Journal of Electroanalytical Chemistry 735 (2014) 68–76

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electrochemical oxygen reduction behaviour of platinum nanoparticles supported on multi-walled carbon nanotube/titanium dioxide composites

K. Jukk [a], N. Kongi [a], A. Tarre [b], A. Rosental [b], A.B. Treshchalov [b], J. Kozlova [b], P. Ritslaid [b], L. Matisen [b], V. Sammelselg [a,b], K. Tammeveski [a,*]

[a] Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia
[b] Institute of Physics, University of Tartu, Ravila 14c, 50411 Tartu, Estonia

ARTICLE INFO

Article history:
Received 24 July 2014
Received in revised form 2 October 2014
Accepted 8 October 2014
Available online 20 October 2014

Keywords:
Oxygen reduction
Electrocatalysis
Carbon nanotubes
Titanium dioxide
Pt nanoparticles
Composite catalysts

ABSTRACT

Pt nanoparticle-titanium dioxide/multi-walled carbon nanotube (Pt–TiO_2/MWCNT) materials were synthesised by combining chemical vapour deposition (CVD), atomic layer deposition (ALD) and magnetron sputtering techniques. These composite materials were employed as electrocatalysts for oxygen reduction reaction (ORR). The surface morphology of the prepared catalysts as well as their supports was examined by scanning electron microscopy (SEM). The SEM images revealed the preferential growth of aligned MWCNTs. The surface composition of Pt–TiO_2/MWCNT catalysts was characterised using X-ray photoelectron spectroscopy (XPS). Their electrocatalytic properties toward the ORR were investigated in acid and alkaline media using the rotating disk electrode (RDE) technique. The ORR activity of Pt–TiO_2/MWCNT was compared with that of commercial Pt/C catalyst and bulk Pt.

1. Introduction

Overcoming fuel cell commercialisation and mass-production challenges by developing catalyst materials with satisfactory activity and stability is of great interest [1,2]. Several factors compromise the fuel cell durability, such as loss of conductivity, membrane degradation and corrosion of carbon support. These issues should be solved for further implementation in automotive fuel cell application. Fuel cell catalyst electroactive area decreases as a result of carbon support corrosion which leads to agglomeration and migration of Pt particles at potentials higher than 0.9 V vs. reversible hydrogen electrode (RHE) [3]. Therefore a great number of alternative catalyst support materials have been proposed in recent studies [4–6]. A great deal of attention has been paid to metal oxides, in particular TiO_2, SnO_2, Nb_xO_y, WO_3, MnO_x, Ta_2O_5 [7–19]. In recent years, intensive research has been focused on the investigation of TiO_2 as a potential candidate support material in the form of nanoparticles, nanotubes or combined with different carbon materials forming a multi-component composite support structure for catalytic nanoparticles [20–29]. Adding TiO_2 into the structure of high-area carbon support helps to achieve anti-corrosion and anti-poisoning properties of electrocatalyst. While Pt acts as catalyst for carbon support corrosion process, TiO_2 component acts as inhibitor of the catalyst degradation process. Parts of the carbon surface may be mechanically protected against progressive electrochemical degradation by the presence of overlaid titania and therefore improve stability properties of the oxygen reduction reaction (ORR) catalysts [30]. Despite the poor electrical conductivity of TiO_2, this metal oxide is frequently utilised in the design of catalytic composite materials due to possible synergistic effect between TiO_2, carbon support and a catalyst. It has been reported earlier, that metal oxides can anchor Pt nanoparticles by interacting with them and thereby inhibit the migration and agglomeration of Pt [31]. It was proposed that chemical interactions between Pt and TiO_2 could alter the electron density in the d-orbitals of Pt and thereby enhance the catalytic activity towards the ORR [32]. Timperman and Alonso-Vante prepared Pt/TiO_2/C catalysts by sol–gel method, which showed 2 times higher Pt mass activity for ORR than commercial Pt/C catalyst [33]. According to previous studies, same research group explained the synergistic effect between Pt and TiO_2 using two models: bifunctional mechanism and electronic effect [34]. Selvaganesh et al. proposed that the introduction of TiO_2 into the catalyst structure does not only help mitigate the aggregation of Pt particles but also protects the

* Corresponding author. Tel.: +372 7375168; fax: +372 7375181.
E-mail address: kaido.tammeveski@ut.ee (K. Tammeveski).

http://dx.doi.org/10.1016/j.jelechem.2014.10.008
1572-6657/

Nafion membrane against peroxide radicals originating from hydrogen peroxide generated during incomplete reduction of O_2 [35].

Recently, TiO_2 nanosheets grafted to carbon nanotube (CNT) backbone were used as a support for Pt catalysts, showing improved catalytic performance and stability for methanol electro-oxidation reaction [36]. In order to increase the electrocatalytic activity of fuel cell catalyst composite materials titania-supported bi- or trimetallic alloys have been proposed [37,38]. Another approach in catalyst template design is to dope TiO_2 with an n-type dopant, such as niobium [39–46]. TiO_2 doped with Pd and Nb was investigated as a support for Pt–Pd alloy catalyst and showed higher Pt mass activity (>130 mA mg^{-1} at 0.9 V vs. RHE) than that of the commercial 47 wt.% Pt/C catalyst (110 mA mg^{-1}), however, the durability of these materials was low [47]. Zhang et al. succeeded to prepare highly corrosion resistant Pt nanocatalyst supported on NbO_2 covered CNTs [45]. Addition of niobium oxide helped to improve adhesion between Pt and carbon support without lowering catalytic properties of Pt. Pt distribution and catalyst support morphology has a crucial impact on electrochemical performance [48]. In their study Xu and co-workers evidenced interactions between Pt catalyst and metal oxide support, which led to modification of the Pt electronic structure, which in turn significantly enhanced the electrocatalytic activity towards the ORR and methanol oxidation reactions [49].

Ruiz Camacho et al. used photo-deposition method to obtain highly active Pt/TiO_2–C, Pt/SnO_2–C and Pt/ZnO–C ORR electrocatalysts in acid media [50]. They observed that synergetic effect

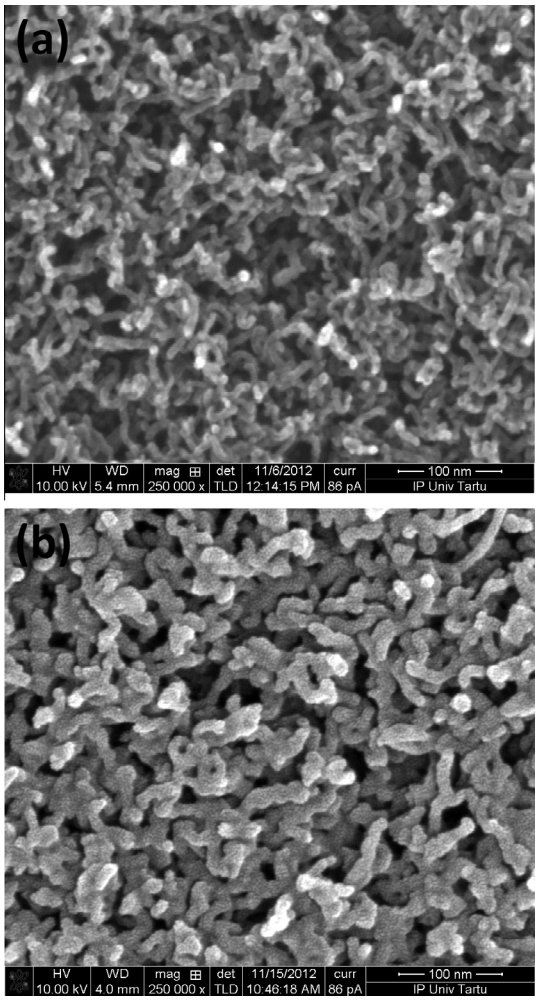

Fig. 1. SEM images of (a) as-prepared MWCNTs and (b) Pt–TiO_2/MWCNT samples.

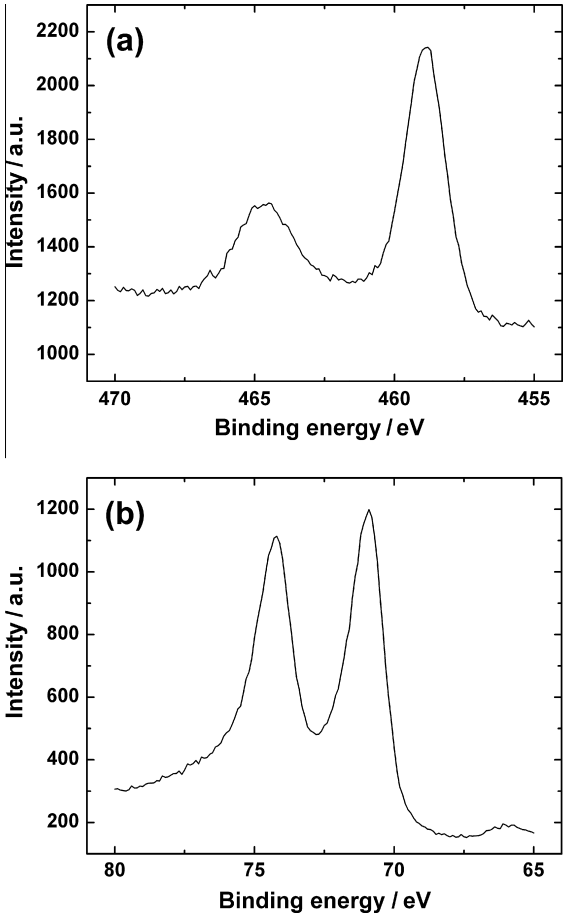

Fig. 2. XPS core-level spectra of 3-Pt–TiO_2/MWCNT samples in (a) Ti2p and (b) Pt4f regions.

arising from strong interaction of Pt centres and Ti metal oxide promotes exceptional activity and stability towards the ORR. Tian and co-workers deposited Pt nanoparticles on TiO_2 by photo-assisted reduction method and the prepared catalyst had 500 times higher vast surface area than bulk Pt electrode [51]. Bauer et al. deposited Pt nanoparticles onto Nb-doped and H_2 reduced TiO_2 nanofibers by chemical reduction with $NaBH_4$ in ethylene glycol. The prepared catalyst support showed improved durability compared to conventional carbon support [52]. Same group reported Pt/TiO_2/C catalyst with comparable ORR mass activity to that obtained for Pt supported on mesoporous carbon, however long-term cycling showed that incorporation of TiO_2 into the substrate matrix noticeably improved durability of the prepared catalyst material [30]. Huang et al. coated CNTs by a nanolayer of TiO_2 with subsequent doping of TiO_2 with carbon and anchoring of Pt nanoparticles by ethylene glycol method [53]. Their study proved that post-thermal treatment of the prepared ORR catalyst can significantly improve catalyst activity and stability. Montero-Ocampo et al. used metal–organic chemical vapour deposition for preparations of Pt–TiO_2–CNT catalysts [27]. These materials showed good catalytic activities for ORR in acid media. Yao et al. synthesised platinised fibre-like Ti_4O_7 which showed superior durability as well as enhanced Pt mass activity in comparison to commercial Pt/C catalyst in 0.5 M H_2SO_4 [54]. Pulsed electrodeposition technique was employed by Zhang et al. to synthesise and deposit Pt nanoparticles onto the TiO_2 nanotube arrays as a support for fuel cells [55]. Dual-gun sputtering technique was used for the preparation of TiO_2 nanotube arrays as carbon-free support for PtCo catalyst. $Pt_{70}Co_{30}$ catalyst had the highest specific surface area and thus the maximum electrocatalytic activity for ORR in 0.5 M $HClO_4$ [56].