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



M.D. Obradović^a, U.Č. Lačnjavec^b, B.M. Babić^c, P. Ercius^d, V.R. Radmilović^{d,e},
N.V. Krstajić^e, S.Lj. Gojković^{e,*}

^a Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia

^b Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1, 11030 Belgrade, Serbia

^c Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia

^d National Center for Electron Microscopy, LBLN University of California, Berkeley, USA

^e Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

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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

* Corresponding author. Tel.: +381 11 3303 753; fax: +381 11 3370 387.
E-mail address: sgojkovic@tmf.bg.ac.rs (S.Lj. Gojković).