

## SHORT COMMUNICATION

# POTENTIODYNAMIC OXIDATION OF ABSORBED AND ADSORBED HYDROGEN ATOMS ON GOLD PROMOTED BY THE DYNAMIC AGEING OF THE OXYGEN CONTAINING LAYER

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Neither hydrogen absorption nor hydrogen adsorption occurs on gold in contact with hydrogen gas[1]. However, it has been recently reported that a gold electrode in aqueous acid solution after it has been potentiostatted for several minutes at a cathodic potential where the net hydrogen evolution takes place, is able to display, under an anodic linear potential sweep an anodic current contribution which is related to absorbed and adsorbed hydrogen[2-5]. These electrochemical characteristics have been also correlated to the optical properties of the electrode surface[2,5]. Furthermore the oxidation of molecular hydrogen on gold[6] as well as the corresponding  $H_2/H^+$  thermodynamic value[7] have been also studied.

This communication describes the application of the multiple train of triangular potential sweeps (Fig. 1) to promote the development of the hydrogen atom electro-oxidation current peaks on gold in acid solution. This perturbation technique has been recently reported to produce the so-called dynamic ageing of the oxygen containing monolayers on various noble metals[8,9].

The perturbation profile (Fig. 1) consists of a combination of repetitive triangular potential sweeps. The switching potentials  $E_{\lambda,c}$  and  $E_{\lambda,a}$  are located, respectively, in the potential region of the hydrogen evolution reaction and in the potential region preceding the oxygen evolution, where the oxygen-containing layer is electrochemically formed. The

intermediate perturbation which last a lapse  $\tau$  is constrained between the switching potentials  $E_{\lambda,a}$  and  $E'_{\lambda,c}$ . During the time  $\tau$  a fraction of the oxygen-containing layer is removed from the surface and reformed periodically. Only the potentiodynamic  $E/I$  profiles which are numbered in Fig. 1 are recorded.

The  $E/I$  displays obtained in 1 M  $H_2SO_4$  at 25°C after the intermediate perturbation (Figs 2 and 3) are remarkably different from the stabilized  $E/I$  profile (1), as  $\tau$  increases the following changes are noticed. The cathodic charge related to the electroreduction of the oxygen containing layer (which is larger than that expected for the electrosorbed oxygen) slightly increases and simultaneously the corresponding current peak becomes sharper and its potential more cathodic. This effect has already been described as a dynamic ageing of the oxygen containing layer[8]. Moreover, as  $\tau$  increases the current associated to the evolution of hydrogen increases. Then, the intermediate perturbation in the anodic potential range produces a noticeable depolarization for the hydrogen evolution reaction at the cathodic switching potential. But the most important feature is the appreciable anodic current in the  $-0.02$  V to 0.68 V potential range. This current contribution which is quite likely the sum of two anodic current peaks is exactly coincident with that recently reported by Chao and Costa[2-5] after continuously cathodizing polycrystalline gold in  $H_2SO_4$  solutions for a relatively long

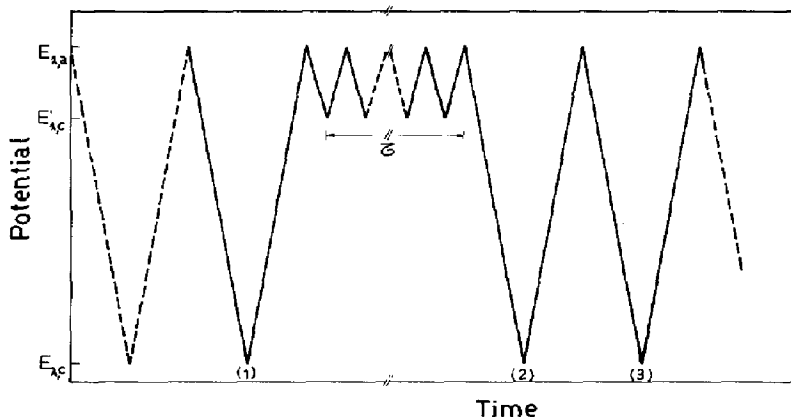


Fig. 1. Potential perturbation programme.

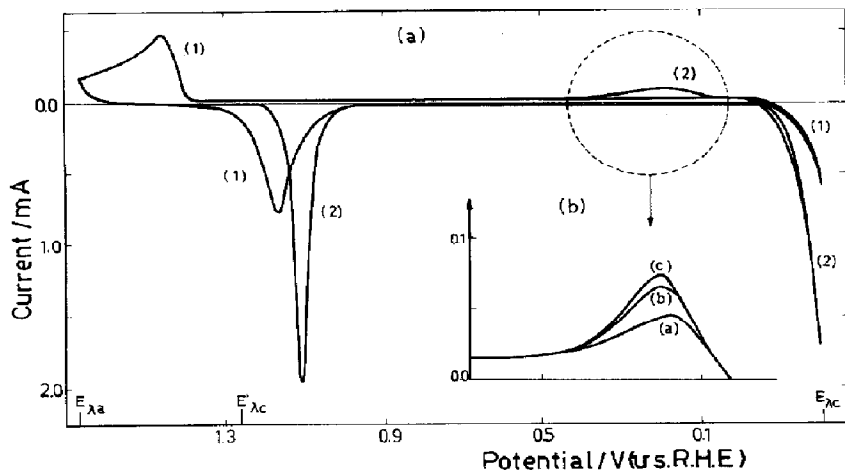


Fig. 2. (a) Potentiodynamic  $E/I$  displays run at 0.2 V/s according to the perturbation programme shown in Fig. 1. The intermediate perturbation was run at 0.2 V/s and  $\tau = 30$  min.

(b) Anodic  $E/I$  displays for the potentiodynamic electrooxidation of hydrogen at 0.2 V/s after the intermediate perturbation at different  $\tau$ . (a)  $\tau = 10$  min; (b)  $\tau = 20$  min; (c)  $\tau = 30$  min.

time. It corresponds to absorbed and adsorbed atomic hydrogen on gold. In the following potential sweeps (4), (5) and so on, one observes that progressively the new anodic current peaks and the cathodic current related to the hydrogen evolution disappear simultaneously.

The potential sweep rate of the intermediate perturbation as well as  $E_{\lambda,a}$  and  $E_{\lambda,c}$  have an appreciable influence on the features of the  $E/I$  profile already described. Thus, for the same  $E_{\lambda,a}$  and  $E_{\lambda,c}$  switching potentials, practically no activation in the hydrogen reaction potential range is obser-

ved at  $v = 20$  V/s after cycling during 5–10 min. It is interesting to note that the maximum depolarizing effect for the hydrogen discharge and also the largest charge pertaining to the electrooxidation of adsorbed and absorbed hydrogen is achieved when the intermediate potential perturbation removes and reforms during each cycle half of the oxygen containing layer. It also appears that the larger the activation for the hydrogen electrode reaction, the smaller the ageing effect in the potential range of the electroadsorbed oxygen layer is. Thus, the activation effect depends directly on the surface

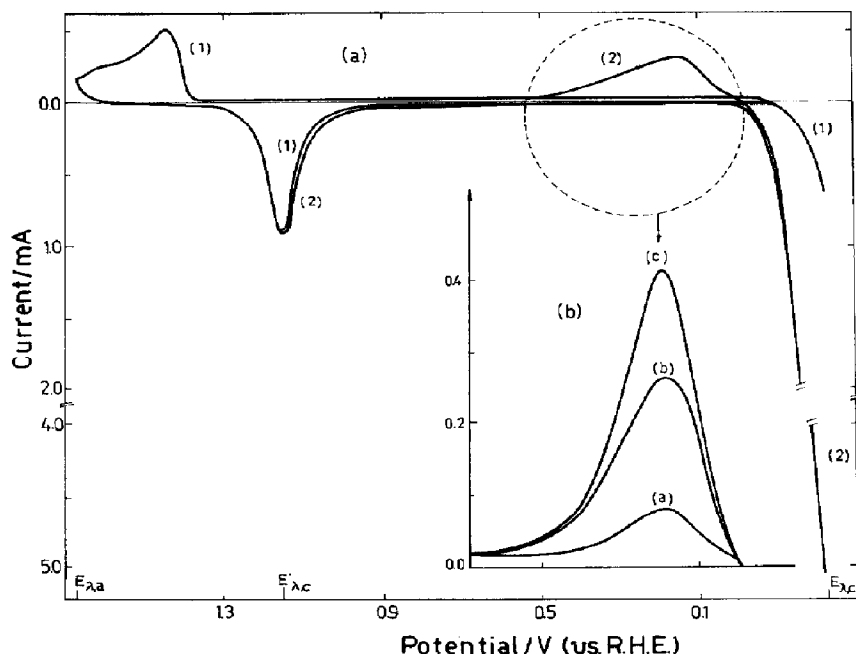


Fig. 3. (a) Potentiodynamic  $E/I$  displays run at 0.2 V/s according to the perturbation programme shown in Fig. 1. Influence of the switching potential of the intermediate perturbation.  $\tau = 30$  min.

(b) Anodic  $E/I$  displays for the potentiodynamic electrooxidation of hydrogen at 0.2 V/s after the intermediate perturbation at different  $\tau$ . (a)  $\tau = 10$  min; (b)  $\tau = 20$  min; (c)  $\tau = 30$  min.

concentration of the non-equilibrium states related to the oxygen-containing layer achieved during the intermediate perturbation.

The influence of any electrode roughness mainly produced by the electro-dissolution of the metal seems rather unlikely because this charge balance as well as the values for the anodic and the cathodic charges determined from the stabilized potentiodynamic profiles before and after the intermediate perturbation period, are satisfactorily reproducible. Therefore, the dynamic ageing of the oxygen-containing layer promotes the activation of gold for the hydrogen adatoms adsorption and absorption. During the dynamic ageing it is most likely that a fast reconstruction of the gold surface takes place together with a minor electro-dissolution of the bare metal[10]. This apparently is also obtained after a number of conventional triangular potential sweeps, where it has been optically shown that the original gold surface is transformed into a structured surface similar to thermal faceting[11]. An equivalent effect is also produced on platinum[12, 13]. The effect of a rapid short potential range intermediate perturbation is explained with the model proposed by Schultze and Vetter[14]. Accordingly, the fast perturbation assists and magnifies the mobility of metal atoms during their delocalization during the oxygen desorption. The anisotropy of the metal surface energy is induced by adsorbed oxygen. Therefore, the surface reconstruction influences equally both the processes related to the oxygen-containing monolayer as well as those of the hydrogen electrode reaction.

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