Electrochemical reduction of oxygen in alkaline solution on Pd/C catalysts prepared by electrodeposition on various carbon nanomaterials

Madis Lüsi, Heiki Erikson, Maito Merisalu, Mihkel Rähn, Väino Sammelselg, Kaido Tammeveski

Abstract

Electrochemical deposition by applying potential steps between −0.25 (or 0 V) and 0.85 V (vs SCE) was used to deposit Pd on different nanocarbon substrates. Influence of overpotential on the electrodeposition process was observed. Obtained Pd/C catalysts were studied with scanning electron microscopy and electrochemically in alkaline solution. Specific activity for the oxygen reduction reaction (ORR) of the catalysts was determined using the rotating disc electrode method. The ORR on all the studied Pd/C catalysts proceeded through a 4-electron pathway with a rate-limiting step of the first electron transfer to the O2 molecule. Pd catalysts deposited on graphene nanosheets showed highest specific activities for the ORR. The prepared catalysts showed higher specific activities than commercial Pd/C catalysts, which can be due to electrodeposition process proceeding without the presence of intrusive additives used in chemical synthesis of nanoparticles. Electrochemical activation was employed to improve the electrocatalytic activity of carbon nanotube-supported Pd catalysts for ORR.

1. Introduction

The electrochemical oxygen reduction reaction (ORR) has been studied extensively for metal-air battery and fuel cell applications. Low-temperature fuel cells are currently using Pt as the cathode catalyst. However, utilising Pt in fuel cell vehicles is not sustainable due to the low abundance and high cost of platinum. In recent years Pd has been studied as a potential replacement for the Pt due to its abundance in the Earth’s crust compared to Pt [1,2]. Pd needs further modification due to its high cost, subpar stability and low electrocatalytic activity for ORR in acidic media. One approach for better Pd utilisation is to disperse it on a high-area carbon support reducing the amount of metal and increasing the specific surface area. In addition, by altering the size and shape of the Pd particles the ORR activity can be increased [3,4]. Furthermore, synergistic effects between support and metal can improve the stability and activity of the catalysts [5]. Electrodeposition is a method, which enables one to control the dispersion, size and shape of metal particles without the presence of intrusive additives, the removal of which from catalyst surface is difficult [6].

Metal electrodeposition mechanism and growth models have been extensively studied on Au electrodes. Bakos and others noted deposition of Pt on Au at the open circuit potential (OCP) with about 5% of a Pt monolayer coverage on the polycrystalline Au electrode, as the value was obtained through potential cycling it is possible that adsorbed PtCl4^-2 species on the surface were reduced [7]. It was shown by Uosaki et al. with the help of electrochemical quartz crystal microbalance and scanning tunnelling microscopy that PtCl4^-2 readily adsorbs onto Au(111) upon immersion of Au(111) electrode into H2PtCl6 solution at OCP [8]. Same group conducted similar experiment with Pd showing that the adsorption of Pd species on Au(111) was similar to that of Pt, furthermore while studying the deposition of Pd they noticed that the adsorption of PdCl4^-2 ions inhibited 3D growth [9,10]. Pd electrodeposition on different Au(hkl) facets was studied by Kibler and co-workers and it was shown that Pd preferably grows on Au defects [11–13]. In their further work they pointed out changes in deposition process when moving from chloride solution to sulphuric acid solution, showing that the growth of Pd in chloride-free solution favours 3D growth mode [14]. Contradicting evidence was found by Wang et al. showing that chlorides did not inhibit 3D growth [15].

Similar deposition mechanisms have also been noted on some carbon materials studied by different groups: glassy carbon (GC) [16–21], carbon black [22–25], carbon paper [26–28], single-walled carbon nanotube [29], multi-walled carbon nanotube (MWCNT)
[25,30], highly oriented pyrolytic graphite (HOPG) [18,31–33], graphene [34–38], graphite [28,39–43], but underpotential deposition is generally not observed on carbon materials though it has been discussed on HOPG, GC [18] and graphite [39]. It has been shown that noble metals favourably deposit on metal seeds, Au [44], Pt [45] and Pd [32] on the carbon material, which leads to growth of larger agglomerates. To overcome this problem that leads to deposition of large particles, different groups have used nucleation on carbon materials applying large overpotential for a short period of time, which forces the creation of larger number of small nuclei [31], this process is sometimes followed by growth of those centres with lower overpotential [16,26]. Morphology, size and dispersion of the Pd nanoparticles is usually varied by changing the support material, deposition potential, concentration of Pd in the solution and presence of ions that preferably adsorb on certain facets of the deposited material. Temperature during the electrodeposition process of Pd was noted to influence only the speed of deposition, yielding similar surface morphology regardless of temperature [28]. Deposition mechanism of Pd has been studied on pencil graphite, where the process follows Stranski-Kranstov growth mechanism with at least three steps: adsorption followed by 2D instantaneous nucleation and diffusion limited 3D growth [40]. Supported materials influence on the electrodeposition of Pd has been shown by Maniam et al., when they changed Vulcan XC72R carbon black with wood apple shell carbon, where Pd displayed larger electrochemical surface area, which was attributed to the increased surface area of the supporting material [24]. Change of dispersion of Pd was also noted by Liu and others on graphene oxide (GO) surface depending on the degree of reduction of GO, where significant reduction of GO leads to the deposition of larger Pd particles and aggregates [34]. Deposited metal morphology dependence on precursor concentration was observed by Xiao and others where they noted the change in morphology of the deposits by lowering the PdCl2 concentration from 1M, this process is sometimes followed by growth of those centres with lower overpotential [16,26]. Salome and others showed that increasing the electrodeposition overpotential from 250 to 500 mV where flowerlike Pd deposits with a cubic core changed into spherical particles forming cubic agglomerates and at intermediate overpotential of 400 mV displayed triangles protruding from the corners of the cubic particles [27]. Our group has previously studied electrodeposition of Pt on MWCNT [46], Pd on GC [20] and Au [47] and AuPd alloy coatings on GC [48]. All these electrodeposited catalysts showed excellent electrocatalytic activity towards the ORR. In this work Pd was electrodeposited onto high-area carbon nanomaterials. The prepared deposits were studied with scanning electron microscopy and transmission electron microscopy. The electrochemical reduction of O2 was observed in alkaline medium to characterise the influence of the support material on the Pd electrodeposition process and the electrocatalytic activity of supported Pd catalyst for ORR. Furthermore, carbon materials were activated using potential cycling and deposits of Pd were studied in alkaline solutions. Electrodeposition was carried out by abrupt change of the potential between −0.25 (or 0 V) and 0.85 V (vs SCE) in a 0.05 M H2SO4 solution containing 1 mM H2PdCl4.

2. Experimental

Glassy carbon (GC) working electrodes with a geometric area of 0.2 cm² were prepared by mounting GC discs (GC-20SS, Tokai Carbon) into Teflon™ holders. Before coating GC electrodes with carbon nano-material they were polished with 1.0 and 0.3 μm alumina slurries (Buehler) and the polishing debris was removed by sonication in Milli-Q water (Millipore, Inc) and isopropanol (99.8%, Honeywell) for 5 min in each using Branson 1510EMTH (Branson™) ultrasonic cleaner.

Graphene nanoplatelets (GNP, Strem Chemicals, Inc.), graphene nanopowder (GNS, Graphene supermarket), carbon black (CB, Vulcan XC-72R Cabot Corp.), carbon nanotubes (CNT, NanoLab, Inc.), and the mixture of GNP and CNT (CNT-GNP) were drop-coated by applying their ink to the cleaned GC surface. Ink of the different nanocarbon materials was prepared by dispersing 1 mg of carbon material in 1 mL of isopropanol and sonicating for 30 min. For electrochemical measurements 5 μL of 0.005% Nafion solution was transferred to the electrode surface after the electrodeposition process to ensure the integrity of catalyst at high rotation speeds during the RDE experiments.

Electrochemical activation of the carbon surfaces was carried out in Ar-saturated 0.1 M KOH solution by potential cycling between 0.1 and 1.6 V at 50 mV s⁻¹ (a is added to the catalyst designation). After which the electrodes were washed and transferred to the deposition bath.

Electrochemical deposition of Pd was carried out in argon-saturated 0.05 M H2SO4 solution containing 1 mM H2PdCl4. Deposition process consisted of 500 potential steps applied between 0 and 0.85 V (subscript L added to the abbreviation) or −0.25 and 0.85 V (subscript H added to the abbreviation) vs saturated calomel electrode (SCE) for 250 ms and 3 s respectively at an electrode rotation rate of 1000 rpm. The electrodeposition solution was prepared from PdCl2 (Sigma-Aldrich), HCl (Sigma-Aldrich) and H2SO4 (Suprapur, Merck).

Scanning electron microscopy (SEM) images were taken with HR-SEM Helios™ NanoLab 600 (FEI) microscope operating at 10 kV. The obtained Pd/C catalyst structure were also explored with transmission electron microscope (TEM) Titan 200 (FEI) operating at 200 kV and using HAAD detector. For SEM studies the catalyst samples were deposited on GC discs and for TEM imaging on Lacey carbon layer coated copper grids.

Oxygen reduction was studied in 0.1 M KOH solution using the rotating disc electrode (RDE) method. The ORR measurements were carried out in a 3-electrode cell with Pt wire separated with a glass frit serving as a counter electrode and a reference electrode of reversible hydrogen electrode (RHE) connected through the Luggin capillary. All the potentials are given with respect to RHE if not stated otherwise. Potential was applied with an Autolab potentiostat/galvanostat PGSTAT30 (Metrohm Autolab B.V.), which was controlled with General Purpose Electrochemical System (GPES) software. The RDE experiments were carried out using an EDI101 rotator and CTV101 speed control unit (Radiometer). 0.1 M KOH solution was prepared using granulated KOH pellets (pro analyti, Sigma-Aldrich) and Milli-Q water. For cyclic voltammetry (CV) studies the electrolyte solution was deaerated with argon (99.999%, AGA). Electrodes were pre-treated by cycling in the potential range of 0.1–0.8 V for 10 cycles after which they were cycled between 0.1 and 1.4 V for 2 cycles at 50 mV s⁻¹. Electroactive surface area was calculated from the Pd oxide reduction peak of the second scan. After CV studies the solution was bubbled with CO (99.97%, AGA) for 30 s while potential was held at 0.1 V to block the Pd surface. To check the complete blockage of Pd, the electrode was cycled between 0.1 and 0.4 V, after which the solution was purged from CO by bubbling Ar for 30 min. The CO stripping experiments were carried out by scanning potential between 0.1 and 1 V at 20 mV s⁻¹. Then the electrode was transferred to O2 (99.999%, AGA) saturated 0.1 M KOH solution where the potential was scanned between 0.1 and 1 V at a scan rate (ν) of 10 mV s⁻¹ varying the rotation rate (ω) between 360 and 4600 rpm. All electrochemical experiments were carried out at room temperature (23 ± 1°C).

3. Results and discussion

3.1. SEM and TEM studies

SEM images of electrodeposited Pd-based catalysts are displayed in Fig. 1. Micrographs of materials deposited at lower overpotential are not shown. From Fig. 1a the Pd deposits on the CNT surface can be observed. Deposition is favoured on the defects and ends of carbon nanotubes. Overpotential does not have great impact when depositing on the surface of CNTs as the obtained structures are similar. By
Fig. 1. SEM images: a) Pd/CNT$_{10}$, b) Pd/CNT$_{20}$, c) Pd/GNS$_{10}$, d) Pd/GNP$_{10}$, e) Pd/CNT-GNP$_{10}$ and f) Pd/CH$_{10}$.
Fig. 2. TEM images of Pd/C catalyst: a) Pd/CNTa, b) Pd/GNP, c) Pd/CB, d) Pd/GNS and e) commercial Pd/C.
deposition on the surface of GNS a more uniform dispersion of spherical Pd particles can be observed, with little to no agglomeration (Fig. 1c), while with TEM larger Pd dendrites can be also observed on some of the graphene sheets (Fig. 2d). Fig. 1d reveals the growth of larger palladium particles onto the surface of GNP, which are surrounded by small particles. The number of small particles is larger at lower deposition potential. Increase in the number of smaller particles has been accompanied by the growth of the larger particles. Similar increase in the number of smaller Pd particles on the highly oriented pyrolytic graphite surface has been noted by Mendoza-Hulzlar et al. [31]. Larger Pd particles on the surface of graphene are mostly shaped as nanowires. Deposition of nanowires without additive has also been noted by Xiao and others [23], where the deposition of such wires was attributed to the presence of Cl− in the deposition bath. Electrodeposition of Pd on CNT-GNP composite material can be seen in Fig. 1e. Regardless of deposition potential leaf-like growth of large particles can be observed, while at higher overpotential there is increased number of smaller Pd particles covering the support surface. Furthermore, the presence of graphene when depositing at higher overpotentials has made it possible for Pd particles to deposit on the surface of CNTs, as there are multiple spherical particles visible, which could not be observed when depositing on CNTs without the addition of graphene. In Fig. 1f the deposition was performed on the surface of Vulcan carbon black. Similarly to the graphene platelets the growth of nanowire-like structures can be observed, but at higher overpotential the Pd nanowires evolve into flower-like structures. Comparing SEM images of Pd deposits on electrochemically activated CNTs (Fig. 1b) it is evident that the activation improved the coverage of Pd on the CNTs as Pd particles can be rarely found on the surface of CNTs in the Pd/CNT catalyst (Fig. 1a). Pd particles deposited on the surface of the activated CNTs have similar shapes as on the surface of GNP with nanowire-like structures and smaller spherical particles, while the agglomerates at the ends of CNTs still remain. By depositing at lower overpotential on the surface of CNTs no Pd particles could be observed.

TEM measurements were used to study Pd grain sizes (Fig. 2). The sizes of individual Pd particles were counted from the TEM image giving average particle size of 5.4, 5.2, 4.2 and 2.3 nm for CNT, GNP, CB and GNS supports, respectively, with GNS having the smallest particle size. This suggests that the support material on the surface of which the electrodeposition is carried out can influence the Pd particle size. For all the catalysts larger agglomerates were also present, when comparing the sizes of Pd particles deposited at lower overpotentials. It is evident that the particles are larger, with wider degree of agglomeration. It is especially evident in the case of GNS where the particle size variation is from 2 to 15 nm when depositing at lower overpotentials, where nicely spread particles that can be seen at higher overpotential have been agglomerated. Average particle sizes are given in Table 1. It is interesting to note that carbon black and graphene promote dendritic growth of Pd nanoparticles (see SEM images in Fig. 1d-f and TEM images in Fig. 2c and d).

### 3.2. CV and CO-stripping studies

Carbon monoxide adsorption-oxidation experiments were carried out to clean the freshly prepared Pd surfaces from chloride contamination. Typical CO stripping voltammograms are shown in Fig. 3. There is a peak centred at ca. 0.87 V representing CO oxidation. In case of CNT-supported catalysts, there is a small peak prior to the main peak observed at 0.79 V, which could be due to the effect of CNTs on the structure of the deposited Pd or because of the prevalence of different faceted Pd particles on the CNT surface. It has been shown by Wandlowski and others that in acid solution the location of the CO oxidation peak is influenced by the facet on which the oxidation takes place [49]. Unfortunately no such study has been carried out in alkaline, which could give further information about the crystallinity. In case of GNS (data not displayed) the CO-stripping peak was wider and could encompass both peaks.

Electroactive surface area (Ae) of Pd could be measured by CO oxidation peak as well the surface oxides reduction peak observed during CV measurements. CV studies were carried out before and after the CO oxidation studies, the area of surface oxide reduction peak increased up to 15% during the CO oxidation studies. Increase of the Pd electroactive area can be attributed to surface cleaning from chloride contamination, as chloride is strongly adsorbed on the surface of Pd in acidic solutions [50]. As the electrodeposition was carried out in

### Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ae by PdO reduction (cm²)</th>
<th>Ae by CO oxidation (cm²)</th>
<th>Average particle size (nm)</th>
<th>SA at 0.9 V (mA cm⁻²)</th>
<th>Tafel slope a (mV)</th>
<th>Tafel slope b (mV)</th>
<th>E1/2 (V)</th>
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<tr>
<td>Pd/CNT-L</td>
<td>0.08</td>
<td>0.07</td>
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<td>0.67</td>
<td>−57</td>
<td>−74</td>
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<td>Pd/CNT-Rh</td>
<td>0.18</td>
<td>0.18</td>
<td>x</td>
<td>0.41</td>
<td>−51</td>
<td>−76</td>
<td>0.81</td>
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<td>Pd/CNT-Bh</td>
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<td>0.12</td>
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<td>−82</td>
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<td>Pd/CNT-Bf</td>
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<td>0.25</td>
<td>x</td>
<td>0.31</td>
<td>−59</td>
<td>−78</td>
<td>0.83</td>
</tr>
<tr>
<td>Pd/GNP-B</td>
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<td>0.55</td>
<td>8.3</td>
<td>0.38</td>
<td>−78</td>
<td>−113</td>
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<tr>
<td>Pd/GNP-Bl</td>
<td>1.17</td>
<td>0.9</td>
<td>2.3</td>
<td>0.37</td>
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<td>−134</td>
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<tr>
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<td>−92</td>
<td>−133</td>
<td>0.77</td>
</tr>
<tr>
<td>Pd/GNP-Br</td>
<td>0.50</td>
<td>0.39</td>
<td>5.2</td>
<td>0.34</td>
<td>−78</td>
<td>−99</td>
<td>0.82</td>
</tr>
<tr>
<td>Pd/GNP-G</td>
<td>0.57</td>
<td>0.46</td>
<td>x</td>
<td>0.35</td>
<td>−74</td>
<td>−111</td>
<td>0.82</td>
</tr>
<tr>
<td>Pd/GNP-GF</td>
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<td>0.9</td>
<td>x</td>
<td>0.32</td>
<td>−90</td>
<td>−123</td>
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<td>Pd/GNP-GFh</td>
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<td>0.26</td>
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<td>−110</td>
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<tr>
<td>Pd/GNPLh</td>
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<tr>
<td>commercial Pd/C [61]</td>
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<td>x</td>
<td>3.5</td>
<td>0.19</td>
<td>−92</td>
<td>−136</td>
<td>0.87</td>
</tr>
</tbody>
</table>

a Low overpotential region.

b High overpotential region.

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**Fig. 3.** Oxidation of pre-adsorbed CO on Pd/C catalysts in Ar-saturated 0.1 M KOH solution, v = 20 mV s⁻¹. Current densities are normalised to the geometric area of GC.
chloride-containing acid solution it seems that washing and transferring into alkaline solution does not seem to be sufficient for cleaning the surface from chloride anions and the CO oxidation process is required. CVs measured after the CO stripping experiments are provided in Fig. 4. The $A_r$ values measured from CV results and CO stripping peaks were in good agreement across the measurements (Table 1). In Fig. 4a CVs of Pd/C deposited at lower overpotential are displayed and the CVs of Pd/C deposited at higher overpotential are displayed in Fig. 4b. CVs were recorded between 0.1 and 1.4 V. On the positive going potentials rise of currents from 0.1 to 0.4 V and from 0.7 to 1.4 V represent desorption of hydrogen and formation of Pd surface oxides, respectively. On the reverse scan the current peak at 0.65 V represents the reduction of formed surface oxides. The increase of current at more negative potentials than 0.3 V represents underpotential deposition of hydrogen on Pd surface. In alkaline media the hydrogen adsorption/desorption peaks are less prominent, thus the electroactive surface area could not be estimated based on HUPD peaks [51]. Large peaks at 0.65 V were used to calculate the $A_r$ values by charge integration under the oxide reduction peak assuming charge density of 424 μC cm$^{-2}$ for a monolayer of Pd oxide reduction [52].

3.3. Oxygen reduction reaction studies

The ORR measurements were carried out after CV studies in 0.1 M KOH solution. The ORR polarisation curves were recorded at different rotation rates by cycling between 0.1 and 1 V at 10 mV s$^{-1}$. Background current was measured in O$_2$-free solution and subtracted from the RDE data. The RDE polarisation data were subjected to the Koutecky–Levich (K–L) analysis:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{nFk_2} + \frac{1}{0.62nF D_{O_2}^{2/3} \nu^{-1/6} C_{O_2}^{1/2}}$$

where $j$ is the overall O$_2$ reduction current density, $j_k$ and $j_d$ are kinetic and diffusion-limited current densities, respectively. $n$ represents electron transfer number, $k$ is the reaction rate constant for O$_2$ reduction, $F$ is the Faraday constant (96,485 C mol$^{-1}$) and $\nu$ is the rotation rate (rad s$^{-1}$). The following values were used for 0.1 M KOH solution for the K–L analysis: kinematic viscosity ($\nu=0.01$ cm$^2$ s$^{-1}$) [53], oxygen concentration in the bulk ($C_{O_2} = 1.2 \times 10^{-6}$ mol cm$^{-3}$) [54] and oxygen diffusion coefficient ($D_{O_2} = 1.9 \times 10^{-5}$ cm$^2$ s$^{-1}$) [54]. $n$ was calculated from the K–L plots and for all catalysts the $n$ value was close to 4, indicating that the ORR follows a 4-electron pathway yielding OH$^-$ as the final product. In acid media, it has been shown using computational methods that on Pt type metals the most likely pathway is direct 4e$^-$ reduction of O$_2$ to water [55]. However, it has also been shown that low palladium content could lead to peroxide formation with almost 100% selectivity [56]. In alkaline the lower working potentials could facilitate desorption of HO$_2^-$ increasing the likelihood of parallel 2e$^-$ + 2e$^-$ pathway. In the present work, a drop in the $n$ value was not observed, which suggests that HO$_2^-$ did not escape during the ORR process even at higher rotation rates [57]. The RRDE method is more suitable to detect the formation of HO$_2^-$.

Depositions by potential steps between 0 and 0.85 V (vs SCE) for 500 cycles were used to prepare first batch of catalysts. Single-wave polarisation curves with well-defined diffusion-limited current plateaus were measured for all the catalysts, with comparisons between the catalysts provided in Fig. 5a and the corresponding Tafel plots are
provided in Fig. 5b. Half-wave potential \( E_{\frac{1}{2}} \) values decrease with decreasing \( A_r \), and Pd/GNS\(_{x}\) has the highest \( E_{\frac{1}{2}} \).

The electrocatalytic properties of catalysts obtained by depositions carried out by potential steps between \(-0.25\) and \(0.85\)V (vs SCE) for 500 cycles are shown in Fig. 6a. There is a noticeable improvement in the half-wave potential for \( \text{O}_2 \) reduction when comparing with the lower overpotential deposited materials, which could be attributed to the lower amount of Pd deposited or the size of the deposited Pd particles. Overpotential had the highest influence on the \( E_{\frac{1}{2}} \) value for Pd/GNP and Pd/CNT with 20mV shift in case of CNTs and 50mV for GNP surfaces. As such the deposition overpotential changes the \( E_{\frac{1}{2}} \) of Pd/GNP to higher values than that of Pd/CBH and Pd/CNTH. As the current efficiency for the Pd deposition is unknown, previously it has been shown to be even lower than 4% at \(-0.6\)V (vs SCE) as such no conclusions can be drawn about the mass of Pd electrodeposited on the surface of carbon nanomaterials [58]. Corresponding Tafel plots are displayed in Fig. 7a. All of the Tafel plots display two slopes in high and low overpotential regions.

In several cases using carbon nanomaterials, various groups have observed better dispersion of the deposited catalyst material on the substrate surface when it was activated [24,59,60]. There are several methods for carbon material activation, but the simplest one would be the electrochemical activation. Maniam and others showed better dispersion of deposited Pd particles on an activated CB surface over non-activated carbon black with less Pd agglomeration observed as well [24]. As such the activation of CNTs was carried out, as the dispersion of Pd and the electrocatalytic activity for \( \text{ORR} \) was poor. From the SEM images it is evident that the activation process made it possible for Pd to be deposited on the surface of CNTs. The ORR polarisation curves comparing the effect of activation are provided in Fig. 7a. Corresponding Tafel plots are displayed in Fig. 7b. Deposition of Pd on the activated CNT surface provided larger electroactive surface area and higher electrocatalytic activity towards the ORR in alkaline media. In contrast with CNT-GNP mixture the effect was reversed. Most of the Pd metal in case of CNT-GNP composites is deposited on the graphene surface.

When we applied this activation process for GNP loss of electroactive surface area was observed, which gives similar effect with the CNT-GNP. Such loss in activity has been observed on GO when it has not been sufficiently reduced, so the oxidation could have lowered the conductivity of the graphene and thus lead to lower \( A_r \) values [34]. It has also been shown that reduction of GO improves the peroxide production on the graphene during the ORR process [61]. From SEM images it can be seen that while the agglomerates remain, some Pd is deposited on the CNT surface, which could be one of the aspects improving the electrocatalytic activity of the Pd/CNT catalyst for \( \text{ORR} \).

To compare the oxygen reduction activity of Pd/C catalysts, specific activities (SA) were calculated:

\[
SA = \frac{i_k}{A_i}
\]

where \( A_i \) is the electroactive surface area and \( i_k \) the kinetic current at a specific potential \( E \). SA values obtained at 0.9 V are listed in Table 1, commercial Pd/C catalyst provided in the Table has been measured in identical conditions to the catalysts in this study [62]. The difference in deposition overpotential changed the \( A_i \) value 1.5–2 fold.
depending on the nanocarbon surface. In case of GNP the increase was only 10%. Activation process for CNTs doubled the electroactive surface area while in case of CNT-GNP a decrease in \( A_e \) was noted. The CNT-supported Pd catalysts have apparently high SA values because determining the value of \( A_e \) is made difficult due to the Pd oxidation peak combining with quinone peaks that can be observed near the same potential [63]. This combination makes the peak hard to distinguish and could lead to underestimation of the \( A_e \) values. This could also explain the lower SA values with activated CNTs where the amount of Pd deposited is significantly larger and thus the contribution for the PdO reduction peak is higher. Loss of activity in the case of CNT-GNP is most likely due to lowering of the conductivity of graphene during electrochemical activation, as most of the Pd metal is deposited on the surface of graphene. Rest of the obtained catalysts had SA values close to that of pure Pd nanocubes observed in our previous work [64]. By comparing with the commercial Pd/C catalyst measured in the same work those catalysts show around 1.5-fold increase in SA. Superior activity could be noted for the electrodeposited catalyst compared to the chemically synthesized graphene quantum dot supported Pd [65]. Lower activity of their structures might be due to additives required for chemical synthesis, which are not present in the electrodeposition experiments. Similarly, Shao and others synthesized Pd shape-controlled nanoparticles, which showed comparable activity to commercial catalyst which also might be due to intrusive additives present during those synthesis methods, while electrochemically deposited Pd particles show higher SA compared to the commercial Pd/C catalyst in alkaline medium [66]. Chemical deposition on the surface of CNT has been performed by Jukk et al., while the obtained electroactive surface area was larger than that obtained with our catalysts, the presence of additives used for one of the synthesis methods yielded lower SA value than that of bulk Pd [67]. Our group has also performed magnetron sputtering of Pd on the surface of CNTs and a comparable SA to that of bulk Pd was achieved and the obtained structures had similar \( A_e \) as compared to our Pd catalysts electrodeposited on CNTs in this work [68]. Excellent electrocatalytic activity was achieved by Lin et al. with Pd/CNT catalyst [69]. Wang and others showed a synthesis route with poly(diallyldimethylammonium chloride) and tungstophosphoric acid additives for CNTs covered by Pd, which had higher ORR activity compared to regular Pd/CNT catalyst [70]. Graphene based catalysts for ORR have been synthesised by Seo and others where they fabricated Pd and Pt based GNS-supported catalysts, where Pd/GNS showed higher mass and specific activity for ORR reduction as compared to the Pt/GNS counterpart [71]. Similarly, Pd/graphene catalysts synthesized by pulse electrodeposition [36] and pulse microwave [72] showed excellent PEMFC performance. Likewise, in our work GNS was the most promising support surface for electrochemical deposition with very high electrochemical surface area and well dispersed Pd particles on the surface of graphene sheets. An advantage of graphene support for Pd catalysts has also been noted with nitrogen-doped graphene [73,74].

In the case of CNT-GNP composite the deposited Pd showed higher \( A_e \) than by depositing on those two materials separately suggesting such composites show promise as electrodeposited catalyst supports. Tafel slope values in high overpotential region for Pd are typically close to −60 mV with general trend for our catalysts showing higher values, which have been also observed previously due to the influence of carbon support on the oxide coverage of Pd [51]. CNT-supported Pd catalysts showed typical Tafel slope value in this region corresponding to the oxide-covered Pd surface. The results show that our nanocarbon-supported Pd catalysts possess high electrocatalytic activity for ORR and can be used as cathodes in alkaline membrane fuel cells. Previous work has shown excellent fuel cell performance using Pd-based cathode materials [78].

4. Conclusions

Electrodeposition of Pd on different carbon nanomaterials was carried out using the same potential step technique for all of the materials, where potential was stepped between −0.25 (or 0 V) and 0.85 V (vs SCE). Surface morphology of the prepared catalysts was studied by SEM and TEM. Pd/C catalysts were compared electrochemically using CO oxidation, CV and the ORR measurements. High specific activity for ORR reduction was obtained with GNS supported Pd catalysts. CNT alone did not prove to be an excellent support material for electrodeposition. The electrochemical activation improved the electroactive surface area, but specific activities were still lower than that of Pd/GNS with significantly lower electrocatalytic surface area. Higher activity of Pd/C catalysts deposited on GNS and CNT-GNP could be attributed to the small spherical Pd particles that cover the surface of graphene sheets with no visible agglomeration, while the activity of Pd/CNT-GNP can be attributed to the small Pd particles deposited on the surface of the CNTs, which could not be observed on pure CNT surfaces. Influence of the overpotential on the deposition process on different substrates can be seen in the electroactive surface areas where depending on the support material there was 1.5−2 fold difference in the surface area. Also the influence of overpotential can be noticed when comparing the sizes of Pd particles deposited at different overpotentials. The results show that higher overpotential promotes the formation of smaller Pd particles and their better distribution on the carbon nanomaterial surface. On all Pd/C catalysts the ORR proceeded via 4-electron pathway. The Tafel slope values for ORR reduction were typical to those obtained for carbon-supported Pd nanoparticles in the literature.

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