

Development of TiO₂-supported RuO₂ composite-incorporated Ni–P electrodes for amperometric measurement of ethanol

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Abstract

An electroless Ni–P coating incorporated with TiO₂-supported nano-RuO₂ was developed as a high performance amperometric ethanol sensor. The electrode was systematically investigated for sensing ethanol in 0.2 M NaOH. The composite electrode exhibited good performance with high anodic current for electrochemical ethanol oxidation. The optimized electrode exhibited a response time of 21 s and a sensitivity of 3.6 μA/(ppm cm²). The incorporation of the catalytic composites in the coating resulted in increased roughness of the coating enhancing the hydroxyl radical adsorption during ethanol oxidation.

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1. Introduction

Advantages such as simplicity, precision and convenience make the method of electrochemical sensing of ethanol superior to other methods used for the determination of ethanol concentration. Generally, nickel-based electrodes are used for the fabrication of ethanol sensors. Alloys of nickel with metallic [1,2] or non-metallic elements such as phosphorous [3] are generally used because of their superior electrocatalytic activity than that of the pure nickel electrode.

The electrocatalytic activity of any electrode during sensing, gas evolution or any other reactions depends on the geometric and electronic factors of the electrode. The geometric and electronic factors of nickel-based electrode can be improved by reinforcing with electrocatalytic metal oxides [4,5]. Ruthenium dioxide is used as a composite metal oxide in nickel-based coatings for improving electrocatalytic activity for various electrochemical reactions [6–9]. Interactions of RuO₂ with Ni have been reported to improve the ethanol sensing performance of RuO₂-coated nickel electrode [10]. Similar interactions could exist between RuO₂ composite and nickel matrix if the Ni–P electrode was incorporated with RuO₂ composite.

The particle size can have significant influence on the electrocatalytic activity. Very high catalytic activity can be predicted if RuO₂ composite particles have size at nano-level since it can result in abundant active sites per unit geometric area. In the present study the effect of incorporation of TiO₂-supported nano-RuO₂ composite into electroless nickel phosphorous coatings were studied and the results are discussed in this paper.

2. Experimental

2.1. Preparation of TiO₂-supported RuO₂ composite

Two different methods were adopted for the preparation of TiO₂-supported RuO₂ mixed oxide. In the first method, TiO₂ powder of ~30 nm particle size (supplied by Merck, India) was soaked in isopropanol solution of RuCl₃. The mixture was cautiously evaporated to dryness. Since the isopropanol content in the mixture may result in the formation of carbon and carbon containing organic fragments during thermal decomposition, the dry mass was further heated at 250 °C for 1 h in an oven to remove isopropanol content. After cooling to room temperature, the dry mass was powdered finely using a mortar and then heated at 250 °C for another hour. The powder was then fired at 450 °C in a muffle furnace for 1 h for complete conversion of RuCl₃ into RuO₂. This method of preparation of TiO₂-supported

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RuO₂ mixed oxide is termed as ‘thermal decomposition’ (TD) method in this paper.

In the second method, nano-ruthenium particles of ~5 nm size were prepared by reducing RuCl₃ in ethylene glycol at 180 °C as reported elsewhere [11]. TiO₂ powder of ~30 nm particle size was added to the ethylene glycol reaction medium containing dispersed Ru particles. The reaction medium containing Ru and TiO₂ was stirred continuously for 1 h using a magnetic stirrer to facilitate adsorption of Ru on TiO₂. Ethylene glycol was removed after diluting with 0.3 M NaNO₃ aqueous solution. The solid particles were filtered and dried at 250 °C in an oven for 1 h. The solid mass was then powdered using a mortar, heated at 250 °C for one more hour and then fired at 500 °C in a furnace for 5 h with sufficient supply of air. This method of preparation of TiO₂-supported RuO₂ mixed oxide is termed as ‘thermal oxidation’ (TO) method in this paper.

The composition and crystalline properties of the TiO₂-supported RuO₂ mixed oxide were analyzed using an X-ray diffractometer (Philips make) using a Cu K α I radiation. The particle size of the mixed oxide was analyzed using a transmission electron microscope (TEM) of 2000 FX-11, JEOL, Japan.

2.2. Electrode preparation

Mild steel coupons containing 0.09% carbon, 0.034% manganese, 0.036% phosphorous, 0.0487% silicon and 0.029% aluminium were used as the substrate for plating. The dimension of the mild steel coupons was 5 cm \times 6 cm \times 0.4 cm. The electroless bath had the composition of 30 g/L nickel sulphate, 25 g/L succinic acid, and 25 g/L sodium hypophosphite. The pH of the electroless bath was adjusted to 4.5 by adding ammonia solution. It has been reported that 10 g/L is the optimum amount of TiO₂ in the electroless nickel bath for the preparation of better quality Ni–P coating incorporated with TiO₂ [12]. In the present study too 10 g/L was the optimum amount of mixed oxide added to the plating bath as the results of the preliminary studies also justified.

After mechanical cleaning, the steel coupons were washed with distilled water. The coupons were treated in 5% NaOH solution for 5 min to remove dirt, abrasive scale, grease and oil from the surface (ASTM B 656). The removal of all traces of oxide from the surface was essential to obtain optimum deposit adhesion. Hence, the coupons were then subjected to acid pickling in 3% HCl solution for 5 min (ASTM B 656). The treated coupons were then sensitized in a solution of 10 g/L SnCl₂ in 40 mL/L HCl (37%). After sensitization, the surface was activated in a solution of 1 g/L PdCl₂ in 10 mL/L HCl (37%). The electroless plating was carried out at 80 °C with continuous stirring for 2 h.

2.3. Physico-chemical characterization

Physical characteristics of the electrodes were evaluated as per the ASTM specifications. Adhesion of the electrodes was evaluated by bend test [ASTM B 571–91]. Thickness and hardness of the electrodes were evaluated as per ASTM B 499–88 and E 364–99, respectively. Porosity of the electrodes was evaluated

by ferroxyl reagent test. A solution of potassium ferricyanide, sodium chloride and agar–agar in hot water was used as ferroxyl reagent. The electrodes were etched in 2% HCl for 2 min prior to morphological analysis using scanning electron microscope (SEM) of Hitachi S 4000. The elemental composition of the electrode was determined by EDX analysis (Oxford make).

2.4. Electrochemical characterization

The electrocatalytic activity of the electrodes for ethanol sensing in 0.2 M NaOH solution containing 1000 ppm ethanol was evaluated by cyclic voltammetric experiments at a scan rate of 10 mV/s. All the potentials were measured with respect to an Ag/AgCl electrode. The sensing performance of the electrodes was evaluated based on the calibration curve obtained from the plot of concentration of ethanol versus current. The impedance analysis was carried out at the sensing potential of 420 mV to study the electrocatalytic activity of the electrodes during sensing. An impedance spectrometer of AUTOLAB PGSTAT with FRA2 software of FRA version 4.9 was used. Platinum and an Ag/AgCl electrodes were used as counter and reference electrode, respectively.

2.5. The sensing system

The sensing system consisted of a three-electrode cell with 0.2 M NaOH solution as the base electrolyte. An Ag/AgCl electrode and a platinum electrode (having 4 cm² exposed area) were used as reference and counter electrode, respectively. The composite incorporated Ni–P electrode having 3 mm² exposed area was used as the working electrode. Potentiostat of BAS (USA, 50 W) was used for the analysis. The applied potential was fixed based on the results of cyclic voltammetric analysis. The sensing process was started after fixing the correct potential at which the mass transfer of ethanol to the working electrode surface was the rate determining step [13]. After the background current became stable, the required concentrations of ethanol was added to the cell in such a way that the total ethanol concentration after each addition increased by 100 ppm. The response time and the amperometric response current of the working electrode were recorded. The sensitivity of the electrode for ethanol sensing was calculated using the formula:

$$S = \frac{\Delta I}{\Delta C A}$$

where ΔI is the response current, ΔC the change in ethanol concentration and A is the area of the working electrode in cm².

3. Results and discussion

3.1. Characterization of the mixed oxide composite

Based on the XRD analysis, the mixed oxide prepared by both TD and TO methods was found to contain rutile RuO₂ and anatase TiO₂ (Fig. 1). The crystalline size of RuO₂ prepared by both TO and TD methods was calculated from the respective

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