



The kinetics of the hydrogen oxidation reaction on WC/Pt catalyst with low content of Pt nano-particles

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ABSTRACT

The catalytic activity of WC/Pt electrocatalysts towards hydrogen oxidation reaction (HOR) in acid solution was studied. Tungsten carbide (WC) prepared by polycondensation of resorcinol and formaldehyde in the presence of ammonium metatungstate salt and CTABr surfactant was used as the support of a Pt electrocatalyst (WC/Pt). The obtained WC/Pt electrodes were characterized by XRD, HRTEM, EDS, EELS and electrochemical measurements. HRTEM analysis showed that the WC particles possess a core-shell structure with a metallic tungsten core and a shell composed of a mixture of tungsten carbides shell (WC and W_2C). The WC/Pt catalyst is composed of well-dispersed sub-nanometer Pt clusters which consist of a few to several tens of Pt atoms. EELS measurements indicate that the WC particles function as nucleation sites for Pt nanoparticles. Based on the Tafel–Heyrovsky–Volmer mechanism the corresponding kinetic equations were derived to describe the HOR current–potential behavior over the entire potential region on RDE. The fitting showed that in the lower potential region HOR on Pt proceeds most likely via the Tafel–Volmer (TV) pathway. The kinetic results also showed that the WC/Pt(1%) when compared to the standard C/Pt(1%) electrode led to a remarkable enhancement of the hydrogen oxidation in an acidic medium, which was explained by H-spill-over between platinum and tungsten carbide.

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1. Introduction

Tungsten carbide (WC) has been considered as an anode material for hydrogen [1] or methanol [2] polymer electrolyte membrane fuel cells (PEMFCs) since Leavy and Boundort [3] first showed that WC materials possess catalytic properties similar to those of platinum group metals, due to their isoelectronic structure to platinum. Unfortunately, WC is not an inert material. When exposed to water, WC undergoes continuous oxidation and dissolution [4,5]. The exact nature of the formed tungsten oxides is difficult to characterize and is strongly dependent on the applied potential, electrolyte composition and surface pretreatment [6]. The relatively undefined composition of the surface oxide layers is probably the major reason for the irreproducible hydrogen adsorption potentials at tungsten carbide [7]. The activity for hydrogen oxidation reaction (HOR) and stability of high area tungsten carbides in acidic electrolytes depend on their preparation method. The activity of WC was related to the carbon deficiency and oxygen replacement in carbon layers of the WC lattice [8,9].

Most significant for the electrocatalysis at tungsten carbide is the presence of oxygen species (tungsten oxides) at the catalyst surface.

Ross and Stonehart [10] discussed the effect of the surface composition of tungsten carbides on the activity for HOR. The HOR activity of the carbon deficient, oxygen containing carbides was significantly higher than that of the stoichiometric carbide. The increased activity of the oxygen substituted carbide was due to a reduced interaction of the surface with the electrolyte, resulting from the covalent tungsten–oxygen bonding. However, when used as an anodic material under PEFC conditions, WC alone exhibits poor electrocatalytic activity although it showed tolerance to CO poisoning [11,12]. The HOR activity of WC was four orders of magnitude lower than that of Pt [10]. One of the reasons is its low specific area, due to a high preparation temperature which lead to formation of rather large particle sizes.

Lately, a great effort has been directed towards studies on the fundamental surface properties and new methods for preparation of WC materials that could be used as an electrocatalyst [13,14]. It has been reported that WC possesses three different crystalline phases (β - W_2C , α -WC, and β - WC_{1-x}) depending on the synthetic route and reaction conditions [15]. In order to improve the catalytic activity of tungsten carbide towards HOR the effect of the addition

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of a second metal, such as Ni, Co, Fe, Mn or Mo was also investigated [16–18]. However, addition of Ni, Fe or Mn resulted in a lower activity for HOR, owing to the reduced surface area of the catalysts. At the same time, Co–WC catalyst carburized at 600 °C exhibited better catalytic activity as compared to WC catalyst [18].

It has been found that combination of Pt with both α -WC [19–21], β -W₂C [22] and β -WC [23] resulted in a high catalytic activity for hydrogen oxidation. While the W₂C/Pt catalyst showed similar HOR activity and kinetics as C/Pt catalyst [22], WC/Pt catalysts prepared with high surface area WC exhibited higher specific activity than C/Pt catalyst [24,25]. It has been postulated that Pt was accelerating the dissociative adsorption of H₂, which was the rate-determining step for the HOR [25] and WC could take over the rest steps in the mechanism of the hydrogen oxidation reaction.

In addition, it has been found that the stability of WC was extended to higher positive potentials in the presence of a small amount of Pt [26]. The enhanced stability of the Pt–WC surface was attributed to the strong bonding between Pt and WC, most likely at defect regions of the WC surface, which prevents the surface oxidation. Some reports found that the charge for H adsorption/desorption on Pt supported on WC was higher compared with that on C supports [27,28], which was explained by H⁺-spill-over between Pt and WC.

According to our best knowledge, in the published reports, the HOR activity of various tungsten carbides or Pt/WC catalysts was mainly treated by comparing RDE polarization curves, or the kinetic currents determined using Koutecky–Levich linear relationship, at the selected potential.

The aim of the present paper is to demonstrate that the kinetics of the HOR at WC/Pt catalysts can be generally treated through the Tafel–Heyrovsky–Volmer pathway, and it is possible to determine kinetic parameters of those elemental steps by analyzing RDE polarization curves. The kinetics of the HOR was investigated at home-made WC/Pt and commercial C/Pt catalysts in order to examine the specific role of WC on enhanced activity of Pt towards the HOR. The Pt catalyst content was very low (1 mass%) in both electrodes, because that is the only way to see any noticeable difference in their RDE polarization curves, taking into account the fact that the HOR is an extremely fast reaction on Pt.

2. Experimental

2.1. Preparation of WC

Mesoporous WC was prepared by polycondensation of resorcinol (99% purity E. Merck) and formaldehyde (Fluka Chemie) in the presence of cetyltrimethylammonium bromide (CTABr) surfactant, using the modified method proposed by Ganesan et al. [28]. In a typical synthesis, 6.14 g of CTABr was dissolved in 20 ml of distilled water and added to the solution containing 4.073 g of ammonium metatungstate (AMT), 1.13 g of resorcinol and 1.7 ml of formaldehyde in 10 ml H₂O. Then the solution was decanted in a glass tube, sealed and placed for 3 days at 25 °C, 1 day at 50 °C and 3 days at 85 °C. During this procedure the solution was transformed to gel from which cryogel was prepared by the freeze-drying method [29]. The gel was immersed in a tenfold higher volume of t-butanol (p.a. quality, Centrohem, Beograd) for one day and rinsed twice with new t-butanol to displace the liquid contained in the gel. The sample was pre-frozen at –30 °C for 24 h. After that, it was dried frozen for 20 h at the pressure of 4 mbar. The red colored cryogel was calcinated at 1173 K for 1 h in Ar flow and 2 h in H₂ flow (2 cm³ s^{–1}) [30].

2.2. Physicochemical characterization

The BET surface area and pore size distribution of the WC sample were calculated from nitrogen adsorption/desorption

isotherms at –196 °C, using the gravimetric McBain method. Pore size distribution was estimated by applying the BJH method [31] to the desorption branch of isotherms, and mesoporous surface and micropore volume were estimated using the high resolution α_s plot method [32].

The phase structure, crystallinity and size of the synthesized WC and WC/Pt catalysts were studied with an X-ray diffractometer (XRD, JEOL 6300F microscope) with Cu K α radiation ($\lambda = 0.154056$ nm).

Transmission electron microscopy (TEM), measurements were performed using the FEI (Fillips Electronic Instruments)–CM200-FEG super-twin and TEAM0.5 ultra-twin transmission electron microscopes, operating at 200 kV and equipped with the Gatan 1k \times 1k and 2k \times 2k CCD cameras, respectively. Specimens were prepared for transmission electron microscopy by making suspension of the catalyst powder in ethanol, in an ultrasonic bath. The suspension was dropped onto clean holey carbon grids and then dried in air. The chemical composition of W–WC core-shell particles were characterized by energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS).

2.3. Catalyst preparation

The Pt catalyst was deposited on a WC support by a conventional borohydride reduction method. The preparation process can be described as follows: 40 mg of the WC powder was dispersed in 20 ml of high-purity water (Millipore, 18 M Ω cm) in ultrasonic bath, and then mixed with appropriate amount of H₂PtCl₆ aqueous solution (10 mg ml^{–1}). The mixture of metal salt and support was reduced by using an excess of sodium borohydride solution. The precipitate was washed with high-purity water and then dried at 80 °C. The Pt loading of the samples was 1 mass% and 10 mass%.

2.4. Electrode preparation

Four milligrams of WC/Pt catalysts was ultrasonically suspended in 1.0 ml of 2-propanol and 50 μ l of Nafion solution (5 mass%, Aldrich) to prepare catalyst inks. Then, 10.0 μ l of ink was transferred with an injector to the clean gold disk electrode (5 mm diameter, with geometric surface area of 0.196 cm²). After volatilization of alcohol, the electrode was heated at 80 °C for 10 min. The Pt loading was 0.4 μ g (1 mass%). In order to compare the catalytic activity of WC/Pt against a conventional C supported Pt catalyst, a commercial catalyst XC-72R/Pt (20 mass%, E-Tek) was thoroughly mixed and homogenized with appropriate amount of XC-72R powder to attain 1 mass% of Pt loading.

2.5. Electrochemical characterization

A conventional three-compartment cell was used for electrochemical characterization. The working electrode compartment was separated by fritted glass discs from other two compartments. A reversible hydrogen electrode (RHE) in the same solution as that of the working electrode was used as the reference electrode. A large-area platinum sheet of 5 cm² geometric area was used as the counter electrode. The electrochemical measurements were performed in 0.5 mol dm^{–3} HClO₄ solution (Spectrograde, Merck), prepared with high-purity water, at the temperature of 25 °C.

The experiments were performed by potentiodynamic method. A PAR Model 273 Potentiostat/Galvanostat was used for all electrochemical experiments. Polarization curves for the HOR were recorded at the scan rate of 2 mV s^{–1}.

The cyclic voltammetry (CV) experiments were carried out in the potential range between hydrogen and oxygen evolution in

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