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Physico-chemical and electrochemical characterization of Ti/RhO_x–IrO_2 electrodes using sol–gel technology

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ABSTRACT

Sol–gel technology has been successfully used for the incorporation of RhO_x–IrO_2 on a Ti substrate. RhO_x–IrO_2 was prepared from chloride precursors of Rh and Ir, for surface studies. These metal oxides were then immobilised on solid Ti substrates via dip withdrawal coating methods to form thin films. The Ti/RhO_x–IrO_2 thin films were extensively characterized in terms of surface characterization and chemical composition and used in the oxidation of phenol. Thermo-gravimetric analysis (TGA) determined the calcination temperature at 700 °C where no further structural changes occurred due to mass loss. The rhodium oxide showed two-phase formations, RhO_2 and Rh_2O_3, which were attributed to high calcinated temperatures compare to one phase IrO_2 which was stable at lower temperatures. The scanning electron microscopy (SEM) showed that the morphology of the film was found to be rough with a grain-like appearance in the 150-nm range. The phase composition of these metal oxides was determined by X-ray diffraction (XRD) technique and found to have crystalline structures. The results obtained from Rutherford backscattering spectrometry (RBS) revealed information regarding the chemical composition of the metal oxides and confirmed the diffusion of Rh and Ir into the Ti substrate. Electrochemical characterization of the Ti/RhO_x–IrO_2 electrode, via cyclic voltammetry (CV), showed distinctive redox peaks: anodic and cathodic peaks associated with the oxidation and reduction of the ferricyanide–ferrocyanide couple was seen at 250 and 100 mV respectively; the peak observed at 1000 mV was associated with oxygen evolution and a broad reductive wave at −600 mV can be ascribed to the Ti/RuO_x–IrO_2 reduction, which proved that the Ti/RhO_x–IrO_2 electrode were electroactive and exhibit fast electrochemistry.

1. Introduction

Transition metal oxides, owing their ability to easily accept and donate electrons as a result of more than one oxidation state, make them versatile materials for chemical and electrochemical reactions. For the same reasons, these oxides exhibit remarkable stability toward chemical and electrochemical attack under appropriate conditions [1].

Noble metals oxides of Ru, Rh, Pt and Ir are known to prevent the accumulation of coke on the catalyst surface during methane conversion reactions. It is also well established that the synthesis method plays an important role in the catalytic performance for methane decomposition. The different synthesis methods generate structural, surface and textural changes in the properties of the materials, influencing their catalytic behaviour, Rh seems to be the metal that better fulfils this requirement with some compromise between activity and stability [2].

Rhodium oxide and its compounds catalyzed reactions such as: the hydrogenation of unsaturated organic molecules [3], the dissociation of nitrogen oxide (NO) [4], Fischer–Trøpsch synthesis [5] and RhO_2 is widely used in the production of Cl_2 and O_2. Swette et al. investigated the electrochemical stability of the prepared RhO_2 electrodes [6]. The results showed that this electrode material was very stable towards both oxygen evolution and reduction. Other researchers have conducted studies on the electrochemical properties of Ti/RhO_x electrodes that were prepared by thermal decomposition of suitable precursors [7,8]. It has been found that RhO_x is more stable than both RuO_2 as well as IrO_2 for hydrogen evolution in acid solution. Slavceva et al. investigated the morphology factor assessing the catalytic active surface of sputtered IrO_2 as electro-catalyts for water splitting. They found that the catalytic efficiency is correlated to the thickness/loading of the sputtered IrO_2 [9]. IrO_2 have also been used in electrochromic devices, optical information storage and pH sensing [10].

As research progressed, it was found that mixtures of these metal oxides showed even more unique properties with regard to electrochemical requirements, such as potential and low consumption rate. They may come in the form of either new oxides or new composite materials containing polymers and oxide blends or the

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new properties associated with nano-structured materials. Recent studies have shown that the electro-catalytic activity and chemical or mechanical stability of oxide electrodes are enhanced by incorporating/doping other metal ions into the oxides. The catalytic properties of existing known metal oxide catalysts can be enhanced by tailoring of the micro- and nano-structure. The applications of the new materials extend to fuel cell applications, energy storage and sensors [11]. The range of such compounds is quite large, but is extended even further by considering ternary and yet more complex compounds, where additional metallic elements are present [12–14].

Aramata et al. [15] studied the influence of Sn-oxide on the electro-catalytic activity of Rh-, Ir-, and Pt-based oxide mixtures [16,17]. In the case of the Rh-based electrode materials, the introduction of tin oxide in the coating caused a negative effect in the catalytic activity, whereas with IrO_2, rhodium directs the hydrogenation of carbon monoxide towards higher alcohols [4].

The electro-catalytic properties of the metal oxides are mainly related to electronic and geometric factors. The electronic factor is related to the chemical composition of the oxide layer and the physical and chemical properties of the constituent oxides (e.g., electronic structure, crystallinity). The geometric factor is directly linked to the morphology of the film. Characterization of the surface properties of electrodes covered with conductive metallic oxide films is therefore of fundamental importance for understanding their electrochemical behaviour. The authors have therefore undertaken to systematically study the surface characteristics of a range of compositions of mixed metal oxides of TiO_2, RhO_2 and IrO_2 as thin films with electro-catalytic properties [18].

In this study, physico-chemical and electrochemical characterization studies on Rh oxide doped with Ir-oxides coated on a Ti substrate were conducted and are reported.

2. Experimental

2.1. Reagents

Reagents $RhCl_3$, $IrCl_3$ and Ti foil were obtained from Aldrich (Germany). Merck's absolute ethanol, potassium chloride and hydrochloric acid were used in the experiments. All reagents were of analytical grade, were used without further purification and were purchased in Johannesburg (South Africa).

2.2. Sol–gel and thin film preparation

Rh and Ir oxides were prepared by dissolving hydrated $RhCl_3$ and $IrCl_3$ in absolute ethanol using a sol–gel technique. The sol–gel synthesis for the Rh and Ir oxides titanium materials was based on synthesis procedures tailored from the literature [19–22]. The samples were prepared with nominal Rh:Ir ratios of 20:80, 40:60, 60:40 and 80:20. The starting materials were placed in a round bottomed flask fitted with a thermometer, and the solutions were well stirred and refluxed for 1 h, before being left to age at room temperature for at least 24 h to ensure ageing of the gel. For the purpose of producing the thin films, the gels were retained in the liquid form. The titanium substrates were cut to size (10 mm × 10 mm), sandblasted and etched in HCl (11 M) for 10 min, rinsed with copious amounts of UHQ water and finally rinsed with absolute ethanol.

The Ti substrates were dipped into the gel solution and then slowly withdrawn at a rate of 80 mm min^{-1}. The titanium substrates onto which thin RhO_x–IrO_2 films were coated were affixed to the rotating disk surface and rotated at full speed (±1000 rpm) for 10 s to give reproducible thin films. The thin films were then annealed in an oxygen-rich atmosphere in a quartz tube furnace at a slow heating rate (1 °C min^{-1}) up to 700 °C and then allowed to cool to room temperature, under ambient conditions.

2.3. Construction of the electrode

The electrical connection was made through a Cu wire welded to the Ti/RhO_x–IrO_2 substrate by means of silver epoxy. The back of the electrode and the copper contact was isolated with an inert-conductive polymer resin to base the results exclusively on the active surface. The composition ratio of the conducting metal oxides was varied to investigate the electro-catalytic activity using cyclic voltammetry (CV).

3. Surface analytical techniques

3.1. Thermal gravimetric analysis (TGA)

The hydrated $RhCl_3$ and $IrCl_3$ precursor samples were analysed by TGA. A TGA instrument (Perkin-Elmer Series, Thermal Gravimetric Analyzer 7) was used to monitor the sample weight loss and to record the temperature change at which the metal oxides are formed. The procedure was as follows: the precursor solution was evaporated at 100 °C and the sample was transferred to the TGA cell. The Rh/Ir precursor samples were heated at 10 °C min^{-1}. The temperature was kept constant at 400 °C for 1 h (i.e. the sample was held for 1 h at 400 °C), and later increased to 900 °C. Air was used as the carrier gas.

3.2. Rutherford backscattering spectrometry (RBS)

Measurements using RBS and particle induced X-ray emission were performed at the Materials Research Group, iThemba LABS (Faure, South Africa). RBS spectra using a 2.0-MeV He^+ beam collimated at 2 mm diameter. Specimens were tilted 10° towards the detector situated at a backscattering angle of 165°. The integrated charge was 20 μC.

3.3. Scanning electron microscopy (SEM), and energy dispersive elemental analysis (EDAX)

The surface morphology of the electrode was analysed by an ABT60 scanning electron microscope (SEM) and complimented by elemental X-ray analysis (EDAX). The SEM pictures were taken at a working distance of 7 mm and an accelerating voltage of 7 kV. The samples were placed horizontally on the stubs from the horizontal and they were not coated for viewing. For the X-ray analysis, the working distance was 12 mm and the accelerating voltage was 25 kV. The samples were tilted at 30°. The SEM cross sections of the thin films were obtain as follows: the samples were left in a resin for 24 h in an oven at 60 °C, cut and polished into small pieces and mounted vertically on the stubs.

3.4. X-ray diffraction (XRD)

The electrode surface was characterized by XRD using a D8 Advance powder diffractometer with a theta–theta goniometer. The X-ray source was a copper tube and a NaI (Tl) scintillation detector that detected the diffracted beam. The film surface was oriented perpendicular to a plane defined by the X-ray tube, sample holder and detector. XRD has been found to be the most useful technique for the determination of crystallographic parameters. XDR measurements identify the crystalline phases of the metal oxides present in an electrode surface.

3.5. Electrochemical measurements

The surfaces of the modified electrodes were characterized by means of cyclic voltammetric curves to evaluate the catalytic response of the electrode surface. All electrochemical experiments were carried out and recorded on a BAS50/W electrochemical analyser (Bioanalytical Systems, Lafayette, IN, USA). All studies were carried out using 0.05 M KNO_3 (Merck) and Milli-Q quality water as the supporting electrolyte, to avoid the usage of the acidic medium, which tends to be harsh and shortens the service life of the electrodes [23]. The cell was degassed with nitrogen for 20 min to exclude any oxygen from the cell. A conventional three electrode system was employed: working (WE) was the Ti/RhO_x–IrO_2 electrode, silver/silver chloride (Ag/AgCl) and a platinum wire were used as reference and auxiliary electrodes,