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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

The Electrochemical Behaviour of Gold in Citric Acid Solutions

by

S. BİLGİÇ and M. KABASAKALOĞLU

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lit by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

The Electrochemical Behaviour of Gold in Citric Acid Solutions

S. BİLGİÇ and M. KABASAKALOĞLU

Department of Physical Chemistry, Faculty of Science;
University of Ankara, Turkey

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ABSTRACT

In this study, current-potential curves have been obtained with gold electrode in 0.5 M H_2SO_4 and citric acid solutions by cyclic voltammetry.

In 0.5 M H_2SO_4, the formation potential of oxide film is 1390 mV. Oxygen evolution occurs at 1930 mV. In citric acid, anodic dissolution and film formation proceed together at 1470 mV. Oxygen evolution was not observed in citric acid. In H_2SO_4 anodic charge Q_a is equal to cathodic charge Q_c. However in citric acid $Q_a > Q_c$. In both media cathodic charge and film thickness change linearly with potential. However, film thickness is thinner in citric acid.

INTRODUCTION

Gold anodes exibit a remarkable passivity in aqueous media and in the absence of corroding anions so that gold electrodes are often used in the electrochemical oxidations of different substances. It is already well known that within the potential range of 1.3 to 1.8 V (v.s N.H.E) gold are covered with a monolayer thick oxide film in sulphuric and perchloric acid solutions [1–7]. This range depends on the electrolyte, temperature and potential-time perturbation [7]. The first aim of the present study was to investigate the effect of citrate ion on the electrochemical formation and reduction of oxide layer on gold. As had been shown previously [8–9] that citrate anion can be used as a corrosion inhibitor for aluminum and iron, the second aim was to understand the inhibition mechanism of citrate.

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EXPERIMENTAL TECHNIQUE

The voltametric curves were recorded with a Tacussel type PRT 10–05 potentiostat and Tacussel type EPL 2 recorder. The potential was changed at a constant rate 50 mV /sec, with a potentiometer and a speedbox in response with the potentiostat and the recorder. Measurements were carried out in a three armed pyrex cell. The counter (Pt), the working and the reference electrodes were dipped within the first, second and the third arms respectively.

The stopcock between the counter and the working electrode compartment was kept close during the experiments. The reference and the working electrode compartments were separated from each other by a luggin capillary and a stopcock.

The working electrode was a gold wire (dia 0.5 mm. approximate length 3 cm, purity 99,999 %) obtained from Johnson Matthey Ltd. Before each measurements it was potentiostatted for seven minutes at 1650 mV in 1 N H_2SO_4. Then it was reduced for seven minutes at 300 mV under a flow of purified nitrogen. As a reference electrode saturated calomel electrode was used and all the potentials given in this work are reported relative to the hydrogen electrode. Solutions were prepared by double distilled water and all the chemicals were chemically pure. Nitrogen was bubbled through the solution for 20 minutes before and throughout the experiment.

RESULTS AND DISCUSSION

1. The curves obtained in 0.5 M H_2SO_4:

Fig.1. shows the current-potantial curve obtained in 0.5 M H_2SO_4. To achieve a reproducible electrode surface and hence reproducible curves, the potential was made to vary linearly from the rest potential of pretreated gold electrode in dearated solutions towards to the anodic potentials until oxygen evolution occurred. Then the potential was reversed and changed linearly to the hydrogen evolution. Progressive current-potential curves between hydrogen and oxygen evolution potentials were obtained without-current interruption. After the second run, current potential curves were the same. The second run was used for interpretation in the present study. Oxide formation on gold occur

at 1390 mV (the point A in Fig.1). The oxygen evolution proceeds at potential $E > 1800$ mV. Only one reduction peak was observed between 1390 and 910 mV at room temperature (The region EFG in Fig.1). The double layer region lay between the potentials 260 and 1390 mV in the anodic region. The region IH shows the hydrogen evolution.

As seen from Fig.1, current-potential curves of gold demostrate the strong hysteresis of oxide formation and reduction. As it is expected that the properties of the oxide not only depend on the oxidation potential but also the oxidation time. The current-potential curves up to the various anodic reversal potential ($E\lambda$) towards to oxygen evolution were obtained at constant sweep rate (Fig.2 and 2a).

Fig.3 shows the variation of the cathodic peak current (Ip_c) and potential (Ep_c) with the anodic reversal potential. As the anodic scan limit is increased, the cathodic peak potentials shift toward to more negative values and the cathodic peak current is increased. The shift of the cathodic peak potential and the increase of the cathodic peak current with the anodic reversal potential reveal that the coverage or the thickness of the oxide layer is increased.

2. The thickness of the oxide layer:

Fig.4 shows the variation of anodic and cathodic charges with the potential of anodic scan limit. The amount of Q_a ($\mu C/cm^2$) and Q_c need for anodic formation and cathodic reduction of oxide film were evaluated by a graphical integration of the current-potential curves in Fig.2 and 2a.

As seen from Fig.4 up to the 1650 mV the cathodic and the anodic charges are equal. Similar results have been reported by other investigators [3–7]. At potentials more positive than about 1650 mV, some other electrochemical reaction, like dissolution of metal or oxygen evolution can be thought.

In the present study, the cathodic charges were taken to evaluate the mean oxide layer thickness, L, from the following equation.

$$L = \frac{M \cdot Q_c}{6F\rho}$$

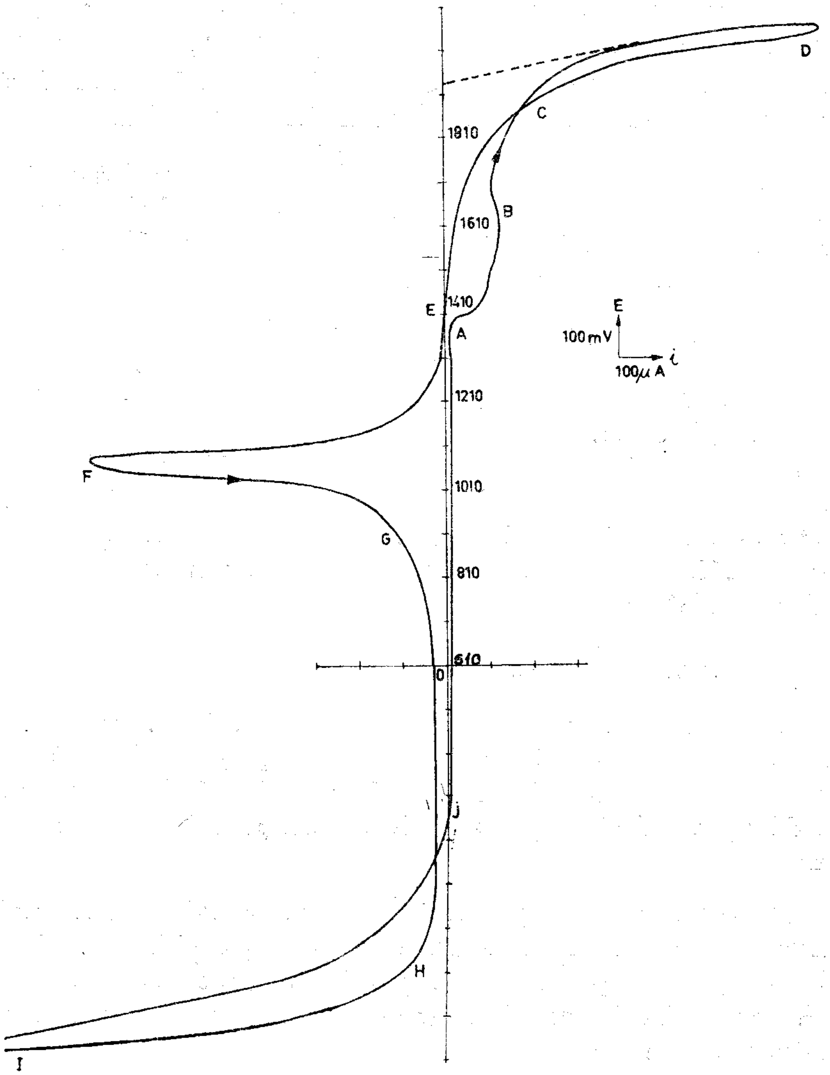

Fig.1. The current-potential curve of gold electrode in 0.5 M H_2SO_4.

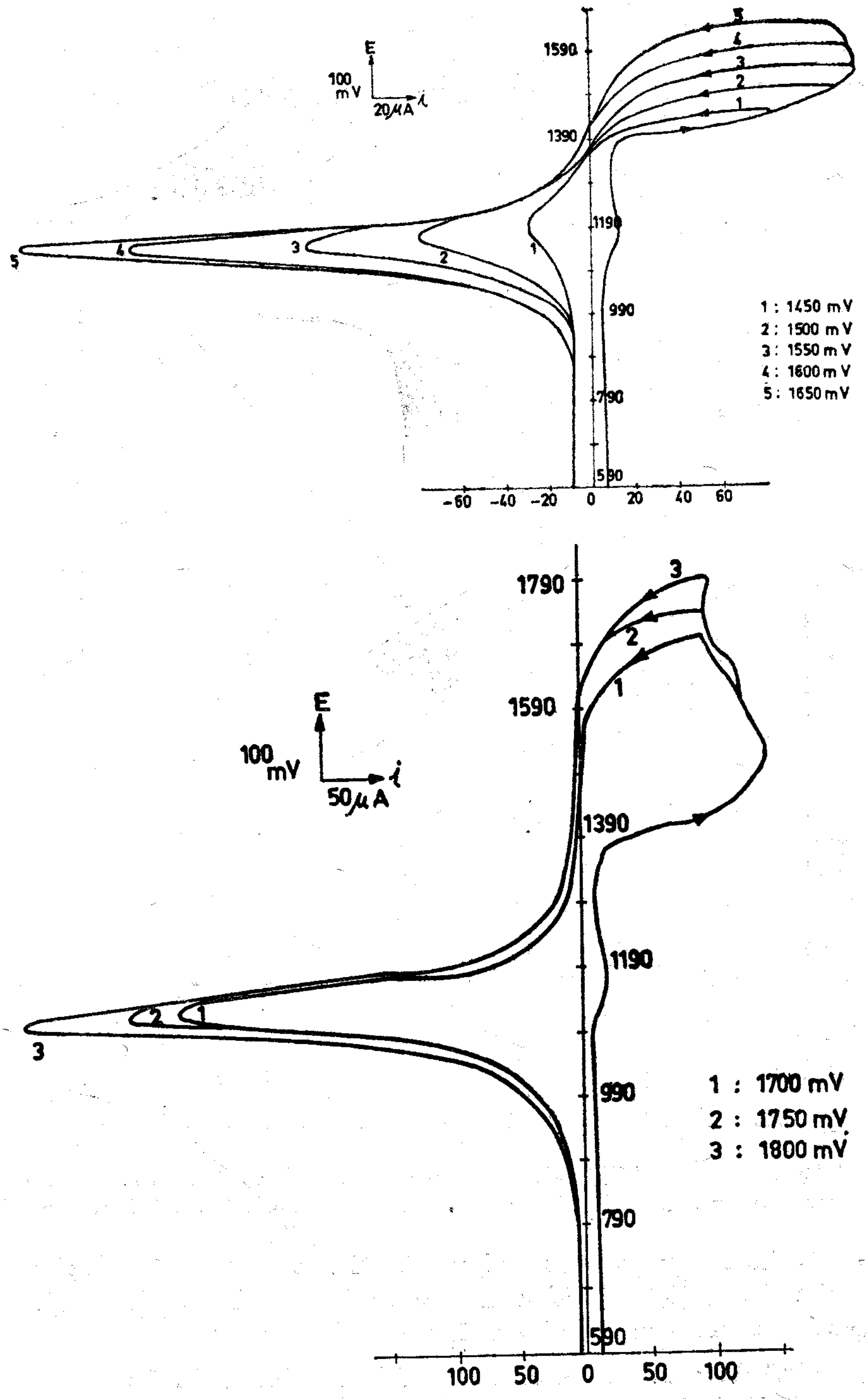

Fig.2. and 2a. The current-potential curves up to the various anodic reversal potential. In Fig. 2 Eλ changes between 1450 mV and 1650 mV. In Fig.2a. Eλ changes between 1700 mV and 1800 mV.

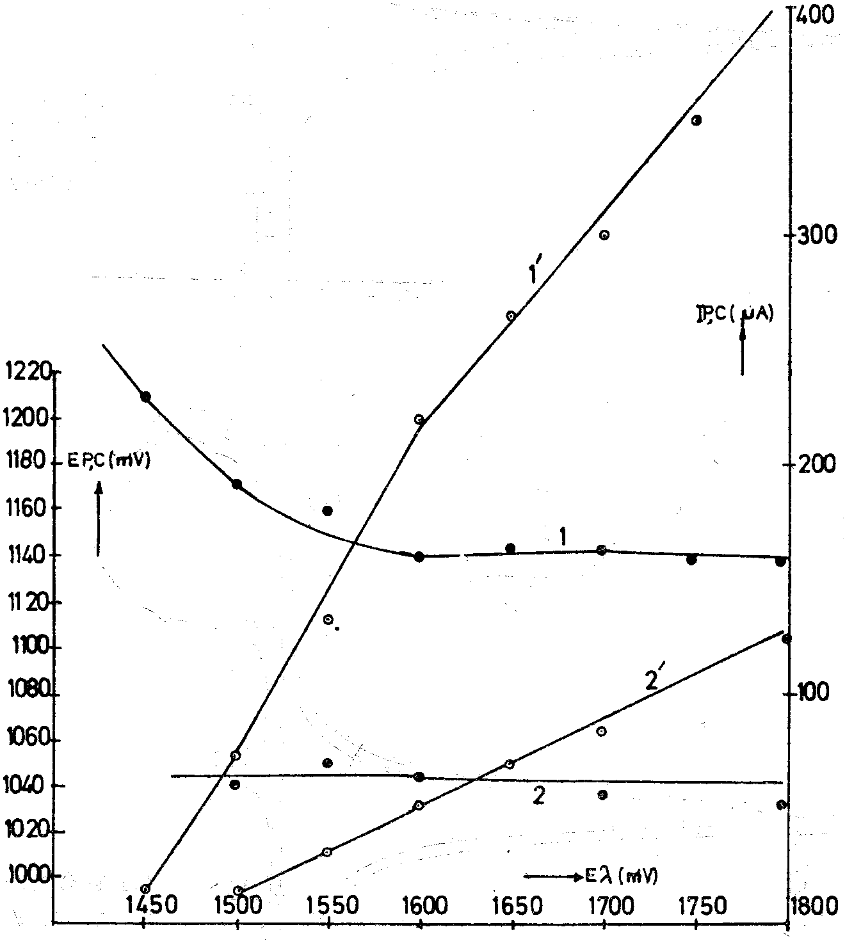

Fig.3. The curve 1 (●) and 1'(⊙). The variantion of Epc and Ipc with Eλ in 0.5 M H_3SO_4 respectively. The curve 2 (●) 2' (⊙). The variation of Epc and Ipc with Eλ in 0.5 M citric acid.

Q_c, is the charge per unit surface area. The oxide layer presumably consists Au_2O_3 [3–7]. (M/ρ) is the molar volume of Au_2O_3. The roughness factor was taken as unity in these experiments.

Fig.5 shows the variation of film thickness with the anodic reversal potential Eλ. This curve shows two different linear regions. The initial oxi-

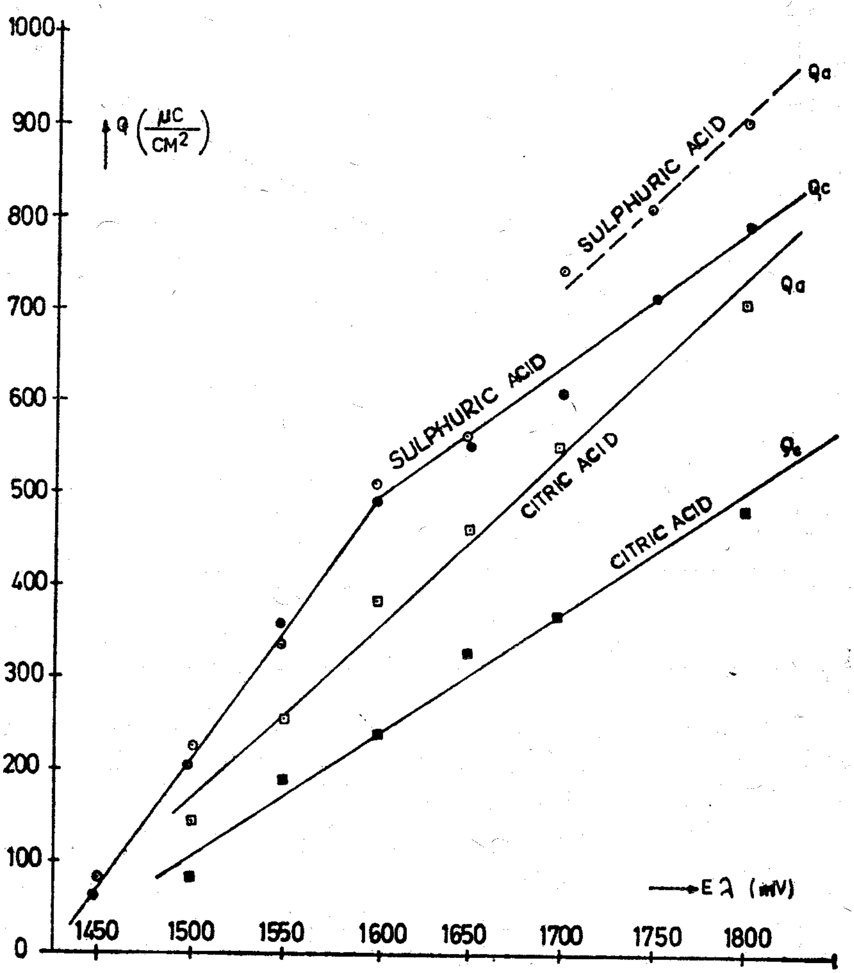

Fig.4. The variation of anodic and cathodic charges with Eλ in 0.5 M H_2SO_4 and 0.5 M citric acid.

de formation region between 1450 and 1600 mV and the further oxide growth (L > 3 A°) between 1600 mV and 1800 mV. The mean field strenght in the oxide can be estimated from the reciprocal slope dE/dL of the curve in Fig.5. The value of $\left(\frac{dE}{dL}\right) = 10^7$ V/cm for the se-

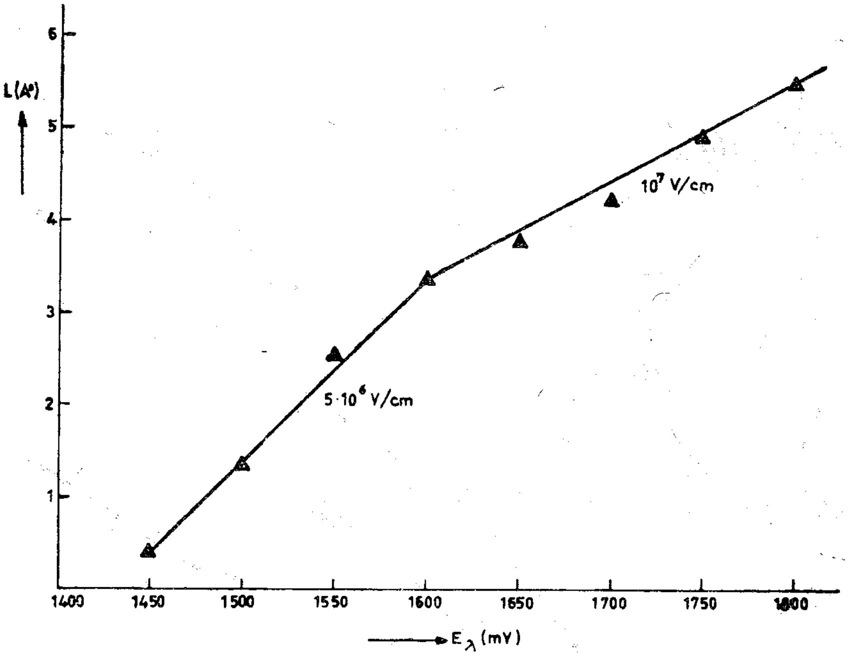

Fig.5. The variation of film thickness with the anodic reversal potential Eλ.

cond region is about two times larger than the value estimated for the initial region below L < 3Å°. The mechanism of oxide growth is mainly determined by the electronic properties of the oxide [10].

The field strenght in the nonconducting oxide is higher than the values for the conducting ones.

The change of field strength at 1600 mV indicates a change in the mechanism of oxide growth and hence the presence of two different oxide layers on gold. The first layer has a better electronic conductivity than the second layer, because of the field strenght in the first layer is lower then the second one.

3. The curves obtained in 0.5 M citric acid:

The curves obtained in 0.5 M H_2SO_4 and 0.5 M citric acid were shown in Fig.6. Anodic film formation in citric acid occurs at 1500 mV. This value is more positive than the value obtained for 0.5 M H_2SO_4. Oxide formation and reduction potentials depend on pH and shifts 59

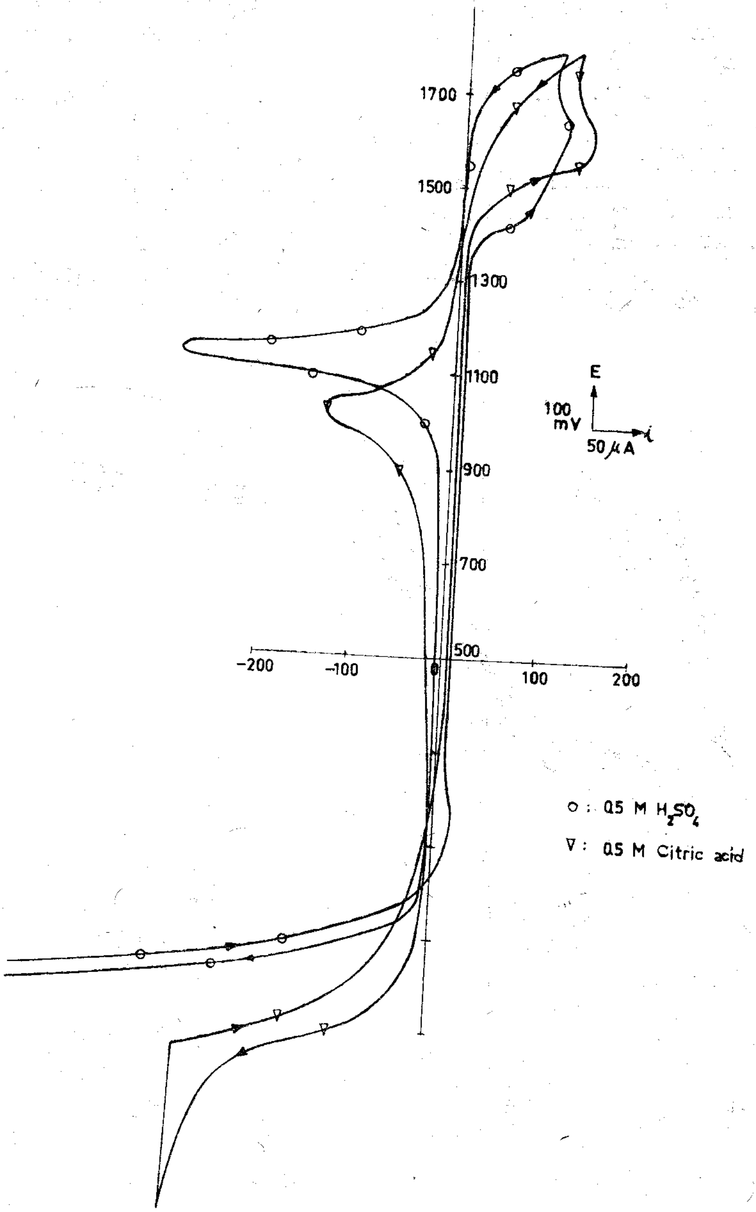

Fig.6. The curves obtained in 0.5 M H_2SO_4 (○) and in 0.5 M citric acid (△).

mV per unit pH [4]. The pH of 0.5 M citric acid is 1.45, so we can expect the oxide formation begins at about 1300 mV, in 0.5 M citric acid, if the formation potential of oxide in 0.5 M H_2SO_4 is taken as a basis. As seen from fig.6 cathodic reduction of oxide film in 0.5 M H_2SO_4 and 0.5 M citric acid occurs at about 1250 mV and 1150 mV respectively. However the difference of anodic film formation potentials in 0.5 M citric and 0.5 M sulphuric acid is not in accordance with the pH shift the difference between the cathodic film reduction potentials corresponds to the shift with pH. So we can say that the adsorption of citric acid molecules or $(H_2Cit)^-$ anion hinder the oxide formation on gold electrode up to the 1500 mV. Fig.7 and 7a show the cyclic voltammograms of gold

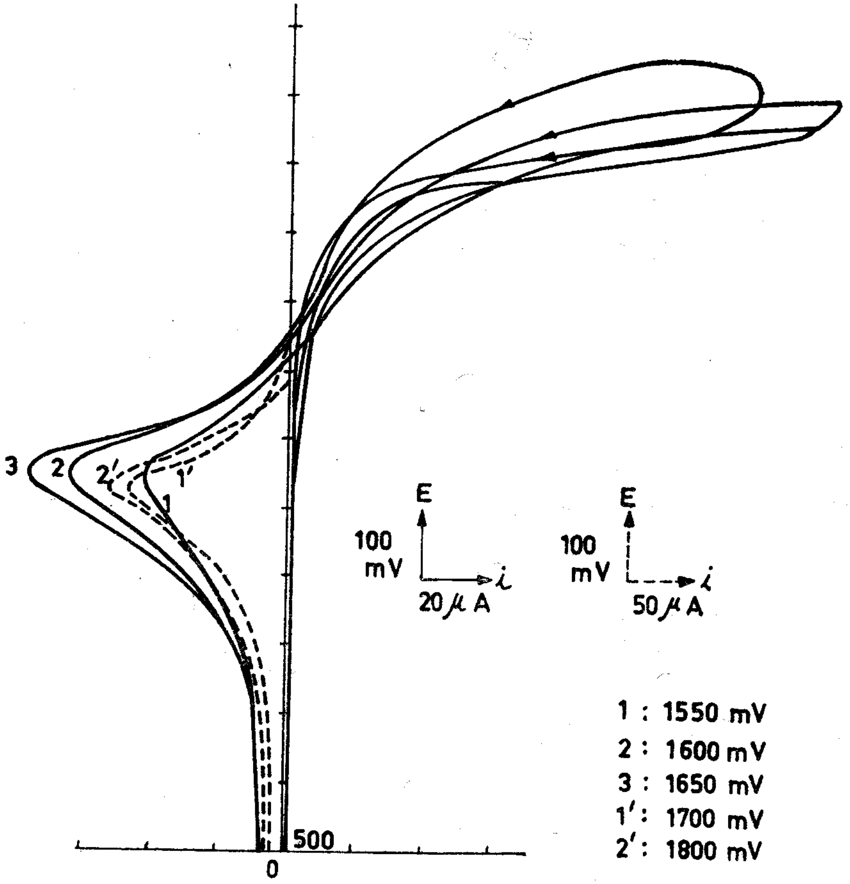

Fig.7. and 7a The current-potential curves up to the various anodic reversal potential obtained in 0.5 M citric acid.

In Fig.7. Eλ changes between 1550–1800 mV.

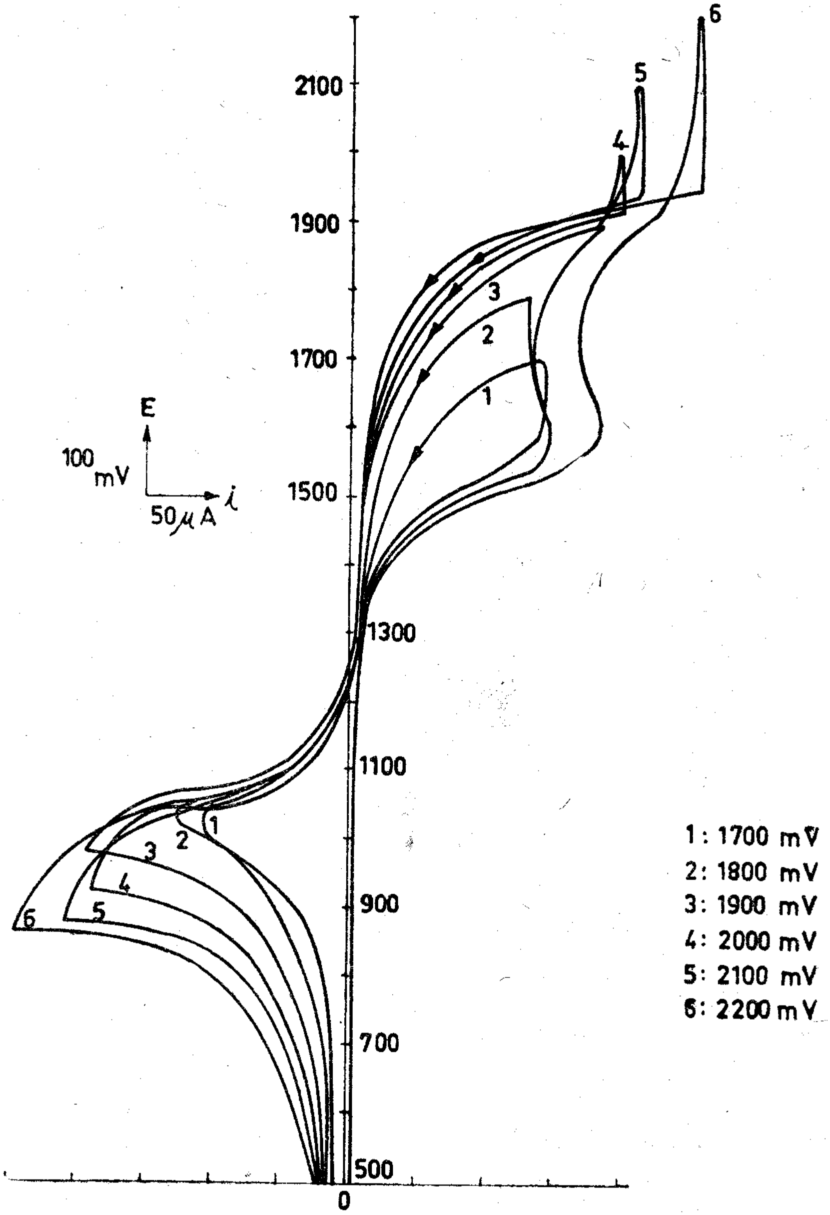

Fig.7a.Eλ changes between 1700–2200 mV.

electrode in 0.5 M citric acid up to various anodic reversal potential. The amount of anodic Q_a ($\mu C/cm^2$) and cathodic charges Q_c ($\mu C/cm^2$) were evaluated as the same way in 0.5 M H_2SO_4 and were shown in Fig.4. In citric acid solutions anodic charges are higher than the cathodic charges and after 1900 mV the difference between them becomes especially higher. Probable reactions in 0.5 M citric acid occur on gold electrode in the anodic region are 1– the formation of oxide film 2– anodic dissolution of gold electrode 3 - the direct anodic oxidation of citric acid 4– the destruction of oxide film by complexing or by some other reaction, like the reaction between adsorbed citrate and oxide film.

The last reaction can not be thought, because in this case, anodic current must begin to rise from the anodic oxide formation potential in citric acid i.e. 1300 mV. The occurence of third reaction, is the anodic oxidation of citric acid between 1500 and 1900 mV has a poor possibility. As can be known, citric acid is three carboxylic acid. The anodic oxidation of carboxylic acids give significant yields at very high potentials i.e. 2.1–2.2V [11]. This is considerably beyond the potential for oxygen evolution in aqueous solution.

The oxide formation in citric acid can be proved by the difference of cathodic peak potentials, in sulphuric and citric acids (100 mV) corresponds to the shift with pH.

The difference between the anodic and cathodic charges in citric acid is due to the anodic dissolution of gold oxide. The redox potential of the reaction

$$Au \longrightarrow Au^{3+} + 3\ e^-$$

is given 1.498 V. This potential is in coincidance with the potential of anodic current increase in 0.5 M citric acid.

This gives an indication that adsorbed citric acid molecules on gold hinder the formation of oxide up to the anodic dissolution potential of gold. When the anodic potential reaches to 1500 mV. i.e. approximately the dissolution potential of gold, citric acid molecules are desorbed by the help of the dissolution process. But the possible reaction at 1500 mV is the formation of oxide layer. As soon as citric acid molecules are desorbed oxide layer is formed on the free sites. In citric acid solution in the anodic oxide region desorption of citric acid molecules, formation of oxide layer, dissolution of electrode metal proceed together.

For noble metals the charge for oxide formation and reduction are independent of pH [4]. As seen from Fig.4 anodic and cathodic charges in 0.5 M citric acid are lower than the ones in 0.5 M H_2SO_4. The difference can be explained by the adsorption of citric acid molecules in oxide region.

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