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Nb–TiO_2 supported platinum nanocatalyst for oxygen reduction reaction in alkaline solutions

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ABSTRACT

Platinum based nanocatalyst at home made Nb–TiO_2 support was synthesized and characterized as the catalyst for oxygen reduction reaction in 0.1 mol dm^{-3} NaOH, at 25 °C. Nb doped TiO_2 catalyst support, containing 5% of Nb, has been synthesized by modified acid-catalyzed sol–gel procedure in non-aqueous medium. BET and X-ray diffraction (XRD) techniques were applied for characterization of synthesized supporting material. XRD analysis revealed only presence of anatase TiO_2 phase in synthesized support powder. Existence of any peaks belonging to Nb compounds has not been observed, indicating Nb incorporated into the lattice.

Nb–TiO_2 supported Pt nanocatalyst synthesized, using borohydride reduction method, was characterized by TEM and HRTEM techniques. Platinum nanoparticles distribution, over Nb doped TiO_2 support, was quite homogenous. Mean particle size of about 4 nm was found with no pronounced particle agglomeration. Electrochemical techniques: cyclic voltammetry and linear sweep voltammetry at rotating disc electrode were applied in order to study kinetics and estimate catalytic activity of this new catalyst for the oxygen reduction reaction in alkaline solution. Two different Tafel slopes were found: one close to −90 mV dec^{-1} in low current density region and other approximately −200 mV dec^{-1} in high current density region, which is in good accordance with literature results for oxygen reduction at Pt single crystals, as well as Pt nanocatalysts in alkaline solutions. Similar specific catalytic activity (expressed in term of kinetic current density per real surface area) of Nb(5%)–TiO_2/Pt catalyst for oxygen reduction reaction in comparison with the carbon supported platinum (Vulcan/Pt) nanocatalyst, was found.

1. Introduction

Electrochemical systems operating in alkaline solutions are subject of growing industrial importance. The most important, among these systems, are alkaline fuel cells (AFCs), as well as chlor-alkali electrolysis and metal air batteries. Overall performance of the fuel cells mostly depends on the cathode performance as at high current density the great extent of cell polarization is due to the oxygen reduction reaction (ORR) that takes place at the cathode [1–6].

The kinetics of oxygen reduction in alkaline solution is generally faster than in acid solution and that is attributed, according to the literature, to a lower degree of specific anion adsorption [1]. However, due to its application in fuel cells with developed proton exchange membrane this reaction has been recently much more studied in acid than in alkaline media. But, development of alkaline anion exchange membrane is under investigation [2], and that will enable benefits of faster kinetics of oxygen reduction in alkaline solutions to be used.

Oxygen reduction reaction in alkaline solutions has been investigated, especially at Pt and Pt group metals [3–7], from single crystals to nanoparticles dispersed on high surface area support, owing the best catalytic activity and corrosion stability of these materials.

It is recognized that the important role in electrochemical nanocatalysis is to provide the adequate support for catalyst. First of all, the support should supply physical surface for dispersion of small catalyst particles, that is necessary to create high active surface area of the catalyst. Since the electrochemical reactions include charge transfer, support material must possess high conductivity to allow transfer efficiently, and should be corrosion inert, as well.

Since carbon or graphite possesses good electronic conductivity it is the most widely used support providing huge surface for catalyst particles dispersion that diminishes the catalyst loading [8–10]. However, the degradation of the catalyst performances with carbon as support during recharge of the fuel cell, at high potentials and

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high temperature, was caused by carbon corrosion reaction so, the temperature at which carbon has been considered as suitably stable in strong alkaline solution has suggested to be lower than 75 °C. With increasing operating time carbon slowly corrodes due to the reaction with the HO_2^- radical formed as an intermediate during oxygen reduction. Despite carbon corrosion, some researchers have found that the use of carbon based supports is advantageous, since the carbon itself has some activity for ORR [1]. It has been found that during oxygen reduction at carbon supported catalyst, carbon significantly contributes to the current only below 0.7–0.8 V vs. RHE [5,11,12], indicating that the contribution of the support may not be helpful in the potential range at which AFCs would ideally operate [1]. Since the two-electron ORR pathway is operated at carbon materials as catalysts [13,14], resulting hydrogen peroxide production, that could increase degradation of fuel cells components [15,16]. Having in mind all mentioned above, the need of new non-carbon catalyst supports for AFCs applications is obvious.

Recently, titanium suboxides (commercially called Ebonex), with the integer formula Ti_nO_{2n-1} ($4 < n < 10$), and between them the most pronounced their first two oxides, *i.e.* Ti_4O_7 and Ti_5O_9, have attracted a lot of attention as new catalyst supports [17–20]. These oxides exhibit electrical conductivity and chemical stability at room temperature similar to these of carbon and graphite. The corrosion stability of these oxides in aqueous electrolytes is very high and they do not form hydrides in contact with hydrogen [21]. All of that make them suitable as a support. Investigation of ORR at Ebonex supported Pt nanoparticles in 0.1 mol dm^{-3} NaOH solutions, revealed similar catalytic activity to polycrystalline Pt [20].

High catalytic activity towards oxygen evolution at PtCo, referred by Slavcheva et al. [22], is related to the formation of surface oxides and electronic interactions between the metallic components of the catalyst and the supportive Ebonex. However, the problem with Ebonex powder is its very low specific surface area.

Sasaki et al. [23] demonstrated that niobium oxide nanoparticles could be adequate support for Pt, reducing at the same time the noble-metal contents of catalyst for oxygen reduction. Since niobium oxides have excellent chemical stability they could diminish the problems of substrate oxidation and corrosion degradation. It has also been reported that, by doping titania with pentavalent niobium ions, these ions get into the anatase titania crystalline structure preventing its phase transformation to rutile. This effect has been attributed to the extra valence of niobium ions, reducing oxygen vacancies in anatase phase and inhibiting the transformation to rutile. Park and Seul [24] referred that $NbTiO_2$ supported Pt catalyst showed an excellent catalytic activity for ORR in acid solution, mainly due to the good dispersion of Pt on $NbTiO_2$.

Zhang et al. [25] investigated ORR activity of Pt electrocatalysts on several forms of niobium oxide in $HClO_4$ solution and excellent stability of Pt/NbO_2 bilayer system has been reported, even after 2500 cyclic voltammetry cycles. Rutile phase niobium doped titanium oxide was tested as supporting material for PEMFCs in acid solution [26]. Half cell accelerated durability test demonstrated high stability and catalytic activity for ORR of $Pt/Nb_xTi_{(1-x)}O_2$ catalyst [26]. Bauer et al. demonstrated higher electrochemical stability of Pt catalyst on Nb doped TiO_2 nanofibers in acid solution, in comparison with carbon supported one [27]. The stability and activity of niobium doped titania supported Pt nanocatalyst were compared to those of Pt/C in PEMFC application. The high potential hold test showed significantly higher stability of the membrane electrode assembly with $Pt/10Nb–TiO_2$ compared to that with Pt/C [28].

In our previous paper [29] we have shown that $Nb–TiO_2$ (0.5%Nb) supported Pt nanocatalyst exhibited higher catalytic activity for ORR in acid solution, by comparing it with carbon supported Pt catalyst. So, the aim of this work was to test the catalytic activity of this new catalyst for ORR in alkaline solution. It has been tested in 0.1 mol dm^{-3} NaOH, compared in term of specific catalytic activity towards ORR with results obtained on Vulcan/Pt catalyst, and discussed it considering the other literature findings.

2. Experimental

2.1. Preparation of Nb-doped TiO_2 support

Nb-doped TiO_2 (5%Nb) nanosized powder was synthesized through modified sol–gel procedure proposed by Boujday et al. [30]. Sol was prepared by adding appropriate amount of hydrochloric acid to the solution of titanium tetraisopropoxide, and an appropriate volume of niobium (V) ethoxide, under vigorous stirring. Mixture was placed in glass tubes, sealed and placed at room temperature, for 5 days. During that time hydrolysis proceeded without forming precipitate, leading to transparent sol. Gellification of the sol was achieved by adding an appropriate amount of water.

The sample was dried by freeze-drying method using Modulyo Freeze Dryer System Edwards, England, consisting of freeze dryer unit at High Vacuum Pump E 2 M 8 Edwards.

In order to activate Nb donor in TiO_2, the nanoparticles were additionally annealed at 400 °C for 2 h under pure H_2 gas flow and cooled to room temperature in H_2 gas atmosphere. Detailed synthesis data have been previously reported in Ref. [29].

2.2. Synthesis of $Nb–TiO_2$/Pt catalyst

The $Nb–TiO_2$ supported Pt (20 wt.%) catalyst ($Nb_{0.05}Ti_{0.95}O_2/Pt$) was prepared by borohydride reduction method. Appropriate amount of H_2PtCl_6 was dissolved in D.I. water. $Nb–TiO_2$ support was dispersed in D.I. water and then mixed by adding metal salt solution with constant stirring. The mixture of metal salt and support was reduced by using excess of sodium borohydride solution. Obtained precipitate was washed with D.I. water and then dried at 80 °C.

The Vulcan/Pt catalyst with Pt loading of 20 wt.%, used as benchmark, was synthesized by modified ethylene glycol method on a commercial Vulcan support. The preparation procedure was fully described in Ref. [31].

2.3. Electrode preparation

Twenty milligrams of $Nb–TiO_2$/Pt catalyst was ultrasonically suspended in 9.5 ml of water and 0.5 ml of Nafion solution (5 wt.% Aldrich solution) in order to prepare catalyst ink. Appropriate amount of prepared ink (Pt loading kept constant – 8 μg) was transferred to a gold disk electrode (with area of 0.128 cm^2). After the water volatilization, the electrode was heated at 80 °C for 10 min.

2.4. Physical characterization of $Nb–TiO_2$ support and $Nb–TiO_2$/Pt catalyst

2.4.1. Adsorption and desorption isotherms

The specific surface area and pore size distribution of $Nb–TiO_2$ support were calculated from adsorption and desorption isotherms of N_2, by gravimetric McBain method. Pore size distribution was estimated by applying BJH method.

2.4.2. XRD analysis

XRD analysis was carried out by Siemens D-500 diffractometer. $CuK_($ radiation was used in conjunction with a $CuK_($ nickel filter. Obtained X-ray diffraction pattern was used to evaluate the crystallite size of the $Nb–TiO_2$ support. The average crystallite size, *D*, was calculated from Scherrer's formula: $D = 0.9\lambda/\beta\cos\theta$, where λ is the wavelength of the X-rays, θ is the diffraction angle, $\beta = (\beta m^2 - \beta s^2)$,