	2-1	48	ordinary	-0.7

Each polarized electrode was washed and introduced together with a non-polarized foil into 10 ml of a normal sulphuric acid, 10^{-12} N in Po, for 20 h. The solution was stirred mechanically while the two foils were kept at equal distance from the stirrer. Each foil was washed and dried and an α -nuclear plate, Ilford C₁ 50 microns then applied for an hour to the surface that was opposite to the stirrer. The plates were then developed by the appropriate photographic technique⁷ and then examined under a microscope.

RESULTS

The microscopic examination of the nuclear plates consisted of establishing the topographic distribution of the trajectories of the α -rays on the metallic surface, by counting their number per field of vision of the microscope (150 fields studied for each plate) and by measuring the ranges of the α -particles in the gelatine (300 per plate). In these studies we have limited our measurements of ranges to the horizontal tracks, *i. e.* those for which practically the total length is visible for the same focussing.

Fig. 1. Prepolarized Pt foil.

Fig. 2. Non-polarized Pt-foil.

Our results show that:

a) The tracks are distributed in all cases at random. No privileged accumulation of the deposited Po atoms was found at certain points of the surface, as was found ⁶ in case of Po in HNO₃ and ²³⁹Pu and ²³⁵U in hydrochloric and nitric acids, respectively ⁸.

b) The velocity of the spontaneous deposition of Po is always greater on a prepolarized than on a non-polarized foil, the ratio between the two velocities being 2 for Pt, 1.64 for Au and 1.75 for Ag.

Figs. 1 and 2 represent, for example, two fields of vision, the first for a prepolarized Pt foil and the other for a non-polarized one.

c) The curves A and B of Figs. 3, 4 and 5 represent the distribution of the ranges of the α -particles of the spontaneously deposited Po atoms on Pt, Au and Ag foils, respectively; A for the non-polarized foils and B for the prepolarized ones.

DISCUSSION

The results obtained indicate that the most probable range of the α -particles of Po in Ilford C₂ plates is $21 \pm 1 \mu$ which is in good agreement with the value found previously ⁶.

The study of the histograms in Figs. 3, 4 and 5 representing the distribution of the ranges of the α -particles of Po shows that the curves are deformed in the case of the prepolarized foils. This deformation corresponds to a relative increase of the apparently shortened ranges. Apparent shortening of the ranges of the α -particles of Po spontaneously or electrolytically deposited on metallic surfaces has been attributed by Haissinsky *et al.*⁶ to penetration of a certain number of Po atoms into the surface. In a recent work ⁸ on the adsorption of Pu on glass and metallic surfaces we admitted that back-scattering of the α -particles from the carrying surface may, together with the penetration factor,

Fig. 3. Histograms of α -particles of Po on platinum foils.

Fig. 4. Histograms of α -particles of Po on gold foils.

play a role in the phenomenon of apparent shortening. However, the observed increase in the apparent shortening in case of prepolarized electrodes cannot possibly be due to an increase in back-scattering since the only possible chemical change of the metallic surface in our experimental conditions would be the inclusion of hydrogen under one form or another. It seems therefore more plausible to suppose that cathodic prepolarization leads to a micro-deformation of the metallic surface connected with the formation of ultramicro pores or lacunae which would facilitate the penetration of a further number of the deposited atoms into the surface. Such deformation may be due to adsorption and desorption of hydrogen, or to the possible formation of a trace of a hydride which may be hydrolysable as in the case of Pt and Pd, or volatile as in the case of Pb and which would as such separate from the surface.

The increased heterogeneity of the metallic surface connected with a more favourable distribution of "active centres" would in general explain the observed effects of prepolarization on the spontaneous and electro-deposition of radio-elements. The higher velocity of spontaneous deposition of Po on prepolarized electrodes may thus be attributed to the increased number of "active centres". A similar explanation might account for the more positive critical deposition potential of Po on prepolarized tantalum. However, in certain particular cases, the chemical changes of the surface have to be taken into consideration together with the physical changes. Such is for example the case of the spontaneous deposition of Pa on anodically prepolarized platinum where atomic oxygen is supposed to play a role⁴. It is again equally important, for the explanation of the induction period in the cathodic

Fig. 5. Histograms of the α -particles of Po on silver foils.

deposition of Rd-Ru, to consider the possible accumulation on the cathodic surface of atomic hydrogen which would effect the reduction of the strong Ru complexes to more easily reducible forms ⁵.

Finally segregation of Po in HNO_3 , as well as of Pu in HCl and U in HNO_3 solution, on metallic and / or glass surfaces was attributed to the possibility of existence of particularly privileged regions having a relatively high energy of adsorption ⁸. However, the absence of the segregation phenomenon in case of Po in $\text{N H}_2\text{SO}_4$ solution, as has been indicated in the present work, seems to suggest that, in addition to the distribution of the energy of adsorption on the metallic surface, one has to consider the role of the solvent and probably also the nature of the deposited atoms.

Acknowledgement. I should like to express my deepest thanks to Professor M. Haissinsky for his continuous advice and encouragement, and to Mademoiselle Albouy for her help concerning the autoradiographic technique.

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Received December 18, 1956.