



Methanol oxidation and photo-oxidation at Pt/WO₃ electrocatalysts on graphite substrates



J. Georgieva^{a,*}, S. Sotiropoulos^b, E. Valova^a, S. Armyanov^a, N. Karanasios^c

^a Rostislav Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

^b Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece

^c Department of Electrical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece

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ABSTRACT

Pt/WO₃ catalyst layers were prepared by electrosynthesis of WO₃ on a graphite (Gr) support and electro-deposition of Cu on WO₃, followed by a galvanic replacement process, involving treatment of the Cu/WO₃/Gr composite electrode with a chloroplatinate solution. Both the platinized and the precursor WO₃/Gr electrodes were characterized by SEM microscopy/EDS spectroscopy and X-ray diffraction. Their electrochemical and photoelectrochemical behavior was assessed by voltammetry and chronoamperometry in the dark and under visible (Vis) light irradiation. The Pt/WO₃/Gr electrode showed more pronounced intrinsic catalytic activity for methanol oxidation than a commercial Pt/C catalyst, which can be further enhanced under Vis light illumination for optimized Pt content. The increased catalytic activity is associated both with a synergistic effect between Pt and WO₃ for methanol oxidation at Pt sites (enhancement of methanol and adsorbed CO oxidation) as well as with the simultaneous occurrence of methanol photooxidation at WO₃ sites.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted much attention as a portable energy source due to their high specific energy at low operating temperature and the ease of handling a clean liquid fuel [1]. However, the high price of the catalyst and low reaction rate of methanol oxidation at the anode, limit DMFCs' performance [2]. Platinum, a well-known catalyst for methanol oxidation reaction (MOR), apart from its high cost and limited abundance, is easily poisoned at room or moderate temperatures by CO, an intermediate in the oxidation of methanol [3]. Various platinum alloys supported on carbon and metal oxides have been studied in order to develop catalysts as anode materials with improved catalytic activity for methanol oxidation, CO tolerance and reduced cost [4,5].

Tungsten oxide (WO₃, an indirect bandgap semiconductor) is a well-known multi-functional material with interesting photoconducting behavior. It is presently used in electrochromic and sensor devices, photoelectrocatalysis and is a potentially low-cost material for solar energy applications [6–10]. Pt catalysts supported on WO₃ have received considerable attention as active catalysts for MOR [11–17]. WO₃ can form a nonstoichiometric and electron

conducting hydrogen tungsten bronze compound (H_xWO₃) in acidic solutions that effectively facilitates the dehydrogenation of methanol molecules adsorbed on Pt, since the spillover of the hydrogen fragments of dehydrogenated species from Pt onto the surface of the hydrogen tungsten bronze can free those Pt sites for further chemisorption of methanol molecules. Hence, the dissociative chemisorption of methanol (first step of the reaction) is catalyzed at Pt/WO₃ electrodes. As far as the removal of poisonous CO_{ads} is concerned this is either attributed to its desorptive hydrogenation [18,19] or to its oxidation by Pt–O/Pt–OH formed at Pt sites that have been freed from H_{ads} fragments after these have passed to neighboring H_xWO₃. In addition, the oxophilic nature of WO₃ also helps in removing the adsorbed CO on adjacent Pt sites [19].

Methods for Pt deposition/incorporation onto/into WO₃ supported layers include electrodeposition [11–14,18], impregnation [16] and the conventional borohydride reduction method [15,17]. During the last decade a new method (known as galvanic replacement or transmetalation) for the introduction of the noble metal onto an electrode support has been developed. This method is based on spontaneous partial replacement of early transition metal layers or particles (Cu, Fe, Ni, Co etc.) by more noble metal (Pt, Pd, Ir, Au etc.) through immersion of the samples into a solution containing the precious metal ions [20–23]. Advantages of the new technique include the fact that it is a fast and room temperature

* Corresponding author. Tel.: +359 2 9793938; fax: +359 2 9712688.

E-mail address: jenia@ipc.bas.bg (J. Georgieva).

process, employs low concentration solutions of the precious metal and can lead to the formation of thin precious metal deposits that may decrease its loading. In recent years this method has been used as an alternative route for the preparation of practical multi-metallic catalysts, supported on high surface area carbon, mainly in search of efficient electrocatalysts for fuel cell related reactions including methanol oxidation [24,25].

In a recent paper platinized deposits have been formed on TiO₂ particulate films supported on Ti substrates [26]. It has been demonstrated that the galvanic replacement of pre-deposited metallic Cu during the immersion of the Cu/TiO₂ coatings into a chloroplatinic acid solution can be successfully applied to semiconductor oxides too. A significant methanol oxidation current enhancement under UV illumination of the platinized rutile-rich electrodes has been observed due to Pt and TiO₂ synergism. It is well known that TiO₂ (one of the most popular photocatalysts) absorbs only UV light and thus it would be desirable for practical applications to develop photocatalysts which exhibit visible (Vis) light response too, aiming at the utilization of solar radiation. WO₃ is a semiconductor of a smaller bandgap, which is active under Vis light [27,28] and to that direction, Pt/WO₃ systems should offer the possibility of enhancing anodic reactions occurring at Pt by means of simultaneous photooxidations at the Vis light-illuminated WO₃ support.

The main objectives of this study have been: (i) preparation of platinized deposits obtained by the galvanic replacement technique on WO₃/Gr electrodes; (ii) microscopic, spectroscopic and crystallographic characterization of the catalysts; (iii) electrochemical and photoelectrochemical characterization of the deposits and (iv), the assessment for the first time of the effect of Vis light illumination on the electrocatalytic activity of these deposits towards MOR.

2. Experimental

2.1. Preparation of WO₃/Gr, Cu/WO₃/Gr and Pt/WO₃/Gr electrodes

Rectangular plates of spectrally pure graphite used as substrates were degreased ultrasonically with acetone and etched in 65% HNO₃ (Riedel) for 120 s before the electrochemical preparation of the WO₃ coatings. WO₃ was deposited in a single direct cathodic deposition step [27,29]. The samples were prepared in a 300-mL three-electrode cell with a graphite substrate (3 cm²) serving as the cathode and a Pt foil as the counter electrode. As a reference electrode, a mercurous sulphate Hg/Hg₂SO₄/H₂SO₄ (0.5 M) electrode (MSE) was employed. An Autolab 30 potentiostat/galvanostat (EcoChemie) was used for electrodeposition. WO₃ was obtained by potentiostatic cathodic deposition at –1.00 V vs. MSE for 20 min from a peroxytungstate solution containing 0.025 M Na₂WO₄ (Na₂WO₄·2H₂O; Merck; pro analysi; >99%), 0.03 M H₂O₂ (30% aqueous solution) and 0.05 M HNO₃ (Riedel, 65%) [30]. The electrodeposited film was heated at 350 °C for 30 min for crystallization (monoclinic WO₃, as confirmed by XRD [31]). WO₃ loadings were in the 1.3–1.7 mg cm^{–2} range. The working area of 1 cm² was fixed one-sidedly with epoxy resin glue.

Constant potential Cu electrodeposition on the WO₃/Gr electrode was carried out at the half-wave cathodic electrodeposition peak potential (–0.125 V vs. saturated calomel electrode (SCE)) of the exploratory deposition voltammetry (Fig. S1) in a 0.1 M HClO₄ (Riedel, ACS reagent, ≥70%) + 0.01 M CuSO₄·5H₂O (Sigma-Aldrich, ACS reagent) deaerated solution. The total charge density passed was 635 mC cm^{–2}.

The Cu/WO₃/Gr electrode was immersed in a chloroplatinic acid solution (0.1 M HCl + K₂PtCl₆ (Sigma-Aldrich, ACS reagent, ≥37.5% as Pt)) for 40 min so that spontaneous Cu galvanic (partial) replacement by Pt occurs, as expected from the difference

between the standard potential values E⁰ of [PtCl₆]^{2–}/Pt (+0.744 V vs. NHE) and Cu²⁺/Cu (+0.340 V vs. NHE) [32]. Two samples with different Pt content (10% and 29% w/w) were prepared, varying the platinum salt concentration (10^{–3} M and 10^{–2} M K₂PtCl₆, respectively).

2.2. Microscopic, spectroscopic and crystallographic characterization of coatings

Scanning electron microscopy (SEM) and Energy dispersive spectroscopic (EDS) elemental analysis were carried out using a JEOL JSM 6390 microscope with INCA Oxford Energy 350 system.

The crystal structure of the Pt–Cu–WO₃/graphite catalysts was examined by XRD on a Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector at room temperature. Two kinds of patterns were recorded: with powder diffraction geometry and with small incidence angle of 5°. Data were collected by scanning scattering angle range 10.000–90.005° in 2θ for the former and 20.000–52.010° for the small incidence angle, with step size for both 0.020°. The position-sensitive linear LynxEye detector allows for high-speed data acquisition measuring simultaneously a range of scattering angles, increasing signal detection and decreasing scan times. Registration time equivalent to 52.5 s per step in the powder diffraction mode and to 175 s per step in 5° incidence mode were set, resulting in increased diffraction pattern intensity, adequate for the small quantity of Pt present in the catalyst.

2.3. Electrochemical and photoelectrochemical characterization of coatings

The electrochemical and photoelectrochemical measurements were performed with the Autolab 100 (EcoChemie) system. Cyclic voltammetry (CV) and chronoamperometry (CA) experiments were carried out in a three-electrode cell equipped with a flat quartz window opposite the working electrode. A Pt foil was used as the counter electrode and a SCE as the reference electrode. The CV experiments were performed in nitrogen deaerated 0.1 M HClO₄ and 0.1 M HClO₄ + 0.5 M MeOH (Chromasolv[®] for HPLC, gradient grade, ≥99.9%) solutions. Voltammograms were run at 10 mV s^{–1} and 5 mV s^{–1} potential sweep rate for at least three consecutive full cycles since preliminary experiments showed that a near-steady state response was observed only after the second run. CA experiments were carried out in the dark and under Vis light illumination. During medium-term constant potential experiments of 300 s, the potential was kept at +0.40 V vs. SCE in a 0.1 M HClO₄ + 0.5 M MeOH deaerated solution, following a conditioning potential protocol. The latter involved initial contact with the solution at –0.30 V vs. SCE for 2 s (where methanol oxidation is minimum), a step to +0.50 V vs. SCE for 2 s (for desorption of adsorbed H and oxidation of CO being formed by methanol oxidation at this potential) and a stay at 0.00 V for 2 s (in the double layer region). A Radium Ralutec 9 W/71 visible light lamp (λ > 400 nm), placed at a distance of 2.5 cm from the sample, was used for front face electrode illumination. The power density on the sample surface position was measured as 3 mW cm^{–2} with a photometer.

For CO oxidation experiment, the electrode was put in a clean deaerated 0.1 M HClO₄, saturated with pure CO gas (>99.99% purity; Air Liquid). The electrode was held at +0.10 V vs. SCE for 5 min, allowing for CO adsorption. The excess of CO in the solution was purged with nitrogen for 10 min. Then the electrode was scanned to more positive potentials at a 10 mV s^{–1} potential sweep rate, for CO monolayer oxidation.

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