Oxygen reduction on electrodeposited Pd coatings on glassy carbon

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**A B S T R A C T**

The electrochemical reduction of oxygen on electrodeposited palladium coatings was studied in acid and alkaline solutions using the rotating disc electrode (RDE) method. Glassy carbon (GC) was used as an electrode substrate and Pd was deposited at a constant potential varying the deposition time. The surface morphology of the palladized electrodes was examined by scanning electron microscopy. It was found that in alkaline media the Pd/GC electrodes show a high specific activity towards oxygen reduction and it does not depend on the deposition time. In acidic solution a little dependence on deposition time was in evidence. The oxygen reduction reaction (ORR) on electrodeposited Pd proceeds mainly through a four-electron pathway in both solutions and the reduction mechanism is similar to that on bulk Pd.

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1. Introduction

In the pursuit to find an alternative catalyst to replace Pt in polymer electrolyte membrane fuel cells (PEMFCs) Pd has received much attention [1,2]. Palladium is a favoured choice due to similar properties with platinum where the mechanistic pathway of oxygen reduction is the same [3,4] and Pd has lower price [2]. Several methods have been used to prepare Pd-based catalysts, e.g. chemical synthesis as well as physical deposition. Overwhelmingly, the oxygen reduction reaction (ORR) has been investigated on chemically synthesised Pd nanoparticles. Salvador-Pascal et al. studied the ORR on nanosized crystalline palladium catalysts which were prepared with NaBH\textsubscript{4} as the reducing agent. The Pd catalyst showed poor ORR activity in relation to Pt electrocatalyst in acid media [5]. Since metal is often incorporated into carbon materials, it is important to know to which extent the pre-treatment of carbon materials affects the kinetics of the ORR [6]. Alvarez et al. studied systematically oxygen reduction on Pd nanoparticles which were synthesised using different reducing agents [7]. Recently good electrocatalytic activity towards the ORR has been shown using Pd nanocubes in both acid [8–11] and alkaline [10,12] solutions and electrodeposited Pd nanorods [13] in acidic media. Oxygen reduction on Pd nanoparticles attached to carbon nanotubes (CNTs) has been investigated by several groups [14–16]. Chakraborty and Raj reported that CNT-supported Pd catalysts showed good electrocatalytic activity and stability in acidic solutions [15]. Seo et al. explored the electroreduction of oxygen on graphene-supported Pd nanoparticles and an excellent ORR activity was observed [17]. Jiang et al. showed that in alkaline solution specific activity of palladium nanoparticles increases continuously by a factor of 3 with increasing particle size from 3 to 16.7 nm without reaching a maximum [18].

Physical methods have been also employed to prepare Pd-based catalysts for ORR [19–22]. With thin Pd films it has been shown that specific activity towards oxygen reduction reaction does not depend on film thickness in perchloric acid [20] nor in potassium hydroxide solution [21] but decreases with film thickness in sulphuric acid [20,21]. Recently magneto sputtering was used to synthesise palladium nanoshells on highly oriented pyrolytic graphite and it was found that Pd nanoshells possess higher ORR activity than Pt thin films of similar electrode thickness and geometric area [22].

Also it is possible to prepare Pd-coated electrodes using electrochemical deposition, the main procedures for this are using constant potential, constant current or potential cycling [23–27]. Naohara et al. and Kibler et al. have studied the mechanism of Pd deposition on Au single crystals and found that the adsorption of PdCl\textsubscript{4}\textsuperscript{2–} complex plays an important role in the layer-by-layer growth of palladium [23–26]. Corduneanu et al. obtained palladium nanoparticles and nanowires on carbon materials by varying deposition parameters. Nanowires were obtained by underpotential deposition at low palladium ion concentrations and spherical Pd nanoparticles by overpotential deposition at higher concentrations.
Yu et al. achieved feather-like structures using highly diluted Pd precursor solution. These feather-like Pd nanostructures exhibited high activity for electro-oxidation of ethanol in alkaline solution [28]. Soreta et al. have studied surface structuring with Pd nanoparticles for signal enhancement. They suggest a method to prepare electrodes with high Pd nanoparticles density with narrow size distribution using 6-ferrocenylhexanethiol [29]. Nohara et al. have studied the reduction of oxygen on ultrathin Pd films on Au(111) and Au(100) substrates and it was found that even a submonolayer of Pd has significant effect on the reaction [30].

In addition to studies on monometallic catalysts several studies on bimetallic Pd catalysts have been carried out. Most often palladium is alloyed with iron, nickel, copper, cobalt, gold or platinum [31–40]. Considerably good activity has been shown for Pd–Co [31–34] and Pd–Fe [34–37] alloys. Alloying of Pd would make it more favourable cathode catalyst in PEMFCs. Earlier work has shown that Pd-based catalysts are electrocatalytically active for ORR [41] in alkaline media and this is a prerequisite for their application in alkaline membrane fuel cells.

In this work the electroreduction of oxygen has been studied on electrochemically deposited Pd on glassy carbon electrodes in acid and alkaline solutions using a rotating disc electrode. The electrodeposition time was varied in order to compare the electrocatalytic properties of Pd/GC electrodes of different Pd loading.

2. Experimental

Glassy carbon (GC) and bulk palladium electrodes were prepared by mounting GC (GC-205S, Tokai Carbon) and Pd (99.95%, Alfa Aesar) disks (diameter 5 mm) into Teflon holders. The surface of the electrodes was polished to a mirror finish using 1.0 and 0.3 μm alumina slurries (Buehler). After alumina polishing, the electrodes were ultrasonically cleaned in Milli-Q (Millipore, Inc.) water for 5 min.

Oxygen reduction was studied in 0.05 M H₂SO₄ and 0.1 M KOH solutions using the rotating disc electrode (RDE) method. The sulphuric acid solution was prepared from 96% H₂SO₄ (Suprapur, Merck) and potassium hydroxide solution was prepared from KOH pellets (p.a. quality, Merck). The solutions were made up using Milli-Q water and were saturated with pure O₂ (99.999%, AGA) or deaerated with Ar gas (99.999%, AGA). A reversible hydrogen electrode (RHE) connected to the cell through a Luggin capillary was employed as a reference and all the potentials reported in this work are referred to this electrode. A Pt wire served as a counter electrode and the counter electrode compartment of the three-electrode cell was separated from the main cell compartment by a glass frit. The potential was applied with an Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie B.V., The Netherlands) and the experiments were controlled with General Purpose Electrochemical System (GPES) software. An EDI101 rotator and CTI101 speed control unit (Radiometer, Copenhagen) were used for the RDE experiments. All experiments were carried out at room temperature ([23 ± 1 °C].

The electrodeposition of palladium was carried out in deaerated 0.05 M H₂SO₄ solution containing 0.1 mM PdCl₂ (99.9%, Sigma–Aldrich). During the deposition the electrode continuously rotated at 960 rpm for faster mass transfer. First, the working electrode was kept at 1.1 V, so that no Pd would be deposited prematurely, then the potential was swept at 50 mVs⁻¹ to 0.78 V where the electrode was kept for 300, 600 or 900 s. Immediately after deposition the electrode was rinsed with Milli-Q water and transferred to another cell containing either 0.05 M H₂SO₄ or 0.1 M KOH, where the electrode was kept at 0.1 V for 300 s so that chloride would desorb.

The as-prepared electrodes were characterised using high resolution scanning electron microscopy (HRSEM) Helios™ NanoLab 600 (FEI).

Prior to the oxygen reduction studies the electrodes were electrochemically pre-treated in Ar-saturated 0.05 M H₂SO₄ or 0.1 M KOH by scanning the potential first between 0.1 and 0.7 V and then additionally for 2 cycles between 0.1 and 1.4 V. After these pre-treatments the electrode was immediately transferred into a third cell, where the solution was saturated with O₂. The oxygen reduction measurements were carried out by scanning the potential between 1.0 and 0.1 V at 20 mVs⁻¹ with different electrode rotation rates.

3. Results and discussion

3.1. Surface characteristics

HRSEM micrographs of Pd coatings on GC deposited for 300, 600 and 900 s are presented in Fig. 1. It can be seen that after 300 s of Pd deposition (Fig. 1a) there are small nanoparticles and also some larger agglomerates. After 600 s (Fig. 1b) more agglomerates have been formed. After 900 s (Fig. 1c) Pd has been deposited on multiple layers, but still some uncoated GC surface can be seen with some small Pd islands on it. The size of small particles was in the range of 3–10 nm and the larger agglomerates were up to 100 nm in diameter. With these deposition parameters Pd grows in the form of nanoparticles as suggested by Bliznakov et al., who also found that if Pd deposition takes place just before hydrogen underpotential deposition, then Pd nanowires would be obtained [42].

3.2. Cyclic voltammetry (CV)

Before the oxygen reduction measurements the electrodeposited Pd and bulk Pd electrodes were subjected to potential cycling in deaerated solution in order to clean and electrochemically characterise the Pd surface. The cyclic voltammograms presented in Fig. 2 show general features characteristic to palladium electrodes. The main characteristics are similar in acid and in alkaline solutions. The broad anodic peak at the potentials above 0.6 V is associated with the formation of Pd surface oxides and reduction of these oxides gives a well-defined cathodic peak between 0.6 and 0.9 V. The current increase between 0.4 and 0.1 V is attributed to hydrogen adsorption and desorption. A minor contribution of hydrogen absorption into Pd is also possible, but it has been shown that in case of thin Pd films at E > 0.1 V this charge is small, as compared to the adsorption charge [43,44]. In acidic media the hydrogen region is better defined than in alkaline solution. This has been attributed to the influence of adsorbed (bi)sulphate ions [45].

The charge corresponding to the Pd oxide reduction peak was used to determine the real electroactive surface area (Aₑ). The value of 424 μC cm⁻² was employed as the charge density for the reduction of a monolayer of PdO [46]. As expected, the value of Aₑ increased with increasing the electrodeposition time.

3.3. Oxygen reduction on Pd/GC electrodes in acid media

The electroreduction of O₂ on electrodeposited Pd/GC electrodes and bulk Pd was studied in O₂-saturated 0.05 M H₂SO₄ using the RDE method. A representative set of polarisation curves of electrodeposited Pd is shown in Fig. 3a; the background current registered in O₂-free solution has been subtracted from the data and only negative-going sweeps are presented and analysed. Similar single-wave polarisation curves were obtained for all the Pd/GC electrodes studied. A comparison of the RDE polarisation curves

Fig. 1. HR-SEM micrographs of electrodeposited Pd on GC. Deposition time: (a) 300, (b) 600 and (c) 900 s.

Fig. 2. Cyclic voltammograms for Pd/GC electrodes in Ar-saturated solutions: (a) 0.05 M H₂SO₄ and (b) 0.1 M KOH. Scan rate: 50 mV s⁻¹.

is shown in Fig. 3b. From this comparison one can observe a positive shift of the half-wave potential of O₂ reduction (E₁/₂) with longer deposition time. The shift is more prominent for 300 and 600 s deposited electrodes being about 100 mV and less prominent between 600 and 900 s deposited Pd electrodes where the difference in E₁/₂ values is about 30 mV. It has been determined in case of platinum that adsorption of bisulphate anions decreases the ORR activity [47]. Same has been determined for epitaxial film of Pd on Pt[1 1 1] [48] and has been proposed for thin Pd films [20].

The RDE data were analysed using the Koutecky–Levich (K–L) equation [49]:

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = -\frac{1}{nFkC^0_\text{O}_2} - \frac{1}{0.62nFD^2_\text{O}_2v^{1/3}C^0_\text{O}_2\omega^{1/2}}
\]

where \(j\) is the measured current density, \(j_k\) and \(j_d\) are kinetic and diffusion-limited current densities, respectively, \(n\) is the number of electrons transferred per oxygen molecule, \(k\) is the rate constant for O₂ reduction, \(F\) is the Faraday constant (96,485 C mol⁻¹), \(\omega\) is the electrode rotation rate, \(C^0_\text{O}_2\) is the concentration of oxygen in the bulk (1.22 × 10⁻⁶ mol cm⁻³) [50], \(D_\text{O}_2\) is the diffusion coefficient of oxygen (1.93 × 10⁻⁵ cm² s⁻¹) [50] and \(v\) is the kinematic viscosity of the solution (0.01 cm² s⁻¹) [51].

The K–L plots were constructed (inset of Fig. 3a) and the number of electrons transferred per O₂ molecule was calculated. The value of \(n\) was close to 4 for 600 s and 900 s deposited Pd electrodes and for 300 s it was somewhat lower, between 3.5 and 3.9 at negative potentials. This indicates that some H₂O₂ is produced. Since
at these potentials the reduction of oxygen is suppressed on GC surface [52] the n value smaller than 4 may not be attributed to two-electron reduction of oxygen on GC, but may be caused by a decreased activity of hydrogen peroxide reduction on Pd nanoparticles in sulphuric acid solution [53]. For bulk Pd the n value was 4 in the whole range of potentials studied.

The negative shift of the half-wave potential with decreasing deposition time is mainly due to decreasing surface area of Pd as can be seen from cyclic voltammograms. In order to compare the intrinsic electrocatalytic activity of electrodeposited Pd the specific activities (SA) were calculated:

\[ \text{SA} = \frac{I_k}{A_r} \]  

where \( I_k \) is the kinetic current at a given potential and \( A_r \) is the real electroactive surface area of palladium. The SA values determined at 0.8 V are rather similar, but some increase with longer deposition time can be observed and for 600 and 900 s deposited Pd the specific activity is comparable with that of bulk palladium (Table 1). The increase in SA values with increasing the Pd film thickness has been observed previously [20,21].

The mass-transfer corrected Tafel plots of \( \text{O}_2 \) reduction shown in Fig. 4 were constructed from the RDE data. For all Pd/GC electrodes the Tafel slope gradually increases with decreasing potential and two regions with distinct slopes can hardly be distinguished. However, the Tafel slope values determined in the potential regions of \( 0.85 \text{V} > E > 0.8 \text{V} \) and \( 0.75 \text{V} > E > 0.7 \text{V} \) (Table 1) were close to \(-60 \text{mV}\) and \(-120 \text{mV}\) that are typical for \( \text{O}_2 \) reduction on palladium catalysts [3,6,7,9,10,20,21], which indicates that the rate determining step for ORR is the transfer of the first electron to \( \text{O}_2 \) molecule.

3.4. Oxygen reduction on Pd/GC electrodes in alkaline media

The electroreduction of oxygen was also investigated in \( \text{O}_2 \)-saturated 0.1 M KOH solution. Fig. 5a shows a typical set of RDE polarisation curves of \( \text{O}_2 \) reduction in alkaline media. Comparison of the RDE results with those obtained in acid solution shows that the electrodeposited Pd electrodes are more active in alkaline environment and well-defined diffusion-limited current plateaus can be observed. On the basis of the RDE data on \( \text{O}_2 \) reduction, the K–L analysis (inset of Fig. 5a) was carried out and from Eq. (1) the value of \( n \) was determined using the following values of oxygen diffusion coefficient and solubility: \( D_{\text{O}_2} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) and \( C_{\text{O}_2} = 1.2 \times 10^{-6} \text{ mol cm}^{-3} \) [54]. For 900 and 600 s deposited Pd as well as for bulk Pd the n value was near to 4 in the whole range of potentials studied. For 300 s deposited Pd the value of \( n \) was between 3.7 and 3.9, indicating that some peroxide is formed. This may be due to the uncovered GC substrate that catalyses the two-electron reduction of \( \text{O}_2 \) to peroxide in alkaline media [55].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tafel slope (mV)</th>
<th>( E_{1/2} ) vs. RHE (V)</th>
<th>SA at 0.8 V (mA cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Region I(^*)</td>
<td>Region II(^*)</td>
<td></td>
</tr>
<tr>
<td>300 s deposited Pd</td>
<td>(-55 \pm 6)</td>
<td>(-123 \pm 14)</td>
<td>0.55 \pm 0.02</td>
</tr>
<tr>
<td>600 s deposited Pd</td>
<td>(-54 \pm 1)</td>
<td>(-136 \pm 1)</td>
<td>0.65 \pm 0.01</td>
</tr>
<tr>
<td>900 s deposited Pd</td>
<td>(-57 \pm 5)</td>
<td>(-138 \pm 8)</td>
<td>0.67 \pm 0.03</td>
</tr>
<tr>
<td>Bulk Pd</td>
<td>(-53 \pm 3)</td>
<td>(-128 \pm 5)</td>
<td>0.71 \pm 0.01</td>
</tr>
</tbody>
</table>

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

Fig. 3. (a) RDE voltammetry curves for oxygen reduction in \( \text{O}_2 \)-saturated 0.05 M \( \text{H}_2\text{SO}_4 \) solution on 600 s deposited Pd at various electrode rotation rates, inset: Koutecky–Levich plot for \( \text{O}_2 \) reduction at 0.3 V and (b) comparison of RDE voltammetry curves in \( \text{O}_2 \)-saturated 0.05 M \( \text{H}_2\text{SO}_4 \), \( \omega = 1900 \text{ rpm} \), scan rate 20 mV s\(^{-1}\).

Fig. 4. Mass-transfer corrected Tafel plots for oxygen reduction on Pd/GC and bulk Pd electrodes in 0.05 M \( \text{H}_2\text{SO}_4 \), \( \omega = 1900 \text{ rpm} \).
values of κ values smaller than 4 have also been reported previously on palladium nanoparticles in alkaline solution [18].

Fig. 5b presents a comparison of the polarisation curves of oxygen reduction on Pd/GC electrodes, bare GC and bulk Pd. From Fig. 5b it is clear that none of the electrochemical characteristics typical to GC remain when it is decorated with palladium. The onset potential of the ORR shifts positive and the second wave on the polarisation curve disappears. It is evident that with shorter deposition time the onset potential is more negative and for 900 s deposited Pd it is basically the same as for bulk Pd. The specific activities were determined at 0.85 V (Table 2). The SA values obtained were somewhat lower than that of bulk Pd.

Mass-transfer corrected Tafel plots were also constructed for O2 reduction in 0.1 M KOH (Fig. 6). The Pd/GC electrodes deposited for 600 and 900 s and bulk Pd showed a rather constant Tafel slope, but for 300 s deposited electrode there were two Tafel regions in evidence. Tafel plots with two different slope values have been observed previously with Pd nanoparticles [10,18,56]. The values of Tafel slope are given in Table 2. Since –60 mV is the typical [10,12,18,21,56] Tafel slope for Pd catalysts at low current densities and –120 mV has also been observed [10,18,56] for nanostructured Pd catalysts, then one may conclude that the mechanism of the ORR on electrodeposited Pd is similar to that on bulk palladium in alkaline as well in acid media.

4. Conclusions

The electroreduction of oxygen on electrodeposited palladium on glassy carbon electrodes has been studied in acid and alkaline solutions. The electrodeposited palladium coatings were more active for O2 reduction in alkaline solution than in acid media and the specific activity did not depend on the deposition time. In acid solution the oxygen reduction activity somewhat decreased for lower deposition time and the specific activities were rather constant and comparable to that of bulk Pd. It was found that on the electrodeposited palladium electrodes the oxygen reduction reaction proceeds mainly via 4e− pathway. The Tafel analysis of O2 reduction indicated that the reaction mechanism on the Pd/GC electrodes studied is similar to that on bulk Pd. The results obtained in this work show that the electrodeposited Pd is a suitable catalyst for oxygen reduction and can be used as a cathode material in low temperature fuel cells.

Acknowledgement

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Table 2

Kinetic parameters for oxygen reduction on electrodeposited Pd on GC and on bulk Pd in 0.1 M KOH. ω = 1900 rpm.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tafel slope (mV)</th>
<th>E1/2 vs. RHE (V)</th>
<th>SA at 0.85 V (mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Region Ia</td>
<td>Region IIa</td>
<td></td>
</tr>
<tr>
<td>300 s deposited Pd</td>
<td>–58 ± 2</td>
<td>–127 ± 15</td>
<td>0.71 ± 0.01</td>
</tr>
<tr>
<td>600 s deposited Pd</td>
<td>–57 ± 2</td>
<td>–56 ± 3</td>
<td>0.77 ± 0.01</td>
</tr>
<tr>
<td>900 s deposited Pd</td>
<td>–57 ± 2</td>
<td>–56 ± 3</td>
<td>0.79 ± 0.01</td>
</tr>
<tr>
<td>Bulk Pd</td>
<td>–57 ± 2</td>
<td>–56 ± 3</td>
<td>0.79 ± 0.02</td>
</tr>
</tbody>
</table>

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

Fig. 5. (a) RDE voltammetry curves for oxygen reduction in O2-saturated 0.1 M KOH solution on 600 s deposited Pd at various electrode rotation rates, inset: Koutecky–Levich plot for O2 reduction at 0.3 V and (b) comparison of RDE voltammetry curves in O2-saturated 0.1 M KOH. ω = 1900 rpm, scan rate 20 mV s⁻¹.

Fig. 6. Mass-transfer corrected Tafel plots for oxygen reduction on Pd/GC and bulk Pd electrodes in 0.1 M KOH. ω = 1900 rpm.
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