

ELECTROCHEMICAL OXIDATION OF ETHANOL AT RUTHENIUM OXIDE COATED TITANIUM ELECTRODE*K ASOKAN and V KRISHNAN*

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Electrochemical oxidation of ethanol in 0.5 M sulphuric acid at ruthenium oxide coated titanium electrode was studied. Results of galvanostatic polarization and chronopotentiometric studies are reported. The data indicate the process to be adsorption controlled and accordingly a probable mechanism is proposed.

Key words: Electro-oxidation, ruthenium oxide coated titanium electrode, galvanostatic polarization, chronopotentiometric studies

INTRODUCTION

Recently there has been growing interest in the electrochemical behaviour of noble metal oxide coated titanium electrodes following their successful achievement as anodes in the electrolytic production of caustic soda-chlorine.

The noble metal oxide coating is mainly based on RuO₂ and is deposited as a mixture with TiO₂ on the titanium substrate by thermal decomposition of a chloride film. The RuO₂ layer plays a number of roles. It prevents passivation of titanium; it acts as a good electronic conductor at the electrode side of the electrode-solution interface [1]; and being a high surface area oxide of a cation which has a wide range of oxidation states, it can adsorb large quantities of (OH) and (O) species which may well be the effective oxidizing agents at this type of interface [2].

Though it is claimed that noble metal oxide coated titanium electrodes can be used for electro-organic syntheses [3,4] literature contains only a few publications dealing with investigation of organic reactions at these electrodes. Electro-oxidation of alcohols at RuO₂ electrodes have been reported [5-8]. In almost all cases the substrate bearing coating was platinum and the RuO₂ coating was obtained by electrodeposition. The kinetics and mechanism of the processes have not been well established. It was thus felt desirable to investigate, in detail the electro-oxidation of alcohols on noble metal oxide coated titanium electrodes.

In the present paper, the results of the studies on the electrochemical oxidation of ethanol at RuO_x coated titanium electrodes are reported.

EXPERIMENTAL

Electrodes were prepared by depositing a thin layer of RuO_x on plain titanium sheets (ASTM Grade II titanium sheet) of 1 mm thick and of size 15 x 1 cm. The substrate was sand blasted, etched in hot hydrochloric acid, washed with distilled water and dried. A 2% solution of RuCl₃ · 2.5H₂O in isopropanol (Analar grade) was prepared and the solution was brushed onto the etched substrate in ten sequential coatings. After each coating, the sample was heated in a drying oven at 373K for 5 minutes to evaporate the solvent and then baked in a preheated furnace at 673K for 10 minutes in the presence of air. Between each of the coatings,

the sample was cooled. After the final coating, the sample was heated at 723 K for one hour and then cooled. Geometric area of the electrode for the studies was taken as 1 cm² on one side only by masking off the remaining area with an adherent inert epoxy resin.

A H-type cell with provisions for gas inlets and Luggin capillary in the working electrode compartment was used. A platinum sheet (of area 2 cm²) was used as counter electrode. Reference electrode was saturated calomel electrode (SCE). N₂ purified through potassium hydroxide solution and pyrogallol was used for deaeration. Ethanol was purified by standard procedures. 0.5M sulphuric acid was used as supporting electrolyte in all cases. Potentials were measured against SCE. All measurements, except for the experiment of temperature dependence, were carried out at 298 ± 0.5K.

For galvanostatic polarisation studies a dc constant current power supply was used to control the polarisation currents precisely and a digital voltmeter to measure electrode potentials. IR drops were corrected by using an interruptor. The polarisation data presented here are those obtained after waiting for 30 seconds at each point. The electrode was potentiostatically polarised at 680 mV for 10 minutes in 0.5M sulphuric acid prior to polarisation studies.

For chronopotentiometric studies, the procedure followed by earlier workers [9-12] for the electrooxidation of organic fuels at platinum electrodes was adopted. The electrode was activated by galvanostatically polarising it anodically in supporting electrolyte (0.5 M sulphuric acid) at a current density of 50 mA · cm⁻² for 5 minutes before each experiment. This ensures complete removal of any oxidisable matter adsorbed on the electrode surface. The activated electrode was kept in a solution of 1M ethanol in 0.5M sulphuric acid for 5 minutes to attain the equilibrium between adsorbed alcohol on the electrode and the alcohol present in the bulk. After that the electrode was taken out, washed well with supporting electrolyte, and replaced into a cell containing supporting electrolyte alone. A constant current pulse was then applied across this electrode and a platinum counter electrode with large surface area to oxidise the adsorbed alcohol. The corresponding potential variation of the test electrode with time was recorded using a storage oscilloscope (Textronix - 7613). Since no ethanol is present in the solution, there is no problem of more adsorbate diffusing to the electrode. From the chronopotentiogram, transition time was determined following the standard procedure [13].

RESULTS

Preparative electrolysis was done and products of oxidation were analysed to be acetaldehyde, acetic acid and carbon dioxide.

Galvanostatic polarisation studies were carried out in 0.5M sulphuric acid with different ethanol concentrations.

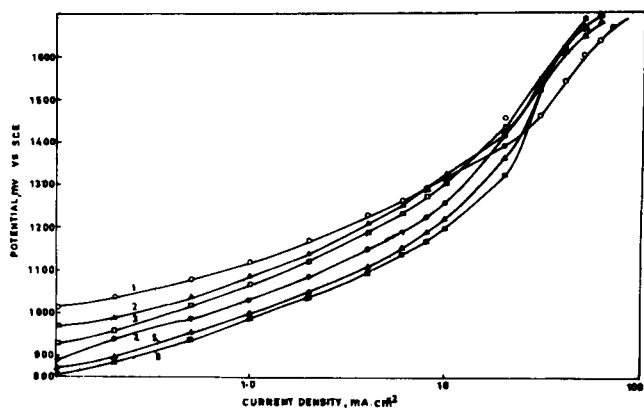


Fig. 1: Logarithm of current density vs potential at RuO_x coated titanium anode in 0.5M sulphuric acid at different concentrations of ethanol at 25°C

(1) 0.2 mol. dm^{-3} (2) 0.5 mol. dm^{-3} (3) 1.0 mol. dm^{-3} (4) 2.0 mol. dm^{-3} (5) 4.0 mol. dm^{-3} (6) 8.0 mol. dm^{-3}

Tafel slopes were invariably $160 \pm 5 \text{ mV decade}^{-1}$, which imply that the reaction is not charge transfer controlled. These values are considerably greater than the value of about $50 \text{ mV decade}^{-1}$, usually quoted for oxygen evolution at such electrodes in the absence of ethanol [14]. Current density values for the electro-oxidation of ethanol increased in an approximately linear manner with increasing concentration of ethanol. The system was studied at different temperatures and increase of temperature was found to decrease polarisation (Fig. 2). A plot of logarithm ethanol concentration against logarithm current density indicates that above 4M, order of reaction with respect to ethanol is zero, whereas below 4M, the order is one (Fig. 3). Energy of activation for the process was found from the slope of the plot of logarithm current density against inverse temperature, the mean value of which was $9.87 \text{ K cal. mole}^{-1}$ in the potential range of 1000 - 1300 mV. Exchange current density was found to be $1.4 \times 10^{-10} \text{ A. cm}^{-2}$ which was obtained by extrapolating the Tafel plot (Fig. 1) to the reversible potential calculated from thermodynamic data.

Chronopotentiometric experiments were conducted at different current densities keeping the ethanol concentration constant after allowing the electrode to adsorb at open circuit as well as at a higher potential. Fig 4 depicts a typical chronopotentiogram. Chronopotentiometric data are shown in Table I. As can be seen from these results the product $iT^{1/2}$ increases with i , which means

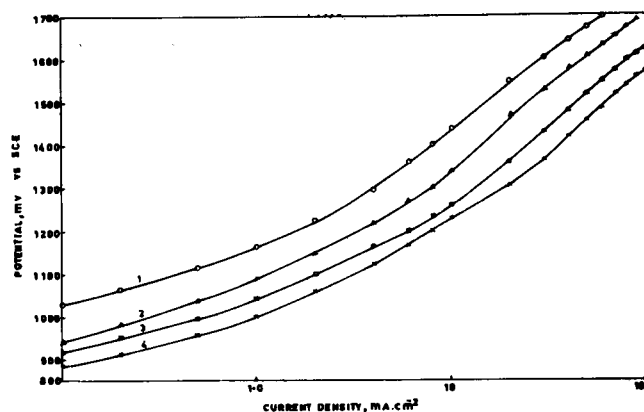


Fig. 2: Logarithm of current density vs potential at RuO_x coated titanium anode in 2M ethanol in 0.5M sulphuric acid at different temperatures. (1) 15°C (2) 42°C (3) 52°C (4) 62°C

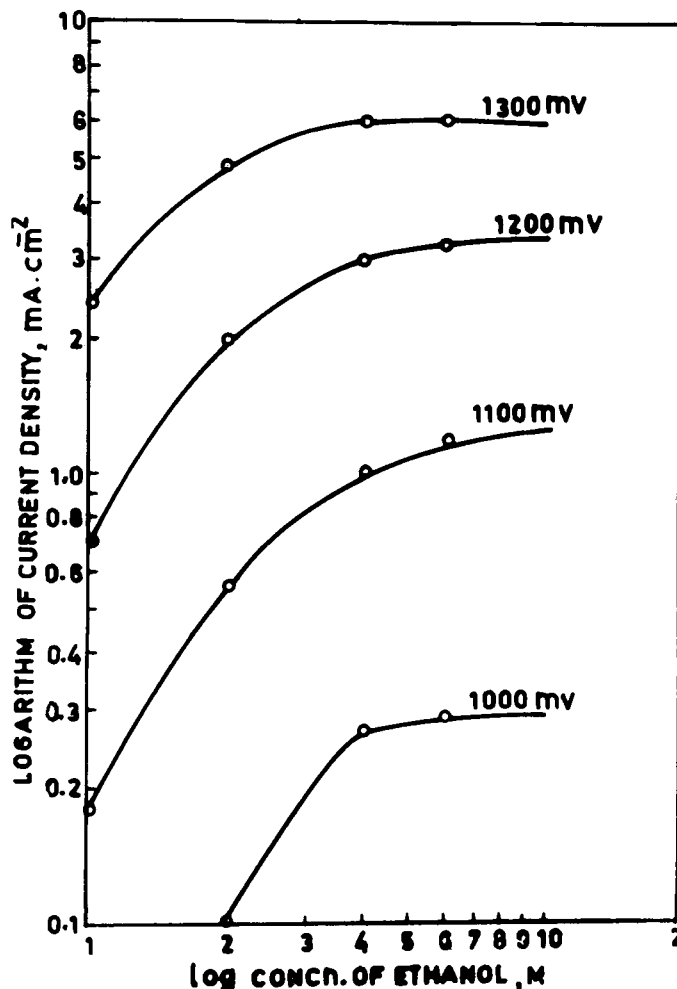
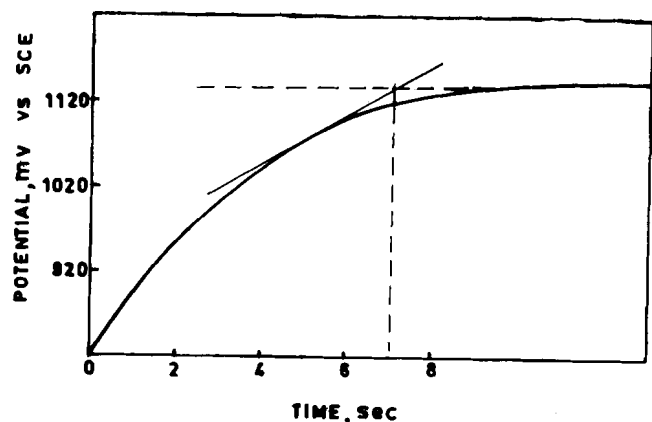


Fig.3: Logarithm of current density vs logarithm of concentration of ethanol at different potentials for the electro-oxidation of ethanol of RuO_x coated titanium anode at 25°C

TABLE-I: Chronopotentiometric results in 1M ethanol in 0.5M sulphuric acid solution

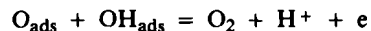
| Current density i (mA. cm ⁻²) | Transition time T (sec) | iT | iT ^{1/2} |
|--|----------------------------|------|-------------------|
| 2 | 7.40 | 14.8 | 5.4 |
| 5 | 3.00 | 15.0 | 8.66 |
| 10 | 1.48 | 14.8 | 12.2 |
| 15 | 1.00 | 15.0 | 15.0 |
| 20 | 0.74 | 14.8 | 17.2 |
| 25 | 0.58 | 14.6 | 19.0 |
| 30 | 0.49 | 14.7 | 21.0 |
| 40 | 0.38 | 15.2 | 24.8 |
| 50 | 0.30 | 15.0 | 27.5 |
| 75 | 0.20 | 15.0 | 33.75 |
| 100 | 0.15 | 15.0 | 39.0 |

Fig.4: Chronopotentiogram for the electrooxidation of 1M ethanol in 0.5M sulphuric acid at RuO_x coated titanium anode at 25°C - current applied 2 mA. cm⁻²

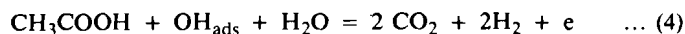
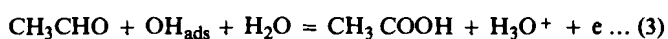
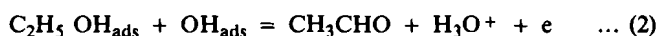
the process is not diffusion controlled. Further, the product iT is constant with increasing i and the slope of a plot of iT^{1/2} vs i is positive. These facts indicate clearly the electrode process to be adsorption controlled [15].

DISCUSSION

One of the major problems in the present work is to account for the high Tafel slope for ethanol oxidation as compared with the low values reported for oxygen evolution under similar conditions. It may well be that more than one species are generated on the anode surface, i.e. OH_{ads} and O_{ads} and that both of these can participate in the oxygen evolution reaction, viz.,



However, only OH_{ads} is (to a large extent) active with respect to organic electro-oxidation. Thus the current for the latter does not increase quite so rapidly with increasing potential. Further, the linear relationship between ethanol concentration and oxidation rate probably reflects the effect of increasing ethanol concentration on the ability of the alcohol to displace water which is quite strongly bonded at oxide surface and reacts with the electrochemically generated intermediate at the hydrated anode surface. From this point of view a mechanism is proposed wherein the chemical reaction between surface species and ethanol is rate determining. The surface reaction can yield acetaldehyde, acetic acid and carbon dioxide according to the following scheme.



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