## DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS 94

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Electrocatalytic reduction of oxygen on carbon nanotube-based nanocomposite materials



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Dissertation in Colloid and Environmental Chemistry

Dissertation is accepted for the commencement of the degree of Doctor of Philosophy in Chemistry on May 3, 2010 by the Doctoral Committee of the Institute of Chemistry, University of Tartu.

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- Commencement: June 21, 2010 at 11.00, Ravila 14A, room 1021

Publication of this dissertation is granted by ESF project FMTDK



Euroopa Liit Euroopa Sotsiaalfond



Eesti tuleviku heaks

ISSN 1406–0299 ISBN 978–9949–19–384–4 (trükis) ISBN 978–9949–19–385–1 (PDF)

Autoriõigus Nadežda Aleksejeva, 2010

Tartu Ülikooli Kirjastus www.tyk.ee Tellimuse nr. 276 To my parents, Niina and Mihhail Aleksejev, for having always stayed behind me and pushing me ahead with the best of gifts ever: education.

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### LIST OF ORIGINAL PUBLICATIONS

This thesis consists of six original articles listed below and a review. The articles are referred in the text by Roman numerals I–VI.

- I N. Alexeyeva, K. Tammeveski, Electrochemical reduction of oxygen on multiwalled carbon nanotube modified glassy carbon electrodes in acid media, *Electrochemical and Solid-State Letters* 10 (2007) F18-F21.
- II N. Alexeyeva, T. Laaksonen, K. Kontturi, F. Mirkhalaf, D.J. Schiffrin, K. Tammeveski, Oxygen reduction on gold nanoparticle/multi-walled carbon nanotubes modified glassy carbon electrodes in acid solution, *Electrochemistry Communications* 8 (2006) 1475–1480.
- III N. Alexeyeva, K. Tammeveski, Electroreduction of oxygen on gold nanoparticle/PDDA-MWCNT nanocomposites in acid solution, *Analytica Chimica Acta* 618 (2008) 140–146.
- IV N. Alexeyeva, J. Kozlova, V. Sammelselg, P. Ritslaid, H. Mändar, K. Tammeveski, Electrochemical and surface characterisation of gold nanoparticle decorated multi-walled carbon nanotubes, *Applied Surface Science* 256 (2010) 3040–3046.
- V N. Alexeyeva, L. Matisen, A. Saar, P. Laaksonen, K. Kontturi, K. Tammeveski, Kinetics of oxygen reduction on gold nanoparticle/multi-walled carbon nanotube hybrid electrodes in acid media, *Journal of Electroanalytical Chemistry* 642 (2010) 6–12.
- VI N. Alexeyeva, K. Tammeveski, A. Lopez-Cudero, J. Solla-Gullón, J.M. Feliu, Electroreduction of oxygen on Pt nanoparticle/carbon nanotube nanocomposites in acid and alkaline solutions, *Electrochimica Acta* 55 (2010) 794–803.

#### Author's contribution

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The author has performed all electrochemical measurements and data analysis. The author is responsible for the interpretations of electrochemical results and writing the papers.

### **ABBREVIATIONS AND SYMBOLS**

A	geometric surface area of an electrode
AFM	atomic force microscopy
$A_{\rm r}$	real surface area of the catalyst
AuNPs	gold nanoparticles
BDD	boron-doped diamond
CNFs	carbon nanofibers
CNTs	carbon nanotubes
$c^{\mathrm{b}}_{\mathrm{O}_2}$	concentration of oxygen in the bulk solution
CV	cyclic voltammetry
$D_{0_2}$	diffusion coefficient of oxygen
Ε	electrode potential
EDS	energy dispersive X-ray spectroscopy
$E^0$	standard potential
$E_{1/2}$	half-wave potential
F	Faraday constant
fr	roughness factor
FWHM	full width at half maximum
GC	glassy carbon
GIXRD	glancing incidence angle X-ray diffraction
HOPG	highly-oriented pyrolytic graphite
HR-SEM	high-resolution scanning electron microscopy
Ι	current
Id	diffusion-limited current
I <sub>k</sub>	kinetic current
j	current density
Jd	diffusion-limited current density
Ĵk	kinetic current density
k	heterogeneous electron transfer rate constant
$k^0$	the apparent electrochemical rate constant for O <sub>2</sub> reduction
K-L	Koutecky-Levich
LBL	layer-by-layer technique
MA	mass activity
MEA	membrane-electrode assembly
MWCNTs	multi-walled carbon nanotubes
n	number of electrons transferred per O <sub>2</sub> molecule
ORR	oxygen reduction reaction
PDDA	poly(diallyldimethylammonium chloride)
PEMFC	proton exchange membrane fuel cells
PG	pyrolytic graphite
PtNPs	platinum nanoparticles
PTFE	polytetrafluoroethylene

Q	charge
R	universal gas constant
r.d.s.	rate-determining step
RDE	rotating disk electrode
RHE	reversible hydrogen electrode
RRDE	rotating ring-disk electrode
RVC	reticulated vitreous carbon
SA	specific activity
SEM	scanning electron microscopy
SCE	saturated calomel electrode
SDS	sodium dodecyl sulphate
SHE	standard hydrogen electrode
SWCNTs	single-walled carbon nanotubes
Т	temperature
TEM	transmission electron microscopy
v	potential scan rate
XPS	X-ray photoelectron spectroscopy
α	transfer coefficient
$\theta$	surface coverage
ν	kinematic viscosity of the solution
$\Phi$	percentage of peroxide formation on the disk
ω	electrode rotation rate

#### I. INTRODUCTION

In recent years a great deal of attention has been given to the study of nanostructured materials due to their application in many fields. Nanostructured material is any solid material that has a nanometre  $(1 \text{ nm} = 10^{-9} \text{ m})$  dimension [1]. Nanoparticles of platinum and other noble metals are used in the preparation of electrodes for fuel cells [2]. The preparation of noble metal catalysts in a highly dispersed form on carbon supports enables to effectively utilise these costly metals in practical devices [3]. There has been much interest in the research of carbon nanotubes since their discovery [4]. Carbon nanotubes have led to many new technical developments and applications due to their excellent properties – high chemical stability, unique electronic properties, high mechanical strength and high surface area. Recent electrochemical studies have demonstrated that CNTs have the ability to promote electron-transfer reactions.

The oxygen reduction reaction continues to be an active research area with different experimental and fundamental approaches focused on understanding the main factors and models of mechanism of its catalysis. The reaction proceeds by either a direct four-electron pathway, where the final product is water or by a two-electron pathway yielding hydrogen peroxide. The reduction of  $O_2$  proceeds on the cathode of a fuel cell and the efficiency of the cell is reduced due to the sluggish kinetics of this reaction.

It was of particular interest in this work to study the effect of different nanocomposite catalyst materials on the kinetics of the ORR. Main attention was focused on electrocatalytic activity of carbon nanotube-supported gold and platinum nanoparticles towards oxygen reduction. The kinetic parameters of  $O_2$  reduction on these catalysts were determined.

In the first part of this work, the electrocatalytic reduction of oxygen has been studied on multi-walled carbon nanotube modified glassy carbon electrodes in acid solution in order to test the properties of MWCNTs as the support material [I]. The oxygen reduction behaviour of oxidatively pre-treated and untreated MWCNT modified GC electrodes was compared.

In the main part of the work the electroreduction of oxygen has been studied on gold nanoparticle/multi-walled carbon nanotubes (AuNP/MWCNT) modified GC electrodes in 0.5 M  $H_2SO_4$  solution [II–V]. The oxygen reduction behaviour of AuNP/MWCNT electrodes was compared with that of a bulk gold electrode.

In the third part, Pt nanoparticles supported on single-walled (PtNP/SWCNT) and multi-walled carbon nanotubes (PtNP/MWCNT) were prepared using two different synthetic routes [VI]. Before use, the CNTs were cleaned to minimize the presence of metal impurities coming from the catalyst used in the synthesis of this material, which can interfere in the electrochemical response of the supported Pt nanoparticles. The reduction of  $O_2$  on PtNP/CNT composites was studied in acid and alkaline solutions.

The surface structure and morphology of new hybrid materials has been examined by transmission electron microscopy, high-resolution scanning electron microscopy, X-ray photoelectron spectroscopy and glancing incidence angle X-ray powder diffraction. Electrochemical experiments were carried out using cyclic voltammetry and the rotating disk electrode method.

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#### 2. LITERATURE OVERVIEW

#### 2.1. The general scheme of oxygen electroreduction

The oxygen reduction reaction is a multielectron reaction that involves a number of elementary steps and various reaction intermediates. The reaction proceeds by either a four-electron pathway, where the final product is water:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
  $E^0 = 1.229 \text{ V vs. SHE}$  (1)

or by a two-electron pathway yielding hydrogen peroxide:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
  $E^0 = 0.67 V.$  (2)

Peroxide can be further reduced:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
  $E^0 = 1.77 V,$  (3)

or catalytically decomposed (disproportionated):

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{4}$$

In alkaline solutions, the corresponding reactions are:

$$O_2 + 2H_2O + 4e^- \to 4OH^ E^0 = 0.401 \text{ V},$$
 (5)

$$O_2 + H_2O + 2e^- \to HO_2^- + OH^- \qquad E^0 = -0.065 \text{ V},$$
 (6)

$$HO_2 + H_2O + 2e \rightarrow 3OH \qquad E^0 = 0.867 V,$$
 (7)

$$2HO_2 \rightarrow 2OH + O_2. \tag{8}$$

[3,5–7].

The simplified reaction pathway is shown in Scheme 1.



**Scheme 1.** Simplified mechanism of oxygen reduction in acid solutions. The rate constants for the different steps in the scheme are indicated in the scheme  $(k_i)$ . (ads) denotes the species in their adsorbed state.

Despite the apparent simplicity, these overall reactions represent a complex electrocatalytic network and involve many elementary steps. The dominating pathway depends on several factors, for example, on the electrode material, solution pH and on electrode potential [6,7].

#### 2.2. Oxygen reduction on bulk carbon electrodes

The oxygen reduction reaction on carbon-based electrodes has been extensively studied. Different types of carbon are of wide research interest, such as pyrolytic graphite, highly oriented pyrolytic graphite, glassy carbon, boron-doped diamond, reticulated vitreous carbon, carbon nanotubes and other carbon materials [8]. Overwhelmingly, the ORR on carbon electrodes has been investigated in alkaline solution, because most of these materials are active catalysts for  $O_2$  reduction at high pH. The only exceptions are basal plane HOPG and BDD, which strongly inhibit this reaction [9]. An interesting  $O_2$  reduction behaviour on different carbon substrate materials has been reviewed for both alkaline and acid solutions [8,10,11]. The mechanism of this reaction at different conditions has been extensively studied; however, there are still many aspects which are unclear. It is generally accepted that in acidic and alkaline media the electrochemical reduction of oxygen on carbon-based electrodes involves the formation of hydrogen peroxide.

In an early work Sabirov and Tarasevich investigated the kinetics of the ORR on PG and GC electrodes [12], showing that the reduction of  $O_2$  on PG in acid and alkaline solutions and on GC in alkaline solution proceeds via intermediate peroxide formation. At E > -0.2 V vs. RHE in 0.5 M H<sub>2</sub>SO<sub>4</sub> peroxide as a stable product of reaction results. The same group of workers investigated the pH-dependence of the ORR on PG electrodes and concluded that in the pH range between 1 and 4 the rate of  $O_2$  reduction is independent of pH [13]. Taylor and Humffray performed the oxygen reduction measurements on GC electrodes in the solutions of various pHs [14]. Their results were in agreement with that suggested for PG by Sabirov et al. proposing that the r.d.s. is the first electron transfer to  $O_2$ , followed by protonation of  $O_2^-$  in solutions for which pH < pKa (HO<sub>2</sub>)  $\approx$  4.8. The pH-dependence of O<sub>2</sub> reduction on bare GC electrodes has been also studied in Ref. [15]. It was found that the  $O_2$ reduction activity was higher in the solutions of a high pH. At lower pH, the nature of active sites on GC changes and as a result, the value of  $E_{1/2}$  for  $O_2$ reduction is almost independent of pH.

It is evident that the kinetics of the ORR strongly depends on electrode pretreatment conditions. Nagaoka et al. found that  $O_2$  reduction on anodised GC was independent of pH [16]. Maruyama and Abe carried out experiments with surface-oxidised GC electrodes and those coated with a Nafion film [17]. The  $O_2$  reduction current was smaller on Nafion-coated GC than on bare GC, which was explained by lower pH environment for the ORR at Nafion-coated GC because the activity for  $O_2$  reduction at carbon electrodes decreases as the pH decreases. Another reason was the blocking of the GC surface by the side chains of the Nafion polymer, caused by interaction between the fluorocarbon part of the side chains and the GC surface having a hydrophobic character. Vaik et al. studied the reduction of  $O_2$  on electrochemically oxidised GC electrodes in 0.1 M KOH [18]. Surface oxidation increased the electrocatalytic activity of GC for  $O_2$  reduction to hydrogen peroxide. However, these electrodes catalyse the further reduction of  $HO_2^-$  at more negative potentials than -0.9 V vs. SCE and as a result the value of  $\Phi$  decreases.

Yano et al. have examined the electrochemical behaviour of highly conductive BDD thin films for the reduction of  $O_2$  in acid solution [19]. Focusing particularly on the electrochemical pre-treatment effect they observed that the ORR was slightly inhibited by mild conditions treatment, which deactivated the catalytic functional groups on the electrode surface, but strong oxidative treatment in base appears to substantially remove the sp<sup>2</sup> carbon impurities. Bennett et al. investigated the effect of sp<sup>2</sup>-bonded carbon impurities on the ORR in 0.1 M HClO<sub>4</sub> and 0.1 M NaOH for BDD thin-film electrodes [20]. The results indicated that the grain boundaries and the sp<sup>2</sup> carbon impurities could have a profound impact on the electrode reaction kinetics for certain redox systems.

Friedrich and Ponce-de-León have reviewed the use of RVC as an electrode material, showing that it can be used for the electrosynthesis of  $H_2O_2$  in aqueous acidic solutions. The presence of Fe(II) in the catholyte extremely reduces the half-life of peroxide [21]. Saleh et al. have characterised the electrochemically oxidised RVC electrode for oxygen reduction in acid solution [22]. At the anodically oxidised RVC the reduction of oxygen occurred at more positive potentials and its rate increased. Compton and co-workers employed RVC for the electrochemical production of peroxide [23]. An increased production of hydrogen peroxide on RVC under insonation was observed.

The reduction of  $O_2$  has been thoroughly studied on bulk carbon materials in alkaline solution [15,24–32]. The half-wave potential of  $O_2$  reduction is still more negative than the reversible potential of the  $O_2/HO_2^-$  couple. The kinetics of  $O_2$  reduction strongly depends on the surface properties of carbon electrodes [29–32]. For instance, the highly oriented pyrolytic graphite electrode is remarkably inactive for  $O_2$  reduction [9,24,27,30]. Obviously, the valences of surface carbon atoms are satisfied for HOPG and  $O_2$  molecules could adsorb only on surface defects or steps [27]. The edge plane of pyrolytic graphite shows a much higher activity towards  $O_2$  reduction than the basal plane of HOPG [24,29,31]. It has been proposed that the enhanced rate of  $O_2$  reduction on carbon materials at high pH is caused by native oxygen-containing species (mostly quinone-type groups) [15,25,27,28]. A detailed discussion on the kinetics and mechanism of  $O_2$  reduction on bulk carbon electrodes in the solution of high pH is outside the scope of the present thesis. The reduction of oxygen is strongly inhibited by modifying the surface of GC electrodes with various aryl groups [33]. The rate of  $O_2$  reduction can be greatly increased by modifying the surface of carbon materials with quinones [9,15,18,27,28]. These aspects have been thoroughly reviewed by Sarapuu [34].

#### 2.3. Oxygen reduction on CNT modified electrodes

Since their discovery by Iijima, CNTs have attracted a great interest as a novel material for electrocatalysis [4] and the potential application of carbon nanotubes in creating new catalysts has been extensively explored [35–38]. These materials show a great promise in the fields of electrocatalysis [39], electroanalysis [40] and biosensing [41]. CNTs can be used as a support material for various catalysts, and for this reason their electrocatalytic properties towards O<sub>2</sub> reduction are of great fundamental and practical importance. In order to achieve a stable and uniform catalyst layer some multifunctional polymers can be used for the attachment of CNTs to the electrode surface. A variety of surfactants have been employed to obtain a uniform dispersion of carbon nanotubes [42]. There is a strong tendency of CNTs to agglomerate in the absence of surfactants. The pH-dependence of oxygen electroreduction has been investigated on MWCNT/GC electrodes [43]. Various surfactants were used in the electrode modification to improve solubility of the nanotubes: dihexadecyl hydrogen phosphate, cetyltrimethylammonium bromide, sodium dodecyl sulphate and Triton X-100. The RDE results revealed that the halfwave potential of  $O_2$  reduction was higher in solutions of high pH. At lower pHs (pH < 10) the value of  $E_{1/2}$  did not essentially depend on the solution pH.

Britto et al. observed a well-defined peak of oxygen reduction at -0.31 V vs. SCE on carbon nanotube modified electrodes in H<sub>2</sub>SO<sub>4</sub> solution (pH 2) [44]. Shanmugam and Gedanken have presented a route for the generation of hydrophilic CNTs [45]. The electrodes prepared were proposed for the studies of the ORR in acid media. Manesh et al. described the O<sub>2</sub> reduction in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution on GC/polyaniline (PANI) grafted MWCNT modified electrode, which showed more positive peak potential (610 mV vs. SCE) compared to that for PANI-modified GC electrode (550 mV vs. SCE) [46]. Conducting polymer is present in this electrode as a connective unit to the MWCNTs.

Recently, the reduction of  $O_2$  on MWCNT/HOPG electrodes of various modifications was studied in 0.1 M KOH [47]. Based on the cyclic voltammetry results it was evident that chemical oxidation of MWCNTs increases the amount of oxygenated functional groups on the surface of MWCNTs. However, the  $O_2$  reduction activity did not change considerably in alkaline solution.

The MWCNT/PTFE nanocomposites also showed a high electrocatalytic activity for O<sub>2</sub> reduction in 0.1 M KOH [48]. The value of  $\Phi$  was determined from the RRDE data and it was about 85% at prewave potentials. These results

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were in a good agreement with those obtained in previous studies with SWCNT and MWCNT modified electrodes in alkaline solution [49–51].

Recent advantages in the field of  $O_2$  reduction electrocatalysis include the application of nitrogen-doped CNTs [52,53]. These are more active catalysts for oxygen reduction as compared to undoped CNTs. Maldonado and Stevenson have explored structural, textural, and compositional features of N-doped and nondoped carbon nanofibers [54]. Their results demonstrate that the incorporation of nitrogen into the carbon nanofibers results in a more facile adsorption of  $O_2$  and the greater activity for  $H_2O_2$  decomposition. An experimental and theoretical study by Sidik et al. showed that carbon radical sites formed adjacent to substitutional N in graphite are active for  $O_2$  reduction to  $H_2O_2$  via an adsorbed OOH intermediate in 0.5 M  $H_2SO_4$  [55].

In recent years the effect of metal impurities of CNTs on their electrochemical properties has been highlighted [56–58]. Metallic components in CNTs originate from catalysts used in the synthesis of this material by chemical vapour deposition. It was shown that a variety of purifying methods do not result in complete removal of impurities from the surface of CNTs. If electrode material contains impurities that are sensitive to the ORR, then these can significantly influence the reaction rate or pathway.

Therefore, the purpose of the first part of this work was to study the reduction of oxygen on oxidatively treated MWCNTs in acid solution and to compare their  $O_2$  reduction behaviour with that of the untreated nanotubes.

#### 2.4. Oxygen reduction on bulk gold electrodes

The kinetics of oxygen reduction has been thoroughly studied on bulk gold electrodes in acid solution [59–64]. This metal shows a modest O<sub>2</sub> reduction activity in acid electrolyte. The structure sensitivity of O<sub>2</sub> reduction on Au(*hkl*) surfaces is well-established in acid media [60,63], the Au(100) and Au(111) being the most active and the least active planes, respectively. In acid electrolytes the O<sub>2</sub> reduction on gold electrodes is much slower than in alkaline media, but shows also a pronounced structural sensitivity [60,64]. The two-electron reduction is the dominating reaction pathway for Au single-crystal surfaces [60]. At more negative potentials the number of electrons transferred is greater than two because of the further reduction of H<sub>2</sub>O<sub>2</sub> [65,66]. The Tafel slope was ca –120 mV dec<sup>-1</sup> for all Au surfaces studied [60]. An attempt has been made to investigate the O<sub>2</sub> reduction process on Au(100) in a large pH range (pH 1–13) [62]. Two- and four-electron transfer regions were mapped depending on pH and the electrode potential.

The electrochemical reduction of oxygen has been extensively studied on bulk polycrystalline and single-crystal Au electrodes in alkaline media [67–73]. Two-wave voltammetry curves for  $O_2$  reduction have been observed for gold electrodes in alkaline solution [67–69]. However, the number of electrons

transferred per  $O_2$  molecule was higher than two at the potentials of the first  $O_2$ reduction wave [67,69] indicating that the reduction does not stop at the peroxide stage. Investigations on well-defined Au single-crystal surfaces gave further information on these processes. Detailed studies on Au single-crystal planes have shown that the reduction of oxygen is dependent on surface structure [6.60, 70-73]. The Au(100) plane was found to be the most active one in alkaline electrolyte [60,70,71]. Not only the half-wave potential of  $O_2$ reduction was significantly higher on this plane, but also the mechanism of reaction was found to be different. It was proposed that this particular plane catalyses the direct 4e<sup>-</sup> reduction of O<sub>2</sub> in the potential region where chemisorbed AuOH is present on the surface [70,71]. The current peak of HO<sub>2</sub><sup>-</sup> reduction appeared at the same potential. Alternative explanation for n > 2 is based on the idea that peroxide catalytically decomposes at the potentials of the first wave and the formed  $O_2$  is recycled in the two-electron process therefore enhancing the number of electrons consumed [69]. It is generally recognised that the first electron transfer is the rate-limiting step of O<sub>2</sub> reduction on gold electrode with a Tafel slope of  $-120 \text{ mV dec}^{-1}$ . The following step is most probably the surface dismutation of superoxide anion [67]. More detailed discussion on the mechanism of O<sub>2</sub> reduction on Au electrodes in alkaline solution is beyond the scope of this thesis.

#### 2.5. Oxygen reduction on AuNP modified electrodes

Gold nanoparticles are frequently employed in the preparation of nanocomposites that are useful in electrochemical and molecular electronics applications [74]. The incorporation of these hybrid materials led to the rapid development of electrode design. The modification of electrodes with nanoparticle-based materials drastically improves the properties of electrodes due to the high surface area-to-volume ratio, chemical stability, and excellent electronic properties.

Recently, the study of gold nanoparticles anchored to the surface of CNTs has grown significantly [75]. This hybrid material can be widely used in electrocatalysis and electroanalysis. Here Au nanoparticle-based nanocomposite materials can be exploited as catalysts for the oxygen reduction reaction.

Compton and co-workers have recently reviewed the methods used for the preparation of CNT-supported metal nanoparticles and their further applications [76]. Carbon nanotubes can be used as a support material for various catalysts.

Obviously, differences in the structure of Au nanoparticles may influence the electrocatalytic behaviour of the AuNP-modified electrodes. The reduction of  $O_2$  on thin-film Au electrodes prepared by vacuum evaporation onto GC substrates has been studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> [77]. It was observed that at low overpotentials the 2e<sup>-</sup> reduction to H<sub>2</sub>O<sub>2</sub> predominates in acid media and at more negative potentials the peroxide intermediate is further reduced. The

specific  $O_2$  reduction activity of the Au-film electrodes was almost constant over the entire range of film thickness (0.25–50 nm). Since the first report by Sarapuu et al. [77], the reduction of  $O_2$  on nanostructured gold electrodes has been extensively investigated [78–110]. Guerin et al. found that the specific activity of vacuum-deposited Au films decreased with decreasing AuNP size below 3 nm [78]. Ohsaka and co-workers studied  $O_2$  reduction on gold nanoparticles electrochemically deposited on different substrates [80–88]. Au nanoparticles-electrodeposited electrodes were remarkably active towards oxygen reduction in acid media [80,81]. However, a fundamental understanding of the origin of the electrocatalytic effect observed has not been attained.

The electrocatalytic activity of Au catalysts has also been examined in neutral and alkaline solutions [84–87,94–110]. It is evident that the nature of gold surface considerably affects the kinetics of electrochemical processes. In the case of  $O_2$  reduction, the formation of  $HO_2^-$  as the final reaction product in the whole potential range studied indicated that the surface of gold nanorods was composed of (111) and (110) domains, while (100) domains were practically absent from the surface [95]. Oxygen reduction has been studied on AuNPs electrodeposited onto NH<sub>2</sub>-terminated boron-doped diamond [96]. Sarapuu et al. examined the electrocatalytic properties of nanostructured gold electrocatalytic activity towards  $O_2$  reduction in alkaline solution. A two-step reduction of oxygen was observed on Au nanoparticles electrodeposited on an organic template [98].

#### 2.6. Oxygen reduction on bulk platinum electrodes

Platinum is one of the best electrocatalysts for  $O_2$  reduction [3]. Early work on oxygen reduction on bulk polycrystalline Pt electrodes has been reviewed in several books and review articles [3,5,7,111,112]. The electrochemical reduction of oxygen on platinum is the cathode reaction in fuel cells, and the four-electron reduction to water is the desired reaction and the two-electron reduction to hydrogen peroxide is to be avoided.

It has been established that in a large region of potentials the platinum electrode surface is covered with oxygen-containing species [111,113] and these affect the kinetics of the ORR. The Tafel slope changed going from the reduced Pt surface to the oxide-covered one. At low overpotentials the Tafel slope was  $-60 \text{ mV dec}^{-1}$  and at more negative potentials the slope changed to  $-120 \text{ mV dec}^{-1}$  in both acid and alkaline solutions [113]. It was found that the slope changed when the surface coverage by adsorbed oxygen became low. It was proposed by Damjanovic and Brusic that the first electron transfer is the r.d.s. for O<sub>2</sub> reduction in both acid and alkaline media [113,114]. The same r.d.s. has been proposed to control the kinetics of the ORR in both Tafel regions

in the case of the slow first electron transfer (assuming  $\alpha = 0.5$ ) the slope of – 120 mV dec<sup>-1</sup> is expected, however, the experimentally observed slope value was –60 mV dec<sup>-1</sup> in the low current density region [113,114]. It was suggested that at the potentials of intermediate coverage by adsorbed oxygen the Temkin conditions of adsorption are operative. At higher current densities the coverage by reaction intermediates decreases and Langmuir conditions of adsorption should become predominant. In those conditions the rate equations for the reduction of oxygen in both acid and alkaline solution have been derived by Damjanovic and co-workers [113–116]. Their results have been summarised in Ref. [117].

Tarasevich reported a similar Tafel behaviour for oxygen reduction on polycrystalline Pt electrodes [118]. The Tafel slope was  $-60 \text{ mV dec}^{-1}$  at the low current density region and  $-120 \text{ mV dec}^{-1}$  at high current densities. It was stated that the kinetics of O<sub>2</sub> reduction could only be explained by taking into account the effect of adsorbed oxygen-containing species. The ORR was inhibited by increasing coverage of adsorbed oxygen. It was assumed that the r.d.s. must ivolve the adsorption of molecular O<sub>2</sub>. Deriving a kinetic expression for the ORR, Tarasevich assumed that the heat of chemisorption decreases linearly with the coverage of adsorbed oxygen. In contrast to Damjanovic it was claimed that the chemisorption of molecular oxygen was affected [118]. The change in the Tafel slope from  $-60 \text{ mV dec}^{-1}$  to  $-120 \text{ mV dec}^{-1}$  was observed at the coverage value of 0.3 in alkaline solution and at a lower  $\theta$  in acid media.

More recently, Markovic and co-workers revisited the derivation of the kinetic expression for  $O_2$  reduction and a slightly modified rate equation for the ORR on Pt has been proposed [119]:

$$j = nFkC_{O_2}^{b} (1 - \theta_{ad})^{x} \exp(-\frac{\beta FE}{RT}) \exp(-\frac{\gamma r \theta_{OH}}{RT})$$
(9)

where *x* is either 1 or 2 depending on the site requirements of the adsorbates,  $\beta$  and  $\gamma$  are the symmetry factors (as assumed to be 0.5) and *r* is a parameter characterising the rate of change of the apparent standard free energy of adsorption with the surface coverage by adsorbing species. All other symbols have their usual meaning. The kinetics of the ORR is determined either by the free Pt sites available for the adsorption of O<sub>2</sub> (1– $\theta_{ad}$  term in Eq. (9)) and/or by the change of Gibbs energy of adsorption of reaction intermediates with  $\theta_{OH}$  ( $r\theta_{OH}$  term in Eq. (9)). This rate expression allows one to analyse the effect of various factors on the kinetics of the ORR. These authors also consider that the reduction of O<sub>2</sub> on Pt catalysts proceeds entirely *via* series pathway [119].

The ORR has been systematically investigated on Pt single-crystal electrodes during the last two decades [120–131]. The main aspects of  $O_2$  reduction on Pt(*hkl*) surfaces have been reviewed by Markovic and Ross [119,132]. It has been established that the structure-sensitivity of the ORR arises mostly due to

the structure-sensitive adsorption of anions (OH<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, etc.) on Pt(*hkl*) planes [119,131,132]. Thus, the strongly adsorbing anions like  $HSO_4$  block the catalytically active centres on the surface of Pt to a large extent and as such inhibit the rate of  $O_2$  reduction more strongly. It is especially evident in the Pt(111) case for which there is a good match between the geometry of the surface and the anion structure. Indeed, the reduction of  $O_2$  in H<sub>2</sub>SO<sub>4</sub> is much more inhibited on this particular plane in comparison to two other low index facets (Pt(100) and Pt(110)). The order of activity for the ORR on Pt single crystal planes in  $H_2SO_4$  solution is as follows: Pt(110) > Pt(100) >Pt(111). The adsorption of perchlorate ions is much weaker than that of  $HSO_4^$ and therefore the electrocatalytically active centres are less blocked in HClO<sub>4</sub> and as a consequence, the rate of the ORR is higher. However, not enough clean  $HClO_4$  solutions may contain traces of Cl<sup>-</sup> ions and these adsorb very strongly on Pt surfaces. As a result, the reduction of O<sub>2</sub> is greatly inhibited in the solution containing Cl ions [122]. Even stronger inhibition of the kinetics of the ORR on Pt(111) has been observed in the presence of Br<sup>-</sup> ions in solution [126]. In 0.1 M KOH, the structure-sensitivity of the ORR is less pronounced and it arises due to the structure-sensitive adsorption of hydroxyl species on Pt(*hkl*) surfaces [130].

#### 2.7. Oxygen reduction on PtNP modified electrodes

The structure sensitivity of the reduction of  $O_2$  on Pt(*hkl*) planes is closely related to the particle size effect [119,124,131,133]. Considering the classical (and most simple) Pt particle geometrical model which is cubo-octahedra [3,133], one can calculate the ratio of Pt(111) to Pt(100) surface atoms as a function of the Pt particle size. These calculations show that the number of surface atoms of the (100) plane starts to significantly decrease when the diameter of Pt particles is smaller than 6 nm and becomes essentially zero when the diameter is 2 nm or below [3,133]. Therefore, one can predict that the specific activity of O<sub>2</sub> reduction (current per catalyst surface area) in H<sub>2</sub>SO<sub>4</sub> solution should also decrease with decreasing Pt particle size, because the rate of  $O_2$  reduction is significantly lower on the Pt(111) plane and the atoms of this plane predominate on the surface of smaller Pt nanoparticles. The supposition that the specific activity in sulphuric acid should decrease with decreasing Pt particle size has been experimentally confirmed using highly dispersed Pt catalysts on carbon supports [134,135]. The investigation of the ORR in acid media is much more important because the acid electrolytes are preferred in the fuel cells systems [3].

The preparation of composite materials using carbon nanotubes supported Pt nanoparticles has been extensively studied during the last decade. The PtNP/CNT nanocomposites have attracted much attention as potential electrocatalysts for the ORR. Thus, several research groups have successfully synthesised

composites of PtNPs on the surface of CNTs using various methods and studied their electrocatalytic behaviour towards  $O_2$  reduction in acid [136–146], alkaline [147,148] and neutral solutions [149–151].

In 1998 Che and co-workers proposed the use of carbon nanotube/PtNP containing membranes to electrocatalyse  $O_2$  reduction in 0.05 M H<sub>2</sub>SO<sub>4</sub> [152]. They reported a large  $O_2$  reduction wave at potentials similar to those characteristics for Pt electrocatalysis in acid solution. In addition, due to the higher electrochemically active surface area, the currents obtained were 20 times higher than those observed at a Nafion-coated Pt electrode of equivalent geometric area.

Well-aligned CNTs were used for the first time as catalyst support for a fuel cell by Tang et al. [153]. These authors reported a uniform deposition of the Pt catalysts on each of well-aligned carbon nanotube arrays by using potential-step electrodeposition methods. The kinetics of the ORR at Pt/CNT electrode was investigated in 0.1 M H<sub>2</sub>SO<sub>4</sub> observing a large O<sub>2</sub> reduction current at 0.36 V (SCE), which is the typical potential for oxygen electroreduction on platinum catalysts in H<sub>2</sub>SO<sub>4</sub> solution. In comparison with a Pt/graphite electrode, the Pt/CNT electrodes yield a higher electrocatalytic activity.

Rajalakshmi and co-workers tested different catalysts containing PtNPs and CNTs for the ORR in a PEMFC, and observed that CNTs have to be functionalised to have a uniform Pt dispersion with a narrow particle size range [154]. Thus, the performance of the PEMFC with different mixtures of PtNP/MWCNTs and PtNP/C was systematically studied in order to find an optimum composition of PtNP/MWCNTs [155]. They found that a cathode catalyst containing 50% PtNP/MWCNTs and 50% PtNP/C provided the best performance due to a better dispersion and good accessibility of MWCNT support and Pt electrocatalysts for ORR in PEMFC.

However, according to the study by Li et al., Pt/MWCNT catalysts did not offer significant advantages over the PtNP/C based systems [156]. The RDE measurements conducted in 0.5 M  $H_2SO_4$  indicated that the overpotential of the ORR for PtNP/MWCNT and PtNP/C catalysts was similar and that the increase in current density for PtNP/MWCNTs was not significant.

Wang et al. compared the effect of the electrochemical surface oxidation between Pt catalysts supported on carbon black (Vulcan XC-72) and MWCNTs for the electrocatalysis of  $O_2$  reduction [157]. The Pt/MWCNT samples showed a lower loss of Pt surface area and ORR activity than those observed for the Pt supported on Vulcan carbon.

Kim and Mitani obtained highly dispersed Pt nanoparticles (1.5 nm) by introducing thiol groups on MWCNT surfaces using organic synthetic methods based on an amide bond formation [158]. The good interaction between Pt nanoparticles and the surface thiol groups on MWCNTs was the reason for a high Pt dispersion. The relationship between catalyst dispersion and the electrocatalytic activity towards ORR of these modified electrodes was investigated in 0.1 M HClO<sub>4</sub> electrolyte. The slight increase of the ORR activity for Pt/t-MWCNT was rationalised by the existence of an optimum particle size of electrocatalyst for ORR (about 3 nm). The specific activity per Pt surface area tends to increase with increasing particle size, although larger particles have smaller active surface areas for ORR [133,159].

A presumed advantage of metal nanoparticle–carbon nanotube system is that the surface of CNTs is convex and therefore the nanoparticles attached are freely accessible to solution-based species and the mass-transfer conditions are much simpler as compared to metal catalysts supported on porous carbon.

#### 3. EXPERIMENTAL

#### 3.1. Chemicals and materials

Single-walled carbon nanotubes (purity > 90%, diameter 1–2 nm, length 5–30  $\mu$ m) were purchased from NanoAmor, Inc. (Houston, TX, USA). Multi-walled carbon nanotubes (purity > 95%, diameter 30±10 nm, length 5–20  $\mu$ m) were purchased from NanoLab, Inc. (Newton, MA, USA). Sodium dodecyl sulfate, HAuCl<sub>4</sub>×3H<sub>2</sub>O, 4-nitrobenzenediazonium tetrafluoroborate, NaBH<sub>4</sub>, poly-(diallyldimethylammonium chloride) (*M*w = 200 000–350 000) in 20% aqueous solution were purchased from Aldrich. A 0.5% Nafion solution used in this work was prepared by diluting the 5% Nafion solution (Aldrich) into ethanol. The electrolyte solutions for studying O<sub>2</sub> reduction were prepared from 96% H<sub>2</sub>SO<sub>4</sub> (Suprapur, Merck) and KOH or NaOH pellets (AristaR, BDH or pro analysis, Merck) in Milli-Q water; these were saturated with O<sub>2</sub> (99.999%, AGA or 99.95%, AGA) or deaerated with Ar gas (99.999%, AGA). All other chemicals were analytical grade reagents and all the solutions were prepared with Milli-Q water (Millipore, Inc.).

Glassy carbon, Au and Pt electrodes employed for RDE experiments were prepared by mounting the GC, Au and Pt disks in a Teflon holder. GC disks were cut from rods (GC-20SS, Tokai Carbon). The geometric area of the electrodes was 0.196 cm<sup>2</sup> and the surface was polished to a mirror finish with 1.0, 0.3 and 0.05  $\mu$ m alumina slurries (Buehler) in Milli-Q water. In some experiments GC disks of 0.0711 cm<sup>2</sup> were used as electrode substrate. After alumina polishing the electrodes were sonicated in a water bath twice for 3 min.

#### 3.2. Acid-treatment of carbon nanotubes

Figure 1 shows the TEM images of the as-received SWCNT (a) and MWCNT (b) samples. In case of the SWCNTs, a high degree of metal impurities can be observed originating from the catalysts used in the synthesis of this carbon nanomaterial. On the other hand, in case of the MWCNTs, the TEM picture clearly shows a rather low degree of metallic impurities. It is important to note that the effect of metal impurities of CNTs on their electrochemical properties has been highlighted in recent years [56-58]. Consequently, cleaning procedures must be developed to ensure the complete removal of these metal impurities, which can significantly influence the reaction rate or the pathway of the system under study.

Both SWCNT and MWCNT materials were purified by refluxing in a  $HNO_3:H_2SO_4$  (1:1) mixture for 2 h at 55 °C and then for 3 h at 80 °C, washed with Milli-Q water and dried under vacuum. The results obtained after this pre-treatment showed, in both cases, an almost complete removal of impurities.

However, in case of the SWCNTs, this cleaning step was too aggressive and results in the destruction of the single-walled carbon nanotubes. No destruction of nanotube material was observed in case of the MWCNTs and consequently the methodology employed was considered to be suitable for purification purposes.



Figure 1. TEM images of SWCNTs (a) and MWCNTs (b) as-received.

In this way, different less-aggressive cleaning treatments were developed to purify the SWCNTs without altering their surface structure. For example, the treatment of SWCNTs in concentrated nitric acid at 80 °C does not result in destruction of SWCNTs surface, although the metal impurities could not be properly removed under these conditions. Finally, after different tests, it was found that the optimal treatment procedure can be achieved if the SWCNTs are treated in concentrated  $HNO_3:H_2SO_4$  (1:1) mixture for 12 h at room temperature. This methodology allows removing a majority of the metal impurities without perturbing the SWCNTs further the structure. Figure 2 presents the TEM micrographs corresponding to the clean SWCNTs (a) and MWCNTs (b) treated under the above mentioned conditions. It is well-established that the acid treatment of both multi-walled and single-walled carbon nanotubes yields carbon–oxygen functionalities on their surface such as carboxylic, phenolic, carbonyl, etc. [160].



**Figure 2.** TEM images of SWCNTs (a) after treatment in a concentrated  $HNO_3:H_2SO_4$  (1:1) mixture for 12 h at room temperature and MWCNTs (b) after treatment in a  $HNO_3:H_2SO_4$  (1:1) mixture for 2 h at 55 °C and then for 3 h at 80 °C. Scale bar: 20 nm.

#### 3.3. Preparation of MWCNT modified GC electrodes

To achieve stable and uniform films of MWCNTs on the GC electrode surface, a 0.5% Nafion aqueous solution was used to solubilise the CNTs. With the aid of ultrasonic agitation (30 min) to give black suspension, 1 mg of MWCNTs was dispersed in 1 mL of 0.5% Nafion solution. The MWCNT-Nafion film was prepared by placing a 20  $\mu$ L aliquot of MWCNT suspension onto the surface of GC and allowing the solvent to evaporate at room temperature. This procedure yields a loading of MWCNTs of about 0.1 mg cm<sup>-2</sup>.

#### 3.4. Preparation of AuNP/MWCNT modified GC electrodes

Functionalisation of MWCNTs with SDS followed a standard procedure described by Zhang et al. [161]. In a typical experiment, 1 mg of MWCNTs were dispersed into 1 mL aqueous solution of 1% SDS, a concentration greater than the critical micelle concentration and the resulting dispersion was sonicated for 30 min to give a homogeneous suspension. The AuNP/MWCNT hybrid was prepared by adding 60  $\mu$ L of 1% aqueous solution of HAuCl<sub>4</sub>×3H<sub>2</sub>O into 2 mL of the aqueous suspension of 1 mg mL<sup>-1</sup> MWCNTs–SDS under vigorous stirring, followed by addition of 60  $\mu$ L of 0.75% NaBH<sub>4</sub> aqueous solution. The mixture was stirred for 5 min, then filtered with a membrane filter (0.22  $\mu$ m, Millipore, Inc.), rinsed twice with Milli-Q water and dried in air. The

aqueous dispersion of the as-prepared AuNP/MWCNT was assembled onto the GC electrode surface by physical adsorption followed by drying in air. The AuNP/MWCNTs-modified electrode was coated with a Nafion film (0.5  $\mu$ m thick) by placing 4  $\mu$ L of a 0.5% Nafion solution in ethanol on the electrode surface and allowing the solvent to evaporate in air.

#### 3.5. Preparation of AuNP/PDDA-MWCNT modified GC electrodes

1 mg of acid-treated MWCNTs were dispersed into aqueous solution of 1 mg mL<sup>-1</sup> PDDA containing 0.5 M NaCl and the resulting dispersion was sonicated for 3 h to give a homogeneous black suspension, which was sonicated for 5 min immediately before preparing the films. Citrate-stabilised AuNP colloidal solution was prepared according to the literature [162,163] and stored in dark glass bottles at room temperature and kept stable for about 1 month. Hydrogen tetrachloroaurate trihydrate (HAuCl<sub>4</sub>×3H<sub>2</sub>O) was used as a precursor of gold nanoparticles.

An electrostatic layer-by-layer technique was employed for the fabrication of the nanocomposite electrodes. The AuNP/PDDA-MWCNT monolayer was prepared by immersing the cleaned GC electrode into MWCNT-PDDA suspension for 30 min at room temperature, then rinsed with Milli-Q water and dried in an inert gas atmosphere for 15 min. Afterwards the electrode was immersed in citrate-stabilised AuNP solution for 30 min, rinsed and dried in Ar atmosphere. To deposit two and three layers of multilayer films onto the GC electrode, the above procedure was repeated two and three times ((AuNP/PDDA-MWCNT)x/GC electrode, where x = 1, 2 or 3). The method of electrode modification used in this work is similar to that employed for the preparation of (PtNP/PDDA-MWCNT)<sub>x</sub>/GC electrodes [164]. Scheme of preparation of the AuNP/PDDA-MWCNT nanocomposite catalyst is shown below (Scheme 2). For comparison, PDDA-MWCNT/GC modified electrode was also prepared.



**Scheme 2.** Preparation of AuNP/PDDA-MWCNT hybrid material using an electrostatic layer-by-layer technique.

#### 3.6. Preparation of AuNP/(NP)MWCNT modified GC electrodes

Functionalisation of MWCNTs with nitrophenyl (NP) groups followed a standard procedure described by Dyke *et al.* [165]. 1 mg of acid-treated MWCNTs were suspended in 10 mM aqueous solution of 4-nitrobenzenediazonium tetrafluoroborate, mixed 30 min and filtered. The investigated AuNP/(NP)MWCNT catalyst was prepared by chemical reduction of 100  $\mu$ L of 1% HAuCl<sub>4</sub>×3H<sub>2</sub>O using 300  $\mu$ L of 0.75% NaBH<sub>4</sub> in an aqueous suspension of functionalised MWCNTs, mixed 30 min and filtered. Scheme of preparation of AuNP/(NP)MWCNT catalyst material is shown below (Scheme 3).



Scheme 3. Preparation of the AuNP/(NP)MWCNT catalyst material.

The modified electrodes were composed of the AuNP/(NP)MWCNT catalysts deposited as a thin layer on a GC electrode surface. A 20  $\mu$ L aliquot of the AuNP/(NP)MWCNT suspension (1 mg mL<sup>-1</sup>) was pipetted onto the GC surface, allowing the water to evaporate at room temperature. Glassy carbon plates of 12×15 mm<sup>2</sup> and 2 mm thick were used as substrates for the X-ray photoelectron spectroscopy studies.

#### 3.7. Preparation of AuNP/MWCNT modified GC electrodes by magnetron sputtering

1 mg of acid-treated MWCNTs were dispersed in 1 mL of isopropanol and the resulting dispersion was sonicated for 30 min to give a homogeneous black suspension and then a 200  $\mu$ L drop was placed on a GC plate for further magnetron sputtering procedure. Acid-treated MWCNTs on the small GC plates were placed in the sputtering chamber and the coating of Au nanoparticles was conducted by sputter-deposition with an Au target in argon atmosphere. For each experiment the same amount of gold was deposited on MWCNTs. The

nominal Au film thickness was 15 nm, which corresponds to Au loading of  $29 \pm 3 \text{ mg cm}^{-2}$ . AuNP/MWCNT composites were further annealed in argon in a tube oven at 250, 300 and 400 °C.

#### 3.8. Preparation of PtNP/CNT modified GC electrodes

Pt nanoparticles supported on single-walled and multi-walled carbon nanotubes were prepared using two different synthetic routes, synthesis of Pt nanoparticles in the presence of citrate (cit) [166], and synthesis of Pt nanoparticles in microemulsion (mic) [167] using in both cases sodium borohydride as a reducing agent. An appropriate amount of carbon nanotubes (nominal metal loading 20 wt%) was added to the nanoparticle suspensions under stirring. In what follows, these catalysts are designated as (mic)PtNP/SWCNTs, (mic)PtNP/MWCNTs, (cit)PtNP/SWCNTs and (cit)PtNP/MWCNTs.

#### 3.9. Instrumentation and measurements

An EDI101 rotator and a CTV101 speed control unit (Radiometer, Copenhagen) were used for the RDE experiments. The electrode rotation rate was varied between 360 and 4600 rpm. A saturated calomel electrode or reversible hydrogen electrode were employed as reference electrodes. The counter electrode compartment of the three-electrode cell was separated from the main cell compartment by a glass frit and Pt wire served as a counter electrode. The potential was applied with an Autolab potentiostat PGSTAT10 or PGSTAT30 (Eco Chemie B.V., The Netherlands) and the experiments were controlled with General Purpose Electrochemical System (GPES) software. All experiments were carried out at room temperature  $(23 \pm 1^{\circ}C)$ .

For all RDE measurements the adhesion of the composite electrocatalysts to the GC disk was excellent and no loss of the catalyst occurred during the measurements as evidenced by an unchanged and stable cyclic voltammogram before and after the ORR testing.

Adsorbed CO oxidation experiments were carried out by bubbling carbon monoxide (N47, AlphaGaz) through the acid electrolyte at 0.05 V until complete blockage of the surface, which was monitored by cycling the electrode between 0.05 and 0.45 V vs. RHE [168]. After that, CO was removed from the solution by bubbling argon. As a general rule, for each minute bubbling CO, 10 min of Ar bubbling were employed. Finally, CO was oxidatively stripped off from the surface and the voltammogram corresponding to the CO-free surface was again recorded. The surfaces were considered suitable when the final voltammetric profile was coincident with that recorded prior to CO adsorption.

Transmission electron microscopy experiments were performed with a JEOL, JEM-2010 microscope working at 200 kV and Tecnai 12 instrument operated at a 120 kV accelerating voltage. The sample for TEM analysis was obtained by placing a droplet of the sample solution onto a formvar/carbon coated copper grid and waiting until the complete evaporation of the solvent in air at room temperature.

The XPS experiments were carried out with a SCIENTA SES-100 spectrometer by using a non-monochromatised Mg K<sub> $\alpha$ </sub> X-ray source (incident energy = 1253.6 eV), electron take-off angle  $\theta = 90^{\circ}$ . A source power of 300W was used. The pressure in the analysis chamber was below 10<sup>-9</sup> Torr. While collecting the survey scan, the following parameters were used: energy range = 600–0 eV, pass energy = 200 eV, step size = 0.5 eV, 1 sweep. For the high resolution scan: energy range = 420–390 eV and 100–70 eV for N1s and Au4f regions, respectively, pass energy = 200 eV, step size = 0.1 eV, 10 sweeps were carried out.

The surface morphology of gold nanoparticle/multi-walled carbon nanotube samples was studied by HeliosTM NanoLab 600 high-resolution scanning electron microscope equipped with energy dispersive X-ray spectrometer Inca Energy with X-Max 50 mm<sup>2</sup> detector (Oxford Instruments). High resolution secondary electron images of the samples were acquired with TLD (Thru-the-Lens Detector) and with the probe electron energy of 2 keV using working distances of 1.8–2.5 mm. A measurement function of the microscope driving program xT Microscope Control was explored for AuNP dimension measurements and for statistical calculations. For a given sample, each SEM image presented in this paper is a representative of numerous images made on different location on the sample.

GIXRD data were measured using a refurbished topographic diffractometer URT-1 (Nauchpribor, Russia). In this instrument, the primary X-ray beam from a fine focus X-ray tube (CuK<sub> $\alpha$ </sub> radiation) working at 40 kV and 30 mA, and collimated with a 0.04° divergence slit, was incident on the sample surface at an angle of 0.3°. The diffracted beam was passed successively through equatorial Soller slits (aperture 0.2°), a 0.03 mm Ni K<sub> $\beta$ </sub> filter, a 4 mm receiving slit and was detected with a NaI:Tl scintillation detector in a step-scanning mode ( $\Delta(2\theta) = 0.1^{\circ}$ , in 100 s) around reflections from (111), (220) and (222) ( $2\theta = 33-50^{\circ}$ , 61–67.5° and 78.7–84.7°) lattice planes of cubic Au. The instrumental broadening of a reflection was determined on a standard material SRM-660 (LaB<sub>6</sub>) and the observed integral breath ( $\beta$ ) from a sample was corrected using the Voigt deconvolution method.

#### 4. RESULTS AND DISCUSSION

# 4.1. Oxygen reduction on MWCNT modified electrodes

Cyclic voltammetric measurements were carried out with both acid-treated and untreated MWCNT modified GC electrodes in  $O_2$ -free 0.5 M H<sub>2</sub>SO<sub>4</sub>. Figure 3 shows typical CV responses of the MWCNT-Nafion film coated GC electrodes in Ar-saturated solution before (curve b) and after acid treatment of MWCNTs (curve a).



**Figure 3.** Cyclic voltammograms for pre-treated (curve a) and untreated (curve b) MWCNT modified GC electrodes in Ar-saturated 0.5 M  $H_2SO_4$  at  $\nu = 100$  mV s<sup>-1</sup>. Curve (c) corresponds to a CV response of a bare GC electrode.

For the MWCNT modified GC electrodes, a clear pair of oxidation and reduction peaks is observed at approximately 0.4 V. These can be assigned to carbon-oxygen functionalities on the surface of the MWCNTs. It is not clear at present, which functional groups are responsible for the quasi-reversible redox behaviour observed, but it is likely that these are quinone-type species. By contrast, the CV curve for a bare GC electrode is almost featureless and the current is rather low (Figure 3, curve c). It can be proposed that the high background current for acid-treated MWCNTs is mainly due to the opening of the ends of CNTs or more hydrophilic properties of oxidised MWCNTs [40,45,169]. The MWCNT modified electrodes were cycled 25 times in order to achieve a stable CV response.

The background-subtracted RDE voltammetry curves of oxygen reduction on a GC electrode modified with untreated MWCNTs are shown in Fig. 4. The RDE measurements were conducted at a scan rate of 10 mV s<sup>-1</sup> in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> between 0.8 and -0.4 V.



**Figure 4.** RDE voltammetry curves for O<sub>2</sub> reduction on untreated MWCNT modified GC electrode in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.  $\nu = 10$  mV s<sup>-1</sup>.

There is an ill-defined current plateau at low rotation rates, whereas at the higher values of  $\omega$  the reduction current increases gradually. The oxygen reduction wave starts at a rather positive potential (approximately 0.3 V). The RDE data were analysed using the Koutecky–Levich (K–L) equation [170]

$$\frac{1}{I} = \frac{1}{I_{\rm k}} + \frac{1}{I_{\rm d}} = -\frac{1}{n F A k C_{\rm O_2}^{\rm b}} - \frac{1}{0.62 n F A D_{\rm O_2}^{2/3} v^{-1/6} C_{\rm O_2}^{\rm b} \omega^{1/2}}$$
(10)

where *I* is the measured current,  $I_k$  and  $I_d$  are the kinetic and diffusion-limited currents, respectively, *n* is the number of electrons transferred per O<sub>2</sub> molecule, *k* is the rate constant for O<sub>2</sub> reduction, *F* is the Faraday constant (96485 C mol<sup>-1</sup>), *A* is the geometric electrode area,  $\omega$  is the rotation rate,  $C_{O_2}^b$  is the concentration of oxygen in the bulk (1.13×10<sup>-6</sup> mol cm<sup>-3</sup>) [171],  $D_{O_2}$  is the diffusion coefficient of oxygen (1.8×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>) [171] and *v* is the kinematic viscosity of the solution (0.01 cm<sup>2</sup> s<sup>-1</sup>) [172].

The K–L plots for  $O_2$  reduction on untreated MWCNT modified GC electrodes are shown in Fig. 5a. Linear K–L plots are observed and from the slope of these lines, the number of electrons transferred per  $O_2$  molecule was calculated. The values of *n* at different potentials (Fig. 5b) indicate that the reduction of  $O_2$  produces  $H_2O_2$ , which reduces further at more negative potentials. These results are in line with the investigation by Wang et al. [173]. In their work the Nafion-wrapped nanotubes were deposited onto a GC electrode in order to monitor an enzymatic reaction by detecting the hydrogen peroxide formed. A significant enhancement of peroxide reduction was observed on CNTs.



**Figure 5.** (a) K-L plots for O<sub>2</sub> reduction on untreated MWCNT modified GC in 0.5 M  $H_2SO_4$  at various potentials: (**•**) -0.4, (**•**) -0.3, (**•**) -0.2 and (**•**) -0.1 V. (b) Potential dependence of the number of electrons transferred per O<sub>2</sub> molecule. Data derived from Fig. 4.

A series of experiments was performed in order to study the electrochemical behaviour of oxidatively pre-treated MWCNT modified GC electrodes. Figure 6 presents the RDE results for  $O_2$  reduction on the pre-treated MWCNT modified electrode. It is clearly seen that the onset potential of  $O_2$  reduction for pre-treated MWCNT modified GC electrode is more negative (approximately 0 V) and the reduction current lower than that of the untreated MWCNT modified GC electrode.



**Figure 6.** RDE voltammetry curves for  $O_2$  reduction on a chemically pre-treated MWCNT modified GC electrode in  $O_2$ -saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.  $\nu = 10$  mV s<sup>-1</sup>.

Banks et al. have demonstrated that the oxygenated species formed as a result of acid pre-treatment of the nanotubes do not significantly influence the heterogeneous charge-transfer kinetics [57]. According to the results obtained

by different research groups, the acid treatment of MWCNTs produces more carboxylic groups [45,174], and these are not electrocatalytically active toward the reduction of oxygen in acid media. The impurity effect on the electrocatalytic properties of CNTs has been discussed recently [58]. Iron oxide impurities which exist in CNTs are generally left behind in the chemical vapour deposition synthesis method. It was shown that acid washing of the as-prepared CNTs does not help to get completely rid of impurities existing in nanotubes [56]. Recently Šljukić et al. reported that these iron oxide impurities are partially overcoated with graphite shells [56]. Obviously, this is one of the reasons why it is extremely difficult to purify the nanotubes from catalyst impurities. It was outside the scope of the present research to determine the content of traces of catalyst after oxidative pre-treatment by using any spectroscopic method. According to the producer, the as-prepared MWCNTs contain ca. 1% of iron [175].

Figure 7a shows the K–L plots obtained from the RDE data presented in Fig. 6. The K–L lines are almost linear. Fig. 7b shows that the value of *n* is slightly higher than 2 at the potentials of  $O_2$  reduction. This indicates that the 2e<sup>-</sup> reduction is the predominant pathway which leads to peroxide formation. The acid-treated, MWCNT modified GC is a less active catalyst for H<sub>2</sub>O<sub>2</sub> reduction than that modified with untreated MWCNTs.



**Figure 7.** (a) K-L plots for  $O_2$  reduction on a pre-treated MWCNT modified GC in 0.5 M  $H_2SO_4$  at various potentials: (**■**) -0.4, (**▲**) -0.25, and (**▼**) -0.2 V. (b) Potential dependence of the number of electrons transferred per  $O_2$  molecule. Data derived from Fig. 6.

A comparison of the  $O_2$  reduction results for the two different MWCNT modified electrodes studied in this work is given in Fig. 8.



**Figure 8.** RDE voltammetry curves for O<sub>2</sub> reduction on: (1) Nafion-coated GC, (2) oxidatively pre-treated MWCNT modified GC, and (3) untreated MWCNT modified GC electrodes in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 1900 rpm.  $\nu = 10$  mV s<sup>-1</sup>.

The value of  $E_{1/2}$  for O<sub>2</sub> reduction on the pre-treated MWCNT modified GC electrodes shifted by ca. 250 mV to more negative potentials as compared to that of the electrodes modified with untreated MWCNTs. This is a significant effect which shows that the metal impurities in CNTs can drastically shift the reduction wave to more positive potentials. We may also consider that at least in part the electrocatalytic activity of pre-treated MWCNTs could be caused by the remaining impurities which were not removed by acid washing. The same pre-treatment of MWCNTs in acid mixture did not alter their electrocatalytic properties for O<sub>2</sub> reduction in alkaline solution to a noticeable degree [47]. Surface functional groups of MWCNTs (most probably quinone-type species) are active catalysts for this reaction in alkaline media and the redox catalysis of O<sub>2</sub> reduction on surface-bound quinones is well-established [28]. Obviously, catalyst impurities of CNTs play only a minor role in the overall reduction of O<sub>2</sub> in the solutions of high pH.

For comparison purposes, the *I*-*E* curve of  $O_2$  reduction for unmodified GC electrode is also shown in Fig. 8. The number of electrons transferred per  $O_2$  molecule on Nafion-coated GC electrode is close to two (i.e., similar to polished GC electrodes on the surface of which the reduction of oxygen proceeds via a  $2e^{-}$  pathway in acid solution [15]). In contrast to GC, the MWCNT modified electrodes possess good electrocatalytic properties for  $O_2$  reduction.

The importance of pre-treatment of CNTs for the ORR is clear, and the effect of metal impurities remaining from the fabrication of the CNTs should be considered for electrocatalytic and electroanalytical applications of CNT modified electrodes.
# 4.2. Oxygen reduction on AuNP/MWCNT modified electrodes

### 4.2.1. Surface characterisation of AuNP/MWCNT samples

TEM revealed that the number density of AuNPs present on the sidewalls of the MWCNTs was relatively low. The reason for this is the poor adhesion between gold and carbon, which limits the possibility of reliable investigations on the electrocatalytic properties of this system. Fig. 9 illustrates a representative TEM micrograph of the low coverage AuNP/MWCNT preparations. The TEM images suggest that most of the AuNPs are attached within the bundles of nanotubes. It is also evident that the size distribution of Au nanoparticles is rather polydisperse. Although individual AuNPs attached to MWCNTs can be observed, larger agglomerates are also present. In order to achieve a better structural integrity of the AuNP/MWCNT catalyst a thin film of Nafion was applied on top of it for the electrochemical experiments.



Figure 9. TEM image for an AuNP/MWCNT sample.

## 4.2.2. Cyclic voltammetry of AuNP/MWCNT modified electrodes

Cyclic voltammetric measurements were carried out with a Nafion coated AuNP/MWCNT modified GC electrodes in  $O_2$ -free 0.5 M H<sub>2</sub>SO<sub>4</sub>. For comparison purposes, the CV curves for unmodified MWCNTs and for polished gold electrodes were also recorded and typical electrochemical responses of these electrodes are shown in Fig. 10. For the MWCNT modified GC electrode, a clear pair of oxidation and reduction peaks is observed at approximately 0.4 V

(Fig. 10, curve 2). These can be assigned to carbon–oxygen functionalities on the surface of the MWCNTs. A large increase in the background current is observed in the presence of MWCNTs. The AuNP/MWCNT modified GC electrodes were cycled twenty times in order to achieve a stable CV response. Typical features corresponding to the attached Au nanoparticles are in evidence (Fig. 10, curve 1). The charge under the cathodic reduction peak for bare gold was  $1.3 \times 10^{-3}$  C cm<sup>-2</sup>, whereas that for the AuNP/MWCNT modified GC electrode was  $2.4 \times 10^{-3}$  C cm<sup>-2</sup>. This difference is probably related to the high surface area of the latter structure. This can only be the case if a threedimensional network is present at the surface so that the electrode has characteristics of a partially porous electrode containing a dispersed metal phase.



**Figure 10.** Cyclic voltammograms for AuNP/MWCNT modified GC (1), MWCNT modified GC (2) and polished gold (3) electrodes in Ar-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $v = 100 \text{ mV s}^{-1}$ . The electrodes were covered with a thin Nafion film (0.5 µm).

An ill-defined anodic peak at ca 1.15 V and a well-defined cathodic peak at ca 0.88 V correspond to the formation and reduction of gold surface oxides. A sharp current increase at potentials close to 1.4 V is related to processes on MWCNTs. This current feature is not observed for bulk gold (Fig. 10, curve 3). The real surface area of AuNPs and bulk gold ( $A_r$ ) was determined by charge integration under the gold oxide reduction peak corrected for the baseline. The charge required for an oxide monolayer was taken as 400 µC cm<sup>-2</sup> [176] and hence, the total area of the gold nanoparticles exceeds the geometric electrode area (A = 0.196 cm<sup>2</sup>) by a factor of six. The roughness factor of the bulk gold electrode ( $f_r = A_r/A$ ) was found to be 3.2.

#### 4.2.3. O<sub>2</sub> reduction on AuNP/MWCNT modified electrodes

The RDE voltammetry curves of oxygen reduction on AuNP/MWCNT modified GC electrodes are shown in Fig. 11.



**Figure 11.** RDE voltammetry curves for O<sub>2</sub> reduction on an AuNP/MWCNT modified GC electrode in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.  $\nu = 10$  mV s<sup>-1</sup>. The electrode was covered with a thin Nafion film (0.5 µm).

The background current has been subtracted from the experimental RDE data. The O<sub>2</sub> reduction wave starts at a rather positive potential (0.2 V vs. SCE). There is an ill-defined current plateau at low rotation rates, whereas at the higher values of  $\omega$  the reduction current increases gradually. At potentials more negative than -0.2 V there is a severe overlap of the currents with the reduction wave for AuNP-free MWCNT modified GC electrodes (data shown below). The RDE data were analysed using the Koutecky–Levich equation (10) [170]. The K–L plots for O<sub>2</sub> reduction on AuNP/MWCNT modified GC electrodes are shown in Fig. 12. Linear K–L plots are observed and the value of *n* calculated from Eq. (10) is close to two, showing that the reduction of oxygen proceeds predominantly by the 2e<sup>-</sup> pathway. The extrapolated K–L line yields intercept close to the origin at -0.1 V, which indicates that the process is primarily controlled by mass-transfer at this potential.



**Figure 12.** Koutecky–Levich plots for  $O_2$  reduction on an AuNP/MWCNT modified GC electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> at various potentials: (**•**) 0 and (**•**) –0.1 V. Data derived from Fig. 11.

A comparison of the  $O_2$  reduction results for the three electrodes studied is given in Fig. 13.



**Figure 13.** RDE voltammetry curves for O<sub>2</sub> reduction on MWCNT modified GC (1), polished gold (2) and AuNP/MWCNT modified GC (3) electrodes in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 960 rpm.  $\nu = 10$  mV s<sup>-1</sup>. All the electrodes were covered with a thin Nafion film (0.5 µm).

The value of the diffusion-limited current ( $I_d$ ) corresponding to the two-electron reduction of O<sub>2</sub> was taken from the K–L plots for the correct determination of the  $E_{1/2}$  values. The value of  $E_{1/2}$  for O<sub>2</sub> reduction on the AuNP/MWCNT catalyst shifted by ca 50 mV to more positive potentials as compared to that of a polished Au electrode covered by a Nafion film of the same thickness (Fig. 13, curves 2 and 3). This is a large effect and shows a remarkable electrocatalytic activity of the AuNP/MWCNT modified electrodes for oxygen reduction. The results shown in Figs. 11 and 13 indicate a significant electrocatalytic effect of gold nanoparticles on oxygen reduction. It has been generally considered that gold is a poor catalyst for this process in acid media. However, these considerations are based on the overpotential for the four-electron reduction of oxygen. Indeed, there is a large potential gap between the half-wave potential of  $O_2$  reduction for Au electrodes and the standard potential of the  $O_2/H_2O$  couple. The 2e<sup>-</sup> reduction of oxygen (Eq. (11)) predominates on the surface of gold electrodes in acid media [63] and the overpotential for this process is much lower.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{11}$$

In the potential range of interest, the unmodified MWCNT surface does not display significant activity towards  $O_2$  reduction, but the reduction current increases for E < 0 V (Fig. 13, curve 1). The origin of the electrocatalytic effect observed is not clear, but it is in line with the observation of the strong changes in the catalytic properties of an inert metal in the bulk when the size of the phase is decreased to nanometer dimensions [177].

# 4.3. Oxygen reduction on AuNP/PDDA-MWCNT modified electrodes

#### 4.3.1. Surface characterisation of AuNP samples

A representative TEM micrograph of the citrate-stabilised gold nanoparticles is shown in Fig. 14a. The TEM examination revealed that the particle size is  $15 \pm 3$  nm. This is in agreement with previous observations for citrate-stabilised AuNPs [162,163]. Fig. 14b presents the size distribution of the gold nanoparticles prepared (100 particles were calculated to obtain the average size).



**Figure 14.** (a) TEM image of gold nanoparticles deposited on an amorphous carbon film, (b) size distribution of gold nanoparticles.

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## 4.3.2. Cyclic voltammetry of AuNP/PDDA-MWCNT modified electrodes

Figure 15 presents CV curves of different modified electrodes in  $O_2$ -free 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 100 mV s<sup>-1</sup>. The MWCNT-modified electrode showed a clear pair of oxidation–reduction peaks at about 0.4 V. This might indicate the presence of carbon–oxygen functionalities on the surface of acid-treated MWCNTs. Moreover, the MWCNT modified electrode has a very large background current compared with bare GC due to the significant increase of the electrode surface area. It was shown on the basis of the RDE results that acid treatment of MWCNTs has a strong effect on the electrocatalytic activity for O<sub>2</sub> reduction in acid solution. The half-wave potential shifted more than 250 mV in the negative direction upon MWCNTs treatment in acids [I]. This shift is related to the removal of catalyst impurities from MWCNTs.

A pair of peaks was observed for the AuNP/PDDA-MWCNT modified electrodes (Fig. 15) showing typical features of gold surface oxidation on the forward scan (a broad anodic peak appeared at ca 1.15 V) and its reduction on the reverse scan (at ca 0.88 V). To estimate the amount of gold present in the nanocomposite electrodes, the real surface area of AuNPs was determined by charge integration under the gold oxide reduction peak corrected for the baseline. The charge under the cathodic reduction peak ( $Q_c$ ) for three AuNP/PDDA-MWCNT modified GC electrodes was determined ( $Q_c = 9.85 \times 10^{-6}$ ,  $1.84 \times 10^{-5}$  and  $4.05 \times 10^{-5}$  C for one-, two- and three-times coated electrodes, respectively). As can be seen, the value of  $Q_c$  and the total area of AuNPs increased with increasing the number of coating cycles. The charge required for the formation of an oxide monolayer was taken as 400  $\mu$ C cm<sup>-2</sup> [176].



**Figure 15.** Cyclic voltammograms for GC electrodes coated with one (curve 1), two (curve 2) and three (curve 3) layers of AuNP/PDDA-MWCNT in Ar saturated 0.5 M  $H_2SO_4$ .  $\nu = 100 \text{ mV s}^{-1}$ .

## 4.3.3. O<sub>2</sub> reduction on AuNP/PDDA-MWCNT modified electrodes

A comparison of the oxygen reduction results for the four electrodes studied in  $O_2$  saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> is given in Figure 16. The RDE results clearly demonstrate the excellent electrocatalytic activity of AuNP/PDDA-MWCNT modified GC electrodes for O2 reduction in comparison with the PDDA-MWCNT/GC electrode. The results presented in Fig. 16 show a significant positive shift of the oxygen reduction wave and an increase in the reduction current at a constant potential. The oxygen reduction wave starts at approximately 0.2 V for AuNP/PDDA-MWCNT modified electrodes. The polarisation curves are similar for all the AuNP/PDDA-MWCNT/GC electrodes studied, but an increase in the electrode activity with increasing number of coating cycles is in evidence. It should also be mentioned that there was some scatter in the RDE results, which primarily arises from the batch-to-batch deviation in the nanocomposite preparation. The modified electrodes used in the present work were remarkably stable during repetitive potential scans. After each set of oxygen reduction measurements at different rotation rates, the experiment was repeated at the scan rate of 360 rpm. These RDE voltammetry curves (i.e. the first and the last scan recorded at the same rotation rate) almost coincided. which suggests that a high stability of modified electrodes was achieved.



**Figure 16.** RDE voltammetry curves for O<sub>2</sub> reduction on AuNP/PDDA-MWCNT (curves 1–3) and PDDA-MWCNT (curve 4) modified GC electrodes in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 1900 rpm.  $\nu = 20$  mV s<sup>-1</sup>. Curves (1–3) correspond to the GC electrodes coated with one, two and three layers of AuNP/PDDA-MWCNT.

Fig. 17 shows the K–L plots obtained from the RDE data presented in Fig. 16. Linear K–L plots are observed and from the slope of these lines the number of electrons transferred per  $O_2$  molecule was calculated. The values of *n* at different potentials (shown in Fig. 18) indicate that the reduction of  $O_2$  produces H<sub>2</sub>O<sub>2</sub>, which reduces further at more negative potentials. The further reduction of H<sub>2</sub>O<sub>2</sub> at high overpotentials (E < -0.2 V) is in agreement with previous observations [77,81,97].





Figure 17. Koutecky–Levich plots for  $O_2$  reduction on AuNP/PDDA-MWCNT modified GC electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> at -0.05 V. GC electrode coated with one ( $\blacktriangle$ ), two ( $\blacksquare$ ) and three ( $\blacktriangledown$ ) layers of AuNP/PDDA-MWCNT.

**Figure 18.** Potential dependence of *n* for AuNP/PDDA-MWCNT modified GC electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub>. GC electrode coated with one ( $\blacktriangle$ ), two ( $\blacksquare$ ) and three ( $\blacktriangledown$ ) layers of AuNP/PDDA-MWCNT.

It was previously observed that the number of electrons involved in the AuNP catalysed  $O_2$  reduction depends on the chemical environment of the gold catalysts [94]. Gopalan et al. [79] observed a 4e<sup>-</sup> reduction of oxygen on poly(aminothiophenol)-Au<sub>nano</sub> modified GC electrode. They stated that the fourelectron pathway for this reaction was presumably due to the presence of poly(aminothiophenol) as a modifier for Au nanoparticles. Huang et al. [178] reported a 2e<sup>-</sup> pathway for O<sub>2</sub> reduction on Au nanoparticles/[tetrakis-(*N*methylpyridyl) porphyrinato] cobalt (CoTMPyP) modified GC electrode. Electrochemical reduction of AuCl<sub>4</sub><sup>-</sup> anions sandwiched between CoTMPyP layers led to the *in situ* formation of Au nanoparticles in the multilayer films. During the formation of Au nanoparticles a CoTMPyP anion was used and a two-electron pathway for oxygen reduction was witnessed.

The values of half-wave potential for O<sub>2</sub> reduction on AuNP/PDDA-MWCNT modified GC electrodes shifted to more positive potentials as compared to that of the PDDA-MWCNT modified electrode ( $E_{1/2} = -320$  mV at 1900 rpm). The  $E_{1/2}$  values were determined to be -102, -92 and -76 mV for the GC electrodes modified with one, two and three layers of AuNP/PDDA-MWCNT, respectively. These results reflect an apparent increase in the electrode activity with increasing number of coating cycles. The specific activity of the AuNP/PDDA-MWCNT modified electrodes was calculated using the Eq. (12).

$$SA = I_k / A_r \tag{12}$$

where  $I_k$  is the kinetic current at a given potential and  $A_r$  is the real surface area of gold. The real area of gold was determined from the stable cyclic voltammograms by charge integration under the oxide reduction peak and using a value of 400  $\mu$ C cm<sup>-2</sup> for the reduction of an oxide monolayer [176]. The SA values were determined at 0.05 V taking into account the real surface area of AuNPs for each electrode (Table 1). The calculated values of SA decreased with increasing catalyst film thickness. These SA values listed in Table 1 are higher than that obtained for the bulk Au electrode in identical conditions (SA =  $0.4 \text{ mA cm}^{-2}$ ). Recently, the effect of Au nanoparticle size on the kinetics of O<sub>2</sub> reduction has been systematically studied by Guerin et al. [78] in acid media and these authors concluded on the basis of their results that the specific activity is constant for particles larger than 3 nm. Apparently, the electrocatalytic activity of the gold nanoparticulate material towards oxygen reduction might depend on the catalyst support and on the particular arrangement of AuNPs within the structure of the three-dimensional nanocomposite film. The better electrocatalytic properties for the lower loadings of the AuNP/PDDA-MWCNT catalyst could be related to better accessibility of these layers to dissolved oxygen molecules. It is suggested that the higher activity of the single-time coated electrodes could be explained by better electron-transfer properties between the GC substrate and the most adjacent layer of carbon nanotubes.

**Table 1.** Results of the electrochemical characterisation of the AuNP/PDDA-MWCNTmodified GC electrodes in  $0.5 \text{ M H}_2SO_4$ .

Electrode	$Q_{c}$ (µC)	$A_{\rm r}$ (cm <sup>2</sup> )	<i>E</i> <sub>1/2</sub> (V vs. SCE)	SA at 0.05 V $(mA cm^{-2})$
(AuNP/PDDA-MWCNT) <sub>1</sub>	9.85	0.025	-0.102	1.6
(AuNP/PDDA-MWCNT) <sub>2</sub>	18.4	0.046	-0.092	1.1
(AuNP/PDDA-MWCNT) <sub>3</sub>	40.5	0.101	-0.076	0.8

Since citrate is used as a stabilizer for colloidal gold, it is important to consider its effect on the electrochemistry of the electrodes prepared. Nichols et al. [179] quantified the adsorption of citrate on Au(111) from citric acid containing electrolytes using *in situ* infra-red spectroscopy. They determined the number of coordinating carboxylate groups, estimated the coverage and provided an approximate value for the average tilt angle of the surface bound groups. Lately, the electrochemical methods have been used to provide a thermodynamic description of the adsorption of citric acid (H<sub>3</sub>A) and dihydrogen citrate (H<sub>2</sub>A<sup>¬</sup>) on the Au(111) surface [180]. In order to test the citrate effect on the electrocatalysis of the ORR in acid solution, an additional experiment with bulk gold electrodes in the absence and presence (4 mM) of citrate was performed. As shown in Fig. 19, the voltammetry curves for O<sub>2</sub> reduction on these electrodes

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do not differ to a noticeable degree. Thus, it can be concluded that the electrocatalytic activity of the modified electrodes towards  $O_2$  reduction in acid solution does not depend on the adsorbed citrate.



**Figure 19.** A comparison of RDE voltammetry curves for O<sub>2</sub> reduction on a bulk Au electrode in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence (curve 1) and absence (curve 2) of sodium citrate (4 mM).  $\nu = 20 \text{ mV s}^{-1}$ ,  $\omega = 1900 \text{ rpm}$ .

The oxygen reduction behaviour of the AuNP/PDDA-MWCNT modified GC electrodes was similar to that observed in previous studies. Sarapuu et al. [77,97] studied O<sub>2</sub> reduction on thin films of gold, with a nominal thickness of 0.25–20 nm. A value of n = 2 was found, but it increased at more negative potentials. The specific O<sub>2</sub> reduction activity of the Au-film electrodes was almost constant over the entire range of film thickness. Their analysis indicated that the O<sub>2</sub> reduction mechanism was the same for thin-film as for bulk Au electrodes. For electrodes with lower Au loading, the apparent electrocatalytic activity decreased which was caused by decrease in real area of active surface. Obviously, differences in the surface structure of the gold nanoparticles may influence the electrocatalytic behaviour of the electrode. These results are important from the point of view of using AuNP/PDDA-MWCNT in the biosensor design. Frequently, the determination of various analytes employing biosensors is carried out in the presence of oxygen. Obviously, such a potential of detection should be applied at which the electrochemical reduction of  $O_2$ does not occur or proceeds only at a negligible rate.

# 4.4. Oxygen reduction on AuNP/(NP)MWCNT modified electrodes

### 4.4.1. Surface characterisation of AuNP/(NP)MWCNT nanocomposites

Surface morphology of AuNP/(NP)MWCNT nanocomposites was investigated by TEM. Fig. 20 shows the representative TEM image of the catalyst. The presence of nm-sized Au particles (average particle size of 5–6 nm) is in evidence. During the preparation of AuNP/(NP)MWCNT composites, the attachment of Au nanoparticles to nanotube sites not covered by nitrophenyl groups could also occur. The number density of AuNPs present on the sidewalls of MWCNTs was relatively high, but some individual unmodified nanotubes were also observed.



Figure 20. TEM image for an AuNP/MWCNT sample.

The electrode surfaces were further characterised by XPS. The XPS survey spectrum of the nitrophenyl modified MWCNTs is shown in Fig. 21a. The carbon peaks, stemming from the MWCNTs and organic layer and oxygen peaks related to surface oxides and nitro groups showed the highest intensity. Figure 21a reveals two peaks in the N1s region pertaining to XPS spectra of nitrophenyl modified MWCNTs. The first peak with the higher binding energy around 406 eV is attributed to -NO<sub>2</sub> groups. The second peak with a lower binding energy around 400 eV is attributed to amines. It has been demonstrated that the second peak can come from chemical reduction of NO<sub>2</sub> groups under the X-ray beam during the XPS experiment [181,182]. Also, the formation of azo-linkages within the NP film has been proposed to explain the N1s peak at ca 400 eV [183]. In the next stage of experiments, the XPS analysis of

AuNP/(NP)MWCNT samples was performed. XPS spectrum confirms the presence of gold nanoparticles on the surface of MWCNTs (Fig. 21b). The XPS spectrum of AuNP/(NP)MWCNTs shows the presence of oxygen (O1s) and a small peak of nitrogen residues. The peaks centered at 83.8 (Au4 $f_{7/2}$ ) and 87.5 eV (Au4 $f_{5/2}$ ) provide a typical signature of metallic Au nanoparticles.



**Figure 21.** (a) XPS survey spectrum of a nitrophenyl modified MWCNTs and (b) high resolution XPS spectrum for Au4f region of an AuNP/(NP)MWCNT sample.

## 4.4.2. Cyclic voltammetry of AuNP/(NP)MWCNT nanocomposites

The strong attachment of nitrophenyl (NP) groups to MWCNTs was confirmed by cyclic voltammetry. Fig. 22 shows the CV response obtained at a scan rate of 100 mV s<sup>-1</sup> for a NP/MWCNT modified GC electrode in 0.1 M KOH. These experiments showed a typical CV behaviour of nitrophenyl modified carbon electrodes in alkaline solution [98]. As has been introduced previously the electrochemistry of nitrobenzene in alkaline solution follows a two-step reduction [98]. The first step is a two-electron irreversible reduction to nitrosobenzene according to:

$$Ph-NO_2 + 2H^+ + 2e^- = Ph-N(OH)_2 - H_2O \rightarrow Ph-NO$$
(13)

Followed by a quasi-reversible two-electron, two-proton reduction to phenylhydroxylamine:

$$Ph-NO + 2H^{+} + 2e^{-} \leftrightarrow Ph-NH(OH)$$
(14)

A pair of CV peaks centered at ca -0.4 V is attributed to the Ph–NO/Ph–NH(OH) redox couple. The reduced NP groups are considered as nucleation sites for AuNP formation.



**Figure 22.** Cyclic voltammograms for a NP/MWCNT modified GC electrode in Ar saturated 0.1 M KOH at  $v = 100 \text{ mV s}^{-1}$ . The number of potential cycles is indicated for each CV curve.

CV experiments were also performed with AuNP/(NP)MWCNT modified GC and bulk gold electrodes in O<sub>2</sub>-free 0.5 M H<sub>2</sub>SO<sub>4</sub>. The electrochemical responses of these electrodes are shown in Fig. 23. For both electrodes compared typical features of gold surface oxidation on the forward scan (at ca 1.15 V) and its reduction on the reverse scan (at ca 0.88 V) were observed. The charge under the gold oxide reduction peak for the AuNP/MWCNT modified GC electrode was  $4.64 \times 10^{-3}$  C cm<sup>-2</sup>. These results indicate that the total area of gold nanoparticles of the hybrid material was higher than that observed in our previous investigation for the AuNP/MWCNT catalyst in the absence of nitrophenyl groups [II].



**Figure 23.** Cyclic voltammograms for polished Au (1) and AuNP/(NP)MWCNT modified GC (2) electrodes in Ar saturated 0.5 M  $H_2SO_4$  at  $\nu = 100$  mV s<sup>-1</sup>.

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#### 4.4.3. O<sub>2</sub> reduction on AuNP/(NP)MWCNT nanocomposites

The RDE polarisation curves of oxygen reduction on a bulk gold electrode in  $O_2$  saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> are presented in Fig. 24. These are typical *I–E* curves for  $O_2$  reduction on gold in acid electrolyte. The reduction current gradually increases with decreasing potential and no diffusion-controlled current plateau is formed prior to the potentials of hydrogen evolution. The RDE results clearly demonstrate the excellent electrocatalytic activity of AuNP/(NP)MWCNT modified GC electrodes for  $O_2$  reduction in comparison to the polished Au electrode. Results presented in Fig. 25 show a significant positive shift of the oxygen reduction wave and an increase in the current density. The oxygen reduction wave starts at approximately 0.25 V.





Figure 24. RDE voltammetry curves for  $O_2$  reduction on a polished gold electrode in  $O_2$  saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $\nu = 10$  mV s<sup>-1</sup>.

**Figure 25.** RDE voltammetry curves for  $O_2$  reduction on a AuNP/(NP)MWCNT modified GC electrode in  $O_2$  saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $\nu = 10$  mV s<sup>-1</sup>.

The Koutecky–Levich plots for  $O_2$  reduction on a bulk gold electrode are shown in Fig. 26a. The K–L lines are almost linear. Fig. 26b shows that the value of *n* is slightly higher than two at the potentials of  $O_2$  reduction. This indicates that the 2e<sup>-</sup> reduction is the predominant pathway, which leads to peroxide formation in the range of potentials studied. This is in agreement with previous observations [60,63].



**Figure 26.** (a) Koutecky–Levich plots for O<sub>2</sub> reduction on a bulk gold electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> at various potentials: ( $\blacktriangle$ ) –0.2 and ( $\triangledown$ ) –0.1 V, (b) the dependence of *n* on potential for oxygen reduction on bulk Au electrode.

Fig. 27a shows the K–L plots obtained from the RDE data presented in Fig. 25. Linear K–L plots are observed and from the slope of these lines the number of electrons transferred per  $O_2$  molecule was calculated. The values of *n* at different potentials (shown in Fig. 27b) indicate that the reduction of  $O_2$  produces H<sub>2</sub>O<sub>2</sub>, which reduces further at more negative potentials. It was previously observed, that the number of electrons involved in the AuNP catalysed O<sub>2</sub> reduction depends on the surface structure of the gold catalysts [94]. The higher value of n of the AuNP/MWCNT catalysts as compared to that of bulk Au at high negative potentials could be, at least in part, related to their higher surface area. Gopalan et al. observed a 4e<sup>-</sup> reduction of oxygen on poly(aminothiophenol)-Au<sub>nano</sub> modified GC electrode [79]. They proposed that 4-electron pathway for this reaction was presumably due to the presence of PATP as a modifier for Au nanoparticles.



**Figure 27.** (a) Koutecky–Levich plots for O<sub>2</sub> reduction on a AuNP/(NP)MWCNT modified GC electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> at various potentials: ( $\blacktriangle$ ) –0.2 and ( $\triangledown$ ) –0.1 V, (b) the dependence of *n* on potential.

Indeed, the AuNP/(NP)MWCNT modified GC is a more active catalyst for  $O_2$  reduction than the bulk Au electrode. The value of half-wave potential for  $O_2$  reduction on AuNP/(NP)MWCNT modified GC electrodes is shifted by 80 mV to more positive potentials as compared to that of the bulk gold electrode.

Fig. 28 shows the Tafel behaviour of oxygen reduction on both electrodes studied. In the region of low overpotentials the Tafel slope values were -127 and -109 mV dec<sup>-1</sup> for the AuNP/(NP)MWCNT modified GC electrode and bulk Au electrode, respectively. This slope corresponds to the transfer of the first electron to the O<sub>2</sub> molecule as the rate-limiting step:



 $O_2 + H^+ + e^- \to HO_2 \tag{15}$ 

**Figure 28.** Mass-transfer corrected Tafel plots for O<sub>2</sub> reduction on bulk gold ( $\bullet$ ) and AuNP/(NP)MWCNT modified ( $\blacktriangle$ ) electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.  $\nu$  = 1900 rpm.

These results are in good agreement with previous work, in which the kinetic parameters of oxygen reduction on thin-film Au electrodes of various thickness were determined [77]. The Tafel slope close to  $-120 \text{ mV} \text{ dec}^{-1}$  was also observed for a bulk Au electrode in acid media in earlier reports [60,63]. The values of specific activity were determined at 0.1 V from the Tafel plots (Fig. 28) taking into account the real surface area for each electrode. In agreement with the results reported by Sarapuu et al. [77] the difference of specific activity for O<sub>2</sub> reduction on AuNP/(NP)MWCNT modified GC and bulk Au electrodes is not remarkable (0.057 mA cm<sup>-2</sup> for AuNP/(NP)MWCNT modified GC and 0.042 mA cm<sup>-2</sup> for bulk gold electrodes). The Tafel behaviour was essentially the same for composite materials and bulk gold electrodes. Nevertheless, the catalytic properties of Au nanoparticles were still different from those of the bulk metal, the higher reduction current and shifting the half-wave potential 80 mV to more positive value compared to bulk gold.

Finally, it is necessary to stress that the effect of Au particle size on the kinetics of O<sub>2</sub> reduction on AuNP-modified electrodes in acid solution is a matter of controversy. The most important kinetic parameter, which has been used for the evaluation of the electrocatalytic activity of nanostructured catalysts for oxygen reduction is the value of SA. Our previous results have shown that the SA of vacuum-evaporated thin Au films is very close to that of bulk Au [77,97]. Guerin et al. observed that the specific activity of O<sub>2</sub> reduction was independent of particle size for AuNPs larger than 3 nm [78]. Inasaki and Kobayashi found a decrease in the SA value with decreasing AuNP size [92]. They used Au catalysts supported on high-area carbon with the mean diameter of 1.7, 4.8 and 13.2 nm. In a similar study Bron reported that the surface specific activity was independent of particle size in the range 2.7–42.3 nm [93].

By contrast, Ohsaka and co-workers reported an extraordinary electrocatalytic activity of relatively large AuNPs (20–200 nm) electrodeposited on a gold substrate [80,81]. The increased O<sub>2</sub> reduction activity has also been observed on AuNPs deposited onto boron-doped diamond substrates [88,89]. Yagi et al. [91] have studied smaller Au particles (>2 nm), which have displayed a positive shift of the O<sub>2</sub> reduction potential and increased current efficiency for the four-electron reduction. However, the specific activity of O<sub>2</sub> reduction for AuNP catalysts has not been determined in these works [80,81,89–91] and therefore one cannot evaluate the intrinsic electrocatalytic activity of the nanostructured gold catalysts studied. Despite the numerous research efforts during the last decade, the physico-chemical origin of the Au particle size effect on the rate of oxygen reduction in acid media is still under debate.

A thorough kinetics investigation of  $O_2$  reduction on well-defined AuNPs over a wide size range (1–20 nm) is needed in order to elucidate this important aspect of electrocatalysis of nanoparticulate gold. Recently, an attempt has been made to calculate theoretically the size effect of gold catalysts on the kinetics of  $O_2$  reduction [184]. An increase in activity with decreasing Au particle size is predicted, even though the results obtained are rather preliminary.

# 4.5. Oxygen reduction on AuNP/MWCNT modified electrodes prepared by magnetron sputtering

#### 4.5.1. Surface characterisation of AuNP decorated MWCNTs

In Fig. 29a a typical image of MWCNTs fixed onto the glassy carbon substrate surface is presented after the gold nanolayer was deposited onto the nanotubes by magnetron sputtering. It can be seen that the nanotubes are covered with a continuous smooth Au layer, the fine grains of which are clearly visible. Clear changes in surface morphology were in evidence after annealing the

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AuNP/MWCNT samples at 300 °C (Fig. 29b): instead of smooth film regularly shaped rounded particles are seen, which are almost uniformly distributed on the nanotubes surface. EDS analysis proved that the particles consisted of pure gold. Particle diameter varies from 5 to 20 nm, their average diameter was ca 11 nm, measured over 300 particles.

When annealing at 400 °C the Au particles of different morphology appeared (Fig. 29c): in addition to well distributed small rounded particles a number of large elongated in one dimension agglomerates can be seen. Their longest dimension reached up to 225 nm for some particles, and the particles average (longest) size increases to ~100 nm. In comparison to the sample annealed at 300 °C, in this case the surface of the nanotubes is less uniformly covered with gold particles, and as a result more uncoated area can be observed.

Annealing at a higher temperature (600 °C) resulted in the formation of large droplets of gold and these were not stable on the MWCNTs surface. It should be noted that the heat-treatment at this temperature that has been applied to Au layers on BDD substrates [185–187] is not suitable for AuNP/MWCNT samples studied in the present work.



**Figure 29.** HR-SEM images of AuNP/MWCNT samples: (a) before annealing, (b) annealed at 300 °C and (c) annealed at 400 °C.

GIXRD analysis of Au nanoparticles deposited on MWCNTs of three different samples, selected for the analysis, showed broad reflections of (002), (100), (101) and (110) from glassy carbon substrate and broad reflections of (111), (220) and (222) from gold crystallites, whereas the last two reflections were too weak for crystallite size analysis. Therefore the strongest reflection (111) from gold particles was used for GIXRD analysis. The GIXRD patterns of all AuNP/MWCNT samples are presented in Fig. 30. One of the samples was measured before and after post-growth annealing at 300 °C. Full width at half maximum of reflection (111) before annealing was in the range of 1.5–1.78 which corresponds to crystallite size of gold particles in the range of 4–5 nm. The size increases up to 2.2 times during annealing that is reflected by a decrease of broadening of reflections.



**Figure 30.** Selected area X-ray diffraction patterns of AuNP/MWCNT samples 1 (a) and 3, 4 (b) before (samples 1 and 3, thin solid line with squares) and after annealing at 300°C for 15 min (samples 1 and 4, thick solid line), correspondingly. Intensity units are counts per 100 s. Broadening of gold reflection from lattice plane (111) is indicated by the FWHM value.

## 4.5.2. Cyclic voltammetry of AuNP/MWCNT modified electrodes

Figure 31 presents the CV curves of selected samples at systematic variation of the applied temperature of the annealing process. The shape of CVs in  $O_2$ -free 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mV s<sup>-1</sup> is nearly identical for all the samples under study. The current response to the applied potential scanning is typical for gold electrodes in sulphuric acid solution. The current peaks corresponding to gold surface oxidation on the forward scan (a broad anodic peak appeared at ca 1.15 V) and its reduction on the reverse scan (at ca 0.88 V) are observed as in earlier studies. A clear pair of oxidation-reduction peaks at about 0.4 V corresponds to quasi-reversible electrochemical behaviour of quinone-type carbon-oxygen functionalities on the surface of acid-treated MWCNTs. The MWCNT modified GC electrode has a very large background current compared with bare GC due to the significant increase of the electrode surface area. The real surface area of gold was determined from the CV curves by charge integration under the oxide reduction peak. For AuNP annealed at 250 and 300 °C,  $A_r$  was approximately the same as the geometric area of the electrode and the  $A_r/A$  ratio decreased only for the catalyst material annealed at 400 °C. This ratio was around 0.5 for this composite electrode.



**Figure 31.** Cyclic voltammograms for GC electrodes coated with AuNP/MWCNT catalysts in Ar saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.  $\nu = 50$  mV s<sup>-1</sup>. The AuNP/MWCNT samples were annealed at 250, 300 and 400 °C.

### 4.5.3. O<sub>2</sub> reduction on AuNP/MWCNT modified electrodes

The electrocatalytic activity for  $O_2$  reduction on the GC and MWCNT substrates is not remarkable in acid media and therefore, the activity of the prepared electrodes is due to the sputtered Au nanoparticles only. Figure 32 shows representative current-potential curves for oxygen reduction; the background current has been subtracted from these data. Single-wave polarisation curves with no well-defined current plateau were observed for all the electrodes studied.



**Figure 32.** RDE voltammetry curves for O<sub>2</sub> reduction on a GC electrode modified with AuNP/MWCNT catalyst in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at different rotation rates.  $\nu = 10$  mV s<sup>-1</sup>. The AuNP/MWCNT sample was annealed at 300 °C.

Linear K–L plots were observed and from the slope of these lines the number of electrons transferred per  $O_2$  molecule was calculated. The values of *n* at different potentials indicate that the reduction of  $O_2$  produces  $H_2O_2$ , which reduces further at more negative potentials. The further reduction of  $H_2O_2$  at high overpotentials (E < -0.2 V) is in agreement with previous observations [77,97,188]. It was previously reported that the number of electrons involved in the AuNP catalysed  $O_2$  reduction depends on the chemical environment of the gold catalysts [79,178,189].

Fig. 33 presents a comparison of the oxygen reduction results obtained with AuNP/MWCNT catalysts heat-treated at different temperatures. The values of  $E_{1/2}$  for O<sub>2</sub> reduction on AuNP/MWCNT modified GC electrodes were determined to be -75, -60 and -85 mV for the composite catalysts annealed at 250, 300 and 400 °C, respectively. From the practical point of view it is of considerable importance to compare the values of SA of O<sub>2</sub> reduction for the electrocatalysts studied. The SA values were determined at 0.1 V taking into account the real surface area of AuNPs for each electrode (Table 2).

Table 2. Kinetic parameters for oxygen reduction on AuNP/MWCNT modified GC electrodes in  $0.5 \text{ M H}_2\text{SO}_4$ .

Catalyst material	$A_r (cm^2)$	Tafel slope $(V dec^{-1})$	<i>E</i> <sub>1/2</sub> (mV)	SA at 0.1 V $(mA cm^{-2})$
AuNP/MWCNT annealed at 250 °C	0.22	-0.195	-75	0.130
AuNP/MWCNT annealed at 300 °C	0.26	-0.200	-60	0.145
AuNP/MWCNT annealed at 400 °C	0.11	-0.194	-85	0.125



**Figure 33.** A comparison of RDE voltammetry curves for O<sub>2</sub> reduction on AuNP/MWCNT modified GC electrodes in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.  $\nu = 10$  mV s<sup>-1</sup>,  $\omega = 1900$  rpm. The AuNP/MWCNT samples were annealed at different temperatures.

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Recently, the effect of Au nanoparticle size on the kinetics of O<sub>2</sub> reduction has been systematically studied by Guerin et al. [78] in acid media and these authors concluded on the basis of their results that the specific activity is constant for particles larger than 3 nm. On the basis of these considerations one might expect that the value of SA is unchanged for the AuNP/MWCNT nanocomposites used in the present work. The average particle size is larger than 5 nm. Apparently, the electrocatalytic activity of the nanogold material towards oxygen reduction might depend on the catalyst support and on the particular arrangement of AuNPs within the structure of the three-dimensional nanocomposite film. Sarapuu et al. studied O<sub>2</sub> reduction on thin films of gold, with a nominal thickness of 0.25-20 nm [77]. The specific O<sub>2</sub> reduction activity of the Au-film electrodes was almost constant over the entire range of film thickness. Their analysis indicated that the O<sub>2</sub> reduction mechanism was the same for thin film as for bulk Au electrodes. For electrodes with lower Au loading, the apparent electrocatalytic activity decreased which is caused by a decrease in real area of active surface. The absolute values of specific activities calculated are similar to previous results, where the SA values were obtained at E = 0.05 V versus SCE for different thin film Au electrodes at  $\omega = 1900$  rpm. The thinnest 0.25 nm Au film had a lower SA value  $(0.08 \pm 0.01 \text{ mA cm}^{-2})$  than the thicker films of 20 nm by a factor of two [97].

The Tafel plots of  $O_2$  reduction for all the AuNP/MWCNT materials studied, obtained from the kinetic currents, are presented in Fig. 34.



**Figure 34.** Tafel plots of O<sub>2</sub> reduction on AuNP/MWCNT modified GC electrodes in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.  $\omega$  = 1900 rpm. The AuNP/MWCNT catalysts were annealed at ( $\blacktriangle$ ) 300 °C, ( $\bullet$ ) 250 °C and ( $\blacktriangledown$ ) 400 °C.

The current densities were normalised to the real surface area of gold. A high Tafel slope value was observed at low overpotentials (ca  $-200 \text{ mV dec}^{-1}$ ). A typical slope value for O<sub>2</sub> reduction on gold in acid solution is  $-120 \text{ mV dec}^{-1}$ 

[77], which corresponds to a slow transfer of the first electron to  $O_2$  molecule. At this stage of work it is not clear what is the reason for a discrepancy in the Tafel slope values. It was shown that the AuNP/MWCNT modified GC is more active catalyst for  $O_2$  reduction than bulk gold. The  $E_{1/2}$  value for  $O_2$  reduction on AuNP/MWCNT modified GC electrodes shifted by 50 mV to more positive potentials as compared to that of the bulk gold electrode [II]. The oxygen reduction behaviour of the AuNP/MWCNT modified GC electrodes was similar to that observed in our previous studies [II,III]. It is worth noting that the modified electrodes used in the present work were remarkably stable during repetitive potential scans. The observed changes in the surface structure and morphology of the sputtered Au films upon annealing lead to essential variations in the electrochemically active surface area. This is of considerable applications, importance for various including electrocatalysis and electroanalysis.

# 4.6. Oxygen reduction on PtNP/CNT modified electrodes

In this section a detailed study of the ORR on composite structures formed by PtNPs and CNTs is presented. The PtNP/CNT nanocomposites were prepared by two different synthetic routes, synthesis of Pt nanoparticles in the presence of citrate [166] and synthesis of Pt nanoparticles in microemulsion [167], using in both cases sodium borohydride as a reducing agent. Both synthetic routes have been shown to yield clean Pt nanoparticles. Subsequently, the electrocatalytic behaviour of these PtNP/CNT catalysts supported on a glassy carbon electrode towards O<sub>2</sub> reduction was investigated by employing the rotating disk electrode configuration both in acid (sulphuric acid) and in basic (sodium hydroxide) media. Despite it is well established that oxygen reduction on platinum in perchloric acid takes place at lower potentials than in sulphuric acid and that perchloric acid does not adsorb on Pt and thus, the reactivity would be comparable to that of membrane-electrode assemblies, we have decided to use sulphuric acid because in this medium the cleanliness of the samples can be easily checked: the hydrogen adsorption-desorption peaks are sharper and better defined in sulphuric than in perchloric acid. It is important to point out that when dealing with nanoparticles, the presence of contamination may be a very important problem because their blank voltammograms are not as wellestablished as those of single crystal electrodes.

#### 4.6.1. Surface characterisation of PtNP/CNT modified electrodes

Prepared catalysts were dispersed ultrasonically in ultrapure water to concentration  $1mg_{catalyst} mL^{-1}$ . Before each electrode modification step, the catalyst suspension was again put into the ultrasonic bath for 3 min. While still in there, an aliquot of the suspension was pipetted onto a polished glassy carbon substrate (3 mm in diameter, 0.071 cm<sup>2</sup> geometric area). It is important to follow the requirements of the RDE theory, which assumes a flat substrate covered uniformly with the catalyst material. After evaporation of the suspension in argon stream, the prepared electrode was transferred (with protection of the surface by means of a drop of ultrapure water) to the electrochemical cell and immersed under potential control (0.05 V) in Ar-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> or 0.1 M NaOH solution.

The freshly prepared PtNP/CNT catalysts were characterised by transmission electron microscopy and Figure 35 presents some typical TEM images of the CNT supported Pt nanoparticles.



**Figure 35.** TEM micrographs of the as-prepared (a) (mic)PtNP/SWCNTs, (b) (cit)PtNP/SWCNTs, (c) (mic)PtNP/MWCNTs and (d) (cit)PtNP/MWCNTs samples.

TEM images indicate a good dispersion of the particles on the surface of the carbon support and a Pt particle size of  $2.4 \pm 0.7$  nm in the case of Pt/CNTs prepared in the presence of citrate and of  $3.8 \pm 1.1$  nm for Pt/CNTs prepared in microemulsion. To determine the particle size, isolated-like particles were taken into account; in each case, about 100 particles were measured for the statistics. TEM observations also show that the effect of concentrated acid mixtures on the degradation of carbon nanotubes was not important and thus, the creation of amorphous carbon impurities was negligible.

## 4.6.2. Cyclic voltammetry and CO stripping of PtNP/CNT modified electrodes

PtNP/CNT modified GC electrodes were cycled in Ar saturated 0.5 M  $H_2SO_4$  or 0.1 M NaOH solutions in the range of potentials from 0.05 to 0.8 V vs. RHE using a sweep rate of 50 mV s<sup>-1</sup>. In order to improve the surface cleanliness of the electrodes the residual impurities were displaced by adsorbing carbon monoxide [190]. The electrochemical stripping of the adsorbed CO was performed in a single sweep up to 0.91 V, at 20 mV s<sup>-1</sup>. Fig. 36 shows the CO stripping voltammograms obtained in acid media as well as the voltammograms obtained after the electrochemical decontamination.



**Figure 36.** CO stripping (dashed line) and cyclic voltammograms (solid line) on (a) (mic)PtNP/SWCNT, (b) (mic)PtNP/MWCNT, (c) (cit)PtNP/SWCNT and (d) (cit)PtNP/MWCNT modified GC electrodes in 0.5 M  $H_2SO_4$ .  $v = 20 \text{ mV s}^{-1}$ .

It is well-established that the CO stripping enables a soft electrochemical decontamination of the nanoparticles without altering its initial surface properties. It is important to remark that a high number of excursions to high potential values, commonly used for surface cleaning, would lead to a decrease in surface area estimated from the charge measured in the hydrogen adsorptiondesorption region because nanoparticles sintering would take place. It has been shown that several mechanisms of catalyst degradation were involved during potential cycling: mobility of platinum particle leading to particle growth and dissolution/redeposition process, etc. [191]. According to previous reports, the CO stripping voltammograms may be also used as a structure sensitive qualitative probe [167]. After CO cleaning, the definition and the symmetry of the hydrogen adsorption states increase in all samples in relation to the un-CO decontaminated samples, thus, indicating the improvement of the surface cleanliness. The voltammograms look similar to those reported for polycrystalline Pt electrodes. Thus, the voltammogram shows the presence of adsorption states associated with (110) and (100) sites at 0.12 and 0.27 V, respectively. Moreover, a shoulder around 0.35 V is apparent, being characteristic of small (100) terraces. The unusual adsorption state around 0.5 V and characteristic of small (111) ordered surface domains cannot be clearly observed due to the high double layer contribution of the carbon materials.

The different CO oxidation profiles could be attributed to modifications in the number and nature of active sites present on the surface of the Pt nanoparticles. In this way, in order to gain information about the number and nature of the surface sites, specific surface reactions (Bi and Ge irreversible adsorption) could be performed [192,193]. Nevertheless, this methodology presents some limitations, because in case of small Pt nanoparticles (<4 nm), the fraction of ordered domains in relation to the total number of active sites is expected to be small. In this way, the determination of charge densities related to irreversibly adsorbed Bi and Ge would imply serious experimental uncertainty [194,195]. Consequently, this kind of analysis was discarded.

## **4.6.3.** O<sub>2</sub> reduction on PtNP/CNT modified electrodes in acid media

The oxygen reduction reaction was studied using the rotating disk electrode method. The RDE measurements were carried out in 0.5 M  $H_2SO_4$  at different electrode rotation rates to access to the kinetics data from the Koutecky–Levich equation and to verify that no hydrogen peroxide was formed at the PtNP/CNT modified GC electrodes. The representative current–potential curves are shown in Fig. 37; the background currents were recorded at 10 mV s<sup>-1</sup> in Ar-saturated electrolyte and were subtracted from these data. Only the positive-going potential scans are presented and further analysed.



**Figure 37.** RDE voltammetry curves for O<sub>2</sub> reduction on (a) (mic)PtNP/SWCNT, (b) (mic)PtNP/MWCNT, (c) (cit)PtNP/SWCNT and (d) (cit)PtNP/MWCNT modified GC electrodes in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at different rotation rates.  $\nu = 10$  mV s<sup>-1</sup>.

Single-wave polarisation curves with a well-defined current plateau were observed for all the electrodes under study and a high electrocatalytic activity of the Pt nanoparticles towards oxygen reduction was evident. The values of halfwave potential for O<sub>2</sub> reduction on modified GC electrodes at  $\omega = 1600$  rpm were determined to be 0.75, 0.71, 0.77 and 0.75 V for (mic)PtNP/ SWCNTs, (mic)PtNP/MWCNTs, (cit)PtNP/SWCNTs and (cit)PtNP/MWCNTs composite catalysts, respectively. The values of  $E_{1/2}$  of the Pt/CNT modified electrodes are very similar to that of bulk Pt, which was determined to be 0.79 V.

The RDE data were analysed using the Koutecky–Levich equation (10) [170]. The value of  $n \approx 4$  was found over the whole range of potentials and different samples studied. The 4e<sup>-</sup> pathway of O<sub>2</sub> reduction on Pt has been confirmed in many studies [3,6], however, it is not possible to unambiguously establish whether the reduction of O<sub>2</sub> proceeds through "direct" 4e<sup>-</sup> pathway or through H<sub>2</sub>O<sub>2</sub> intermediate that is subsequently reduced. From the K–L plots it is obvious that the process of O<sub>2</sub> reduction on PtNP/CNTs is controlled by the diffusion of oxygen to the electrode surface in a large range of potentials.

Similar behaviour was observed for GC electrodes modified with PtNP/CNT nanocomposites in previous studies [156]. The catalytic activity of acid-treated CNTs is very low in acid solution [I] and consequently, the O<sub>2</sub> reduction current at potentials E > 0.5 V is exclusively due to the Pt nanoparticles. Moreover, the stability of the PtNP/CNT modified GC electrodes was tested by RDE using repetitive potential cycling and negligible changes in the reduction current density were observed, indicating that the composite PtNP/CNT materials employed possess high stability during oxygen reduction.

In Fig. 38a, the mass-transfer corrected Tafel plots constructed from the RDE data are presented. Fig. 38b shows the potential dependence of the  $O_2$  reduction kinetic current density per real area of Pt.



**Figure 38.** (a) Mass-transfer corrected Tafel plots for O<sub>2</sub> reduction on PtNP/CNT modified GC electrodes in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.  $\omega = 1600$  rpm. (b) Potential dependence of O<sub>2</sub> reduction kinetic current density per real Pt surface area. Catalysts: ( $\blacktriangle$ ) (mic)PtNP/SWCNT, ( $\bullet$ ) (mic)PtNP/MWCNT, ( $\blacksquare$ ) (cit)PtNP/SWCNTs and ( $\blacktriangledown$ ) (cit)PtNP/MWCNT.

Two Tafel regions with characteristic slopes near to -110 and -180 mV dec<sup>-1</sup> are clearly distinguished. The values of Tafel slopes listed in Table 3 do not suggest a clear dependence on the nature of composite materials studied, indicating that the mechanism of oxygen reduction on PtNP/CNT nanocomposites is the same. In earlier investigations a lower slope value (approximately -60 mV dec<sup>-1</sup>) has been observed for Pt electrodes at low current densities [3]. As suggested previously, the change of the slope is attributed to the potential-dependent coverage of surface oxides that inhibit the adsorption of O<sub>2</sub> and reaction intermediates [119,123,126,196]. The Tafel behaviour of oxygen reduction observed here is similar to that reported recently by Shih et al. [197]. In the high current density region, (cit)Pt/CNT composites showed a slightly higher Tafel slope than (mic)Pt/CNT composites.

The specific activity of  $O_2$  reduction for the PtNP/CNT modified GC electrodes was calculated using equation (12), where  $I_k$  is the kinetic current at a given

potential and  $A_r$  is the real electroactive area of platinum. The SA values were determined at 0.85 V (activation region) and the results obtained for PtNP/CNT catalysts of different preparation were rather similar (Table 3).

Electrode	$A_{\rm r}$ (cm <sup>2</sup> )	Tafel slope (mV dec <sup>-1</sup> ) I region*	Tafel slope (mV dec <sup>-1</sup> ) II region*	<i>E</i> <sub>1/2</sub> (mV)	SA at 0.85 V (mA cm <sup>-2</sup> )
(mic)PtNP/SWCNT	0.088	-111	-153	751	0.45
(mic)PtNP/MWCNT	0.016	-105	-164	713	1.28
(cit)PtNP/SWCNT	0.196	-115	-187	774	0.33
(cit)PtNP/MWCNT	0.092	-108	-205	749	0.39

**Table 3**. Kinetic parameters for O<sub>2</sub> reduction on PtNP/CNT modified GC electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $\omega$  = 1600 rpm.

\* Region I corresponds to low current densities and Region II to high current densities.

There is a large body of evidence that the reduction of  $O_2$  on Pt is a structure sensitive reaction in H<sub>2</sub>SO<sub>4</sub> solutions [119,124,125,127,128,198]. The structure sensitivity of the ORR on Pt(*hkl*) primarily arises from different adsorption strength of (bi)sulphate ions on Pt low-index planes. Based on these considerations a Pt particle size effect towards O<sub>2</sub> reduction has been proposed [133] and the SA value should decrease with decreasing particle size according to the model predictions assuming a cubo-octahedral shape of the Pt nanoparticles. Early work on size effects was reviewed by Kinoshita [3] and the results showed that the specific activity decreased as the size of Pt particles decreased. A decrease in specific activity with particle size in sulphuric acid solutions has been also observed in recent studies [199–202]. The origin of this effect is mostly explained by (bi)sulphate ion adsorption, which inhibits the reduction of oxygen more strongly for smaller particles for which the (111) sites predominate. The size effect could be, at least in part, related to size-dependent adsorption of oxygenated species on Pt nanoparticles. For smaller particles the adsorption of these species is stronger and inhibits the rate of oxygen reduction [203]. However, in some other studies the particle size effect has not been observed [204] and these aspects are still under debate in the literature.

### 4.6.4. O<sub>2</sub> reduction on PtNP/CNT modified electrodes in alkaline media

The electrochemical reduction of oxygen on PtNP/CNT composite electrodes was also studied in 0.1 M NaOH solution using the RDE method. It was of special interest to study this process in alkaline electrolyte, because it is well-known from earlier investigations that the kinetics of  $O_2$  reduction is enhanced

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in this media as compared to acid solutions containing strongly adsorbed anions [205]. The representative current–potential curves are reported in Fig. 39.



**Figure 39.** RDE voltammetry curves for O<sub>2</sub> reduction on (a) (mic)PtNP/SWCNT, (b) (mic)PtNP/MWCNT, (c) (cit)PtNP/SWCNT and (d) (cit)PtNP/MWCNT modified GC electrodes in O<sub>2</sub> saturated 0.1 M NaOH at different rotation rates.  $v = 10 \text{ mV s}^{-1}$ .

Single-wave polarisation curves with a well-defined current plateau were observed for all the electrodes under study. By comparison, the activities of the Pt nanoparticles synthesised by the two different methods do not show much difference throughout the whole range of potentials. The RDE data were analysed using the Koutecky–Levich equation. Linear and parallel K–L plots are observed, indicating first order kinetics with respect to molecular oxygen [206]. The slope of these plots gives the values of parameter B = 0.45 mA rpm<sup>-1/2</sup>. This value is in good agreement with the theoretical value calculated for a four-electron reduction of oxygen in 0.1 M NaOH solution (taking the data for  $D_{O_2} = 1.9 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> and  $C_{O_2}^b = 1.2 \times 10^{-6}$  mol cm<sup>-3</sup> from Ref. [207]). It is important to mention that the electrocatalytic properties of unmodified carbon nanotubes at E < 0.7 V should be also taken into account. As it has been previously reported, due to their intrinsic electrocatalytic properties in alkaline

media, the CNTs are active catalysts for the two-electron reduction of  $O_2$  to hydrogen peroxide at low overpotentials [43,47,208].

The mass-transfer corrected Tafel plots for all PtNP/CNT materials are presented in Fig. 40a. The current densities were normalised to the geometric surface area. Fig. 40b shows the potential dependence of  $O_2$  reduction kinetic current density per real area of Pt.



**Figure 40.** (a) Mass-transfer corrected Tafel plots for O<sub>2</sub> reduction on PtNP/CNTmodified GC electrodes in O<sub>2</sub> saturated 0.1 M NaOH.  $\omega = 1600$  rpm. (b) Potential dependence of O<sub>2</sub> reduction kinetic current density per real Pt surface area. Catalysts: ( $\blacktriangle$ ) (mic)PtNP/SWCNT, ( $\bullet$ ) (mic)PtNP/MWCNT, ( $\blacksquare$ ) (cit)PtNP/SWCNTs and ( $\blacktriangledown$ ) (cit)PtNP/MWCNT.

As can be seen from Fig. 40, a transition in slope occurs at potentials between 0.75 and 0.8 V. The ORR mechanism on platinum nanoparticles in alkaline media has been less studied than in acidic solutions. Although the reduction of oxygen on platinum in alkaline media is considered to proceed by a multistep process, there is no general agreement on the precise mechanism [7,132]. As in acidic media, also in alkaline solution the electrodes are characterised by two Tafel slopes and the results are given in Table 4. According to previous studies the Tafel slope for bulk platinum in alkaline solution is close to  $-60 \text{ mV} \text{ dec}^{-1}$  at low current densities and  $-120 \text{ mV dec}^{-1}$  at higher current densities [130]. Our results show that the Tafel behaviour of the PtNP/CNT modified electrodes towards O<sub>2</sub> reduction in alkaline solution differs from that reported previously for polycrystalline Pt. At low overpotentials the slope value was ca -90 mV dec<sup>-1</sup>, which indicates that the first charge transfer is the rate determining step for the ORR. However, in the second Tafel region the slope is much higher (close to  $-200 \text{ mV dec}^{-1}$ ), in agreement with the results obtained in an earlier work in which the reduction of oxygen was studied on nanostructured platinum electrodes in alkaline solution [209,210]. A high Tafel slope value at high current densities has been also observed on bulk Pt and this has been attributed

to the change in the rate-limiting step or adsorption conditions at high overpotentials [211,212]. According to the results obtained in the present work, the adsorption conditions are the same on all the PtNP/CNT modified GC electrodes under study.

Electrode	$A_{\rm r}$ (cm <sup>2</sup> )	Tafel slope (mV dec <sup>-1</sup> ) I region*	Tafel slope (mV dec <sup>-1</sup> ) II region*	<i>E</i> <sub>1/2</sub> (mV)	SA at 0.85 V (mA cm <sup>-2</sup> )
(mic)PtNP/SWCNT	0.209	-77	-217	800	0.31
(mic)PtNP/MWCNT	0.049	-87	-219	725	0.52
(cit)PtNP/SWCNT	0.106	-103	-160	766	0.55
(cit)PtNP/MWCNT	0.171	-104	-205	761	0.31

**Table 4**. Kinetic parameters for O<sub>2</sub> reduction on PtNP/CNT modified GC electrodes in 0.1 M NaOH at  $\omega = 1600$  rpm.

\* Region I corresponds to low current densities and Region II to high current densities.

The SA values were also determined for all PtNP/CNT catalysts in alkaline media (at 0.85 V vs. RHE). According to previous studies the specific activities should be higher in 0.1 M NaOH than in 0.5 M H<sub>2</sub>SO<sub>4</sub> [119]. This is due to the site-blocking effect of (bi)sulphate anions. Hydroxide ions are not strongly adsorbed on platinum and therefore the reduction of O<sub>2</sub> is inhibited to a lesser degree in 0.1 M NaOH. However, in the present work the values of SA were rather similar in both solutions. This may indicate that the method of cleaning employed was more effective in acid media. The results obtained in 0.1 M NaOH are in good agreement with previous reports on the kinetics of O<sub>2</sub> reduction on Pt nanoparticles in alkaline solution [209,210,213]. Recent work has also shown that Pt nanoparticles supported on high-area carbon are rather active catalysts for the ORR in alkaline solution [214–217]. For very small Pt particles (<3 nm) the specific activity was found to be lower than that of bulk Pt [216]. Oxygen reduction on Pt/C catalysts proceeds mainly through 4e<sup>-</sup> route and only small amounts of hydrogen peroxide are produced [214–216].

Pt-based nanoparticles are still the catalyst of choice for low-temperature fuel cells. The investigation of the kinetics of oxygen reduction on these nanoscale materials is important for the development of highly active cathode catalysts for fuel cells [218].

### 5. SUMMARY

The electrochemical reduction of oxygen on carbon nanotube-supported gold and platinum nanoparticles modified glassy carbon electrodes has been studied. The kinetic parameters for this reaction have been determined.

The reduction of oxygen was also studied on GC electrodes modified with oxidatively pre-treated and untreated MWCNTs in 0.5 M  $H_2SO_4$  [I]. The RDE results show that oxidative pre-treatment of MWCNTs has a strong effect on the electrocatalytic activity for O<sub>2</sub> reduction in acid solution. The half-wave potential shifted more than 250 mV in the negative direction upon MWCNTs treatment in acids. According to CV results it is evident that chemical oxidation of MWCNTs increases the amount of oxygenated species on the surface of nanotubes, but these groups do not enhance the ORR in acid solution. The untreated CNTs contain a high degree of metal impurities (mostly Fe, Co) which are used as catalysts for their preparation and can be largely removed by treatment in acids.

The reduction of oxygen has been studied on AuNP/MWCNT catalyst materials prepared by four different procedures. The AuNP/MWCNT catalysts were prepared by: (1) functionalisation of MWCNTs with SDS followed by deposition of AuNPs [II], (2) using an electrostatic layer-by-layer technique [III], (3) using chemical deposition of AuNPs onto MWCNTs spontaneously grafted with 4-nitrophenyl groups [IV] and (4) using a magnetron sputtering technique [V]. The AuNP/MWCNT catalysts showed a pronounced electrocatalytic activity towards O<sub>2</sub> reduction in acid media. The value of  $E_{1/2}$  for O<sub>2</sub> reduction on the AuNP/MWCNT catalyst shifted by ca 50 mV to more positive potentials as compared to that of a polished Au electrode covered by a Nafion film of the same thickness [II]. For AuNP/PDDA-MWCNT catalysts the calculated values of SA decreased with increasing catalyst film thickness. These SA values are higher than that obtained for the bulk Au electrode in identical conditions [III]. In the region of low overpotentials the Tafel slope values were -127 and -109 mV dec<sup>-1</sup> for the AuNP/(NP)MWCNT modified GC electrode and bulk Au electrode, respectively. This slope corresponds to the transfer of the first electron to the  $O_2$  molecule as the rate-limiting step [IV]. The values of half-wave potential for O<sub>2</sub> reduction on sputtered AuNP/MWCNT modified GC electrodes were determined to be -75, -60 and -85 mV vs. SCE for the composite catalysts annealed at 250, 300 and 400 °C, respectively. The SA values were 0.130, 0.145 and 0.125 mA cm<sup>-2</sup> (determined at 0.1 V) [V]. The results clearly demonstrated that MWCNTs can be used as support for a threedimensional electrocatalytic layer containing a dispersed metal that specifically catalyses the reduction of oxygen to hydrogen peroxide. These nanocomposites were simple to construct and their electrochemical response was stable during long-term testing.

PtNP/SWCNT and PtNP/MWCNT composite materials were prepared using two different synthetic routes [VI]. TEM experiments revealed that the amount of platinum deposited onto the treated carbon nanotubes support is sufficient although some of the Pt particles are agglomerated and the experimental conditions still need to be improved. Soft electrochemical decontamination, which is able to clean the samples without altering the initial properties of platinum nanoparticles, was performed using CO stripping. The PtNP/CNT catalysts exhibited promising electrocatalytic activity for oxygen reduction to produce H<sub>2</sub>O through a four-electron reduction pathway with high stability. The RDE results were rather similar for all the PtNP/CNT modified electrodes studied [VI].

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### KOKKUVÕTE

# Hapniku elektrokatalüütiline redutseerumine süsiniknanotorudel põhinevatel nanokomposiitmaterjalidel

Doktoritöös uuriti hapniku elektrokeemilist redutseerumist süsiniknanotorudele seondatud kulla ning plaatina nanoosakestega modifitseeritud klaassüsinikelektroodidel kasutades pöörleva ketaselektroodi meetodit. Saadud andmete põhjal määrati hapniku redutseerumisreaktsiooni kineetilised parameetrid nendel elektroodidel.

Hapniku elektrokeemilist redutseerumist uuriti happes töödeldud ning töötlemata süsiniknanotorudega modifitseeritud klaassüsinikelektroodidel 0,5 M H<sub>2</sub>SO<sub>4</sub> lahuses. Tulemused näitasid, et nanotorude oksüdatiivne eeltöötlemine mõjutab oluliselt O2 redutseerumise elektrokatalüütilist aktiivsust happelises lahuses. Poollainepotentsiaal nihkus pärast nanotorude eeltöötlemist hapete segus rohkem kui 250 mV võrra negatiivses suunas [I]. Tsüklilise voltamperomeetria andmetele toetudes võib väita, et süsiniknanotorude keemiline oksüdeerumine suurendab süsinik-hapnik funktsionaalrühmade hulka nanotorude pinnal, kuid need funktsionaalrühmad ei mõjuta oluliselt hapniku redutseerumise kineetikat happelises lahuses. Doktoritöös saadud tulemused annavad tunnistust sellest, kui olulist efekti avaldavad O2 redutseerumise kineetikale nanotorudes sisalduvad lisandid. Süsiniknanotorude valmistamiseks keemilise aurufaasist sadestamise meetodil kasutatakse katalüsaatorina raua või koobalti ühendeid, mis väikestes kogustes jäävad nanotorudesse või selle materjali pinnale. Need lisandid võivad mõjutada hapniku elektroredutseerumist ning seetõttu on väga oluline need kõrvaldada.

Hapniku redutseerumist uuriti neljal erineval sünteesimeetodil valmistatud AuNP/MWCNT katalüsaatormaterjalidel. Need katalüsaatorid valmistati: (1) süsiniknanotorude funktsionaliseerimisel naatriumdodetsüülsulfaadiga, millele järgnes Au nanoosakeste sadestamine HAuCl<sub>4</sub> lahusest [II], (2) kasutades elektrostaatilist kiht-kihi haaval modifitseerimismeetodit [III], (3) kasutades AuNPde seondamist nanotorudele, mis olid spontaalselt modifitseeritud 4-nitrofenüülrühmadega [IV], ning (4) kasutades magnetrontolmustamise meetodit [V]. AuNP/MWCNT komposiitmaterjalid olid elektrokatalüütiliselt aktiivsed O<sub>2</sub> redutseerumisel happelises lahuses. Hapniku redutseerumise poollainepotentsiaali väärtus AuNP/MWCNT katalüsaatoril nihkus ca 50 mV võrra positiivsemas suunas võrreldes poleeritud Au elektroodiga [II]. AuNP/PDDA-MWCNT katalüsaatori eriaktiivsuste väärtused kahanesid katalüsaatori kihtide arvu suurenemisega. Need väärtused olid suuremad kui samades tingimustes määratud kompaktse Au elektroodi eriaktiivsus [III]. Madalate ülepingete alas olid Tafeli tõusude väärtused -127 ning -109 mV AuNP/MWCNT-ga modifitseeritud klaassüsinikul ja kompaktsel Au elektroodil. See tõus näitab, et kiirust limiteeriv staadium on esimese elektroni ülekanne  $O_2$  molekulile [IV]. Poollainepotentsiaalide väärtused magnetrontolmustamise meetodil sadestatud

AuNP/MWCNT-ga modifitseeritud GC elektroodidel olid -75, -60 ning -85 mV vastavalt 250, 300 ning 400 °C juures kuumutatud materjalidel. Eriaktiivsuste väärtused olid 0,130; 0,145 ning 0,125 mA cm<sup>-2</sup> (määratud 0,1 V juures) [V]. Tulemused näitasid, et süsiniknanotorusid võib edukalt kasutada kolmedimensionaalse elektrokatalüütilise kihina, mis sisaldab kulla nanoosakesi ning mis spetsiifiliselt katalüüsib hapniku redutseerumist vesinikperoksiidi tekkeni. Saadud nanokomposiitmaterjale on lihtne valmistada ning nende elektrokeemiline käitumine on stabiilne pikaajalisel kasutamisel.

PtNP/MWCNT ja PtNP/SWCNT komposiitmaterjalid valmistati kasutades kahte erinevat sünteesimeetodit [VI]. Läbiva elektronmikroskoobi abil teostatud mõõtmised näitasid, et eeltöödeldud nanotorudega seondatud plaatina kogus oli piisav, kuid mõned Pt nanoosakesed esinesid aglomeraatidena ning eksperimentaalsed tingimused vajavad optimeerimist. Pehmetes tingimustes elektro-keemiline puhastamine, mille käigus säilib Pt nanoosakeste esialgne struktuur, teostati kasutades CO adsorptsiooni ja oksüdatsiooni pinnal. PtNP/CNT katalü-saatorid näitasid kõrget elektrokatalüütilist aktiivsust hapniku neljaelektronilisel redutseerumisel. Pöörleva ketaselektroodi meetodil saadud tulemused olid sarnased kõikide PtNP/CNT-ga modifitseeritud elektroodide korral.

### ACKNOWLEDGEMENTS

Above all, I would like to thank my supervisor, Assoc. Prof. Kaido Tammeveski. This thesis would not have been possible without his help, support and patience. His good advice has been invaluable on both an academic and a personal level, for which I am extremely grateful.

I wish to thank the staff at the Institute of Physics, especially Peeter Ritslaid for performing magnetron sputtering experiments, Dr. Leonard Matisen for the XPS measurements, Dr. Hugo Mändar for GIXRD and SAXS studies, Prof. Väino Sammelselg and Jekaterina Kozlova for HR-SEM measurements.

I also thank Prof. Kyosti Kontturi and Drs. Timo and Päivi Laaksonen at Helsinki University of Technology for performing the TEM measurements.

I wish to thank Prof. Juan M. Feliu (University of Alicante) for the possibility to work in his group. Dr. Jose Solla-Gullón, Dr. Francisco José Vidal Iglesias and Dr. Ana Lopez Cudero for being my supervisors during our research work at the University of Alicante.

I would like to thank Prof. David J. Schiffrin (University of Liverpool) for a fruitful collaboration.

I would also like to thank my colleagues and friends from the Chair of Colloid and Environmental Chemistry: Dr. Ave Sarapuu, Marko Kullapere and Ivar Kruusenberg.

I would like to acknowledge the financial, academic and technical support of the University of Tartu, particularly financial support from Graduate School on Functional Materials and Technologies, University of Tartu and Tallinn University of Technology, ESF project 1.2.0401.09-0079, Archimedes Foundation and World Federation of Scientists.

The financial support from the Estonian Science Foundation (Grants Nos. 5831 and 7546) and European Union Framework VI program, NENA project (Contract No. NMP3-CT-2004-505906) is gratefully acknowledged.

I am most grateful to my family and Maret-Mai Otsa Vishneva, who have given me their unequivocal support throughout, as always, for which my mere expression of thanks likewise does not suffice.

Last, but by no means least, I thank my friends in Estonia, Spain, Finland and elsewhere for their support and encouragement throughout (Pavel Starkov wants to appear in the acknowledgements section too –, so here you are).

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