



Ru_xTi_{1-x}O₂ as the support for Pt nanoparticles: Electrocatalysis of methanol oxidation



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ABSTRACT

Two binary Ru–Ti oxides, Ru_{0.1}Ti_{0.9}O₂ and Ru_{0.7}Ti_{0.3}O₂, were synthesized by the sol–gel method and used as an electrocatalyst support. The system was characterized by XRD, EDS, TEM and cyclic voltammetry. The Ru_{0.1}Ti_{0.9}O₂ and Ru_{0.7}Ti_{0.3}O₂ consist of two phases of anatase and rutile structure. An average size of the Pt nanoparticles supported on them is ~3.5 nm and they are deposited on both Ru and Ti-rich domains. The supports exhibited good conductivity and electrochemical stability. The onset potentials of CO_{ads} oxidation on the synthesized catalysts and on commercial PtRu/C are similar to each other and lower than that on Pt/C. This suggests that in Pt/Ru_{0.1}Ti_{0.9}O₂ and Pt/Ru_{0.7}Ti_{0.3}O₂ the Pt nanoparticles are in close contact with Ru atoms from the support, which enables the bifunctional mechanism. The activity and stability of the catalysts for methanol oxidation were examined under potentiodynamic and potentiostatic conditions. While the activity of Pt/Ru_{0.1}Ti_{0.9}O₂ is unsatisfactory, the performance of Pt/Ru_{0.7}Ti_{0.3}O₂ is comparable to PtRu/C. For example, in the potentiostatic test at 0.5 V the activities after 25 min are 0.035 mA cm⁻² and 0.022 mA cm⁻² for Pt/Ru_{0.7}Ti_{0.3}O₂ and PtRu/C, respectively. In potentiodynamic test the activities at 0.5 V after 250 cycles are around 0.02 mA cm⁻² for both catalysts.

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1. Introduction

Current polymer electrolyte membrane fuel cell (PEMFC) technology employs carbon black as the anode and cathode catalyst support [1]. Although this kind of support possesses high electrical conductivity and high surface area necessary for fine dispersion of the catalyst particles, its oxidation under typical fuel cell operating conditions is inevitable [2–5]. Partial oxidation of carbon induces the formation of oxygen-containing functional groups on the surface that weakens Pt–C bond, thus facilitating surface diffusion of Pt nanoparticles and their agglomeration, especially in the case of the Pt nanoparticles smaller than 2 nm [6]. If the carbon support is oxidized to CO or CO₂, Pt nanoparticles detach from the surface [2]. Both processes reduce the electrochemically active surface area (EASA) of the catalyst system. The focus of recent research is to improve the catalyst stability by replacing carbon materials with

metal oxides as the catalyst support [7,8]. Among the oxides, TiO₂ distinguishes itself due to high stability in acid media [9]. In the past several years TiO₂ has been successfully tested as a Pt catalyst support as a pure mesoporous oxide [10,11], doped by Nb [12–15] or as binary oxides such as Ti_{0.7}W_{0.3}O₂ [16], Ru_xTi_{1-x}O₂ [17], hydrous and anhydrous TiO₂–RuO₂ [18] and Ti_{0.7}Ru_{0.3}O₂ [19,20]. The addition of foreign atoms into the TiO₂ crystal lattice increases the conductivity of otherwise low-conducting TiO₂ but can also promote the catalyst activity, i.e., transform a catalyst support to a co-catalyst.

TiO₂ supports containing Ru are particularly interesting, because Pt–Ru surfaces are unsurpassed electrocatalysts for methanol oxidation reaction (MOR) owing to a combination of a bifunctional mechanism [21] and the electronic influence of Ru on Pt atoms [22]. According to bifunctional mechanism, Ru sites provide oxygen-containing species at less positive potentials than Pt, which facilitates oxidative removal of CO and other methanol residues from the Pt sites. Transfer of electron density from Pt to Ru, which can be comprehended as lowering of the d-band center of Pt [23], weakens the CO bonding to the Pt sites but also strengthens

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the bonding of OH and CO species to Ru sites [24]. The bifunctional mechanism is considered to be predominant over the electronic effect in the MOR promotion on Pt–Ru surfaces [25].

$\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ (x between 0.17 and 0.75) prepared by the sol–gel routine [17] revealed that the samples with Ru mole fraction higher than 0.27 were electronically conductive after 30 min of heat treatment at 450 °C. Concerning the phase composition, a two phase mixture was found when the Ru mole fraction was below 0.5, while a solid solution was formed when the Ru fraction was higher than 0.5. The crystal structure corresponded to anatase for the oxides with $x < 0.25$ and to rutile at higher Ru fraction. Pt nanoparticles were supported on $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ (loading from 17 to 40 mass%) and examined by cyclic voltammetry. High Ru content was shown to increase the amount of electrochemically active surface area of Pt by a factor of two between the supports with $x = 0.27$ and $x = 0.71$.

X-ray diffraction (XRD) examination of hydrous $\text{RuO}_2\text{–TiO}_2$ prepared by a wet chemical method [18] showed only anatase TiO_2 without the features of RuO_2 . After annealing at 450 °C two distinct phases of anatase TiO_2 and rutile RuO_2 were found, with no incorporation of Ru inside the TiO_2 crystallites. The annealing process i.e., phase structure of $\text{RuO}_2\text{–TiO}_2$ did not influence the particle size of the supported Pt. However, Pt catalysts on the annealed support presented better electrochemical stability. The Pt/ $\text{RuO}_2\text{–TiO}_2$ samples in that study were also tested for oxygen reduction reaction (ORR). Although their activity was below the Pt/C benchmark, it is expected that optimization of the Pt particle size and electrode structure may make them suitable for the application in fuel cells.

Hydrothermal synthesis of $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$ performed at low temperature (200 °C) yielded a single phase solid solution with TiO_2 in the anatase form [19]. The material was hydrated with 0.23 mole of water per mole of $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$ and possessed BET surface area of 275 $\text{m}^2 \text{g}^{-1}$. The electrocatalytic activity of Pt nanoparticles supported on $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$ was examined for CO and methanol oxidation. Both reactions were significantly enhanced compared to Pt/C and PtRu/C, which was ascribed to the bifunctional mechanism owing to high proton conductivity of hydrated $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$. The same $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$ was also used as a supporting material for Pt nanowires and tested for ORR and MOR [20].

As literature survey showed that studies of $\text{TiO}_2\text{–RuO}_2$ oxides as the catalyst supports are scarce and that very few of them examined MOR on Pt supported on such materials, we synthesized $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ employing a sol–gel method followed by thermal treatment with the aim to be used as an active support for Pt in MOR. Two samples of $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ powder with $x = 0.1$ and $x = 0.7$ were prepared and modified by Pt nanoparticles. The Pt/ $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ catalysts were tested for the activity towards CO and methanol oxidation.

2. Experimental procedures

2.1. Preparation of $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ and Pt/ $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$

The synthesis of the $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ powders was based on an acid-catalyzed sol–gel method proposed for TiO_2 nanoparticles [26] and modified by addition of Ru [27]. In 40 mL of 97% solution of titanium(IV) isopropoxide, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ (Alfa Aesar) an appropriate amount of 0.82 mol dm^{-3} aqueous solution of RuCl_3 (Merck) is added to achieve the Ru:Ti atomic ratio of 0.1:0.9 and 0.7:0.3. Soles were prepared by adding a 0.9 cm^3 of 12 mol dm^{-3} HCl solution (Merck) to the mixture of Ti and Ru precursors under vigorous steering at room temperature. The mixtures were placed in glass tubes, sealed and left for 5 days at room temperature. In the presence of such amount of HCl, the hydrolysis proceeded without forming a precipitate, leading to a transparent sol. Gelification of the sol was achieved by adding an appropriate amount of water.

The samples were dried by a freeze-drying method using Modulyo Freeze Dryer System (Edwards) consisting of freeze dryer unit at High Vacuum Pump E 2 M 8 (Edwards). Samples were pre-frozen in the deep-freeze refrigerator at –30 °C for 24 h. After that, the samples were freeze-dried in an acrylic chamber with shelves mounted directly on the top of the condenser of the freeze dryer. The vacuum during freeze-drying was around 4 mbar. The dried samples were heated in a conventional furnace at 400 °C for 2 h to obtain crystallized phases and to remove traces of organic residues. After the treatment, the furnace was cooled at room temperature.

Pt/ $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ catalysts with a nominal Pt loading of 20 mass% were prepared by modified borohydride reduction method [28]. 80 mg $\text{RuO}_2\text{–TiO}_2$ powders were dispersed in 80 mg of water in an ultrasonic bath. Then an appropriate volume of 10 mg cm^{-3} H_2PtCl_6 aqueous solution was added into suspension under continuous stirring. After adjusting the suspension pH to 10 by adding 0.1 mol dm^{-3} NaOH solution, the metal salt was slowly reduced in the presence of excess of 0.5 M NaBH_4 solution under continuous stirring at 40 °C. The precipitate was rinsed with water and dried at 80 °C in inert atmosphere.

2.2. Physico-chemical characterization

Adsorption and desorption isotherms of N_2 were measured on $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ supports at –196 °C using the gravimetric McBain method. The specific surface area, S_{BET} , was calculated from the isotherms using the Brunauer–Emmett–Teller (BET) method. Pore size distribution was estimated by applying the Barrett–Joyner–Halenda (BJH) method [29] to the desorption branch of the isotherms.

The phase composition of the $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ supports was investigated by XRD. A Siemens D-500 diffractometer was employed with $\text{CuK}\alpha$ radiation of wavelength 0.154056 nm in conjunction with a $\text{CuK}\beta$ nickel filter.

The average elemental composition of the $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ supports and the Pt/ $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ catalysts was performed by energy-dispersive X-ray spectroscopy (EDS) using a scanning electron microscope Tescan VEGA TS 5130MM coupled with an EDS system INCAPentaFET-x3, Oxford Instruments.

Transmission electron microscopy (TEM) was employed to analyze the morphology and elemental distribution of the Pt/ $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ catalysts. The samples were sonicated in ethanol and a drop of the suspension was placed on a Cu grid (300 mesh) covered by lacey carbon film and dried in air. A combination of high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and electron energy loss spectroscopy (EELS) was applied. HAADF-STEM image intensity has a strong correlation with atomic number making it easy to distinguish between heavy elements such as Pt and a light support such as $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$. The measurements were performed on TEAM 0.5 TEM with aberration-correction operated at 80 kV accelerating voltage. EDS mapping was performed on a CM200-FEG TEM operating at 200 kV by using an Oxford Instruments EDS system with INCA software. Crystallographic information from individual Pt particles was obtained by numerical Fourier filtering (Fast Fourier Transformation, FFT) of the digital image intensity spectra. All TEM characterization was done at the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory.

2.3. Electrochemical characterization

For the electrochemical characterization, the Pt/ $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ catalysts were applied on a glassy carbon (GC) substrate in the form of a thin-film [30]. The GC electrode (Tacussel rotating disk electrode, 5 mm in diameter) was polished with Al_2O_3 slurry and washed ultrasonically with water before use. The ink was made by

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