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Electroreduction of oxygen on carbon-supported gold catalysts

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1. Introduction

The electroreduction of oxygen is one of the most extensively studied reactions in electrochemistry, as it finds application in many technologies, most importantly, in fuel cells and metal-air batteries [1,2]. The most active electrocatalyst for this reaction is platinum, but due to its high cost and scarcity, investigations are directed also to other materials. Gold electrodes show modest activity towards O_2 reduction in acidic solutions, but in the alkaline media it is greatly increased, especially on Au(100) single crystal face [2,3].

In the last decade gold nanoparticles (AuNPs) have gained attention for unique catalytic properties for several reactions, for example, low temperature CO oxidation [4,5]. O₂ reduction has been studied on Au nanoparticles supported on bulk carbon electrodes [6–27] prepared by various methods, such as electrodeposition [10–19], vacuum evaporation and sputter deposition [20–22,24–27]. The reduction of O₂ has been also investigated on colloidal AuNPs attached to self-assembled monolayers [28,29]. The morphology of the nanostructured Au has a large influence on its electrocatalytic activity towards O₂ reduction, because this reaction is highly structure sensitive [2,3]. In acidic solution, the activity increases in the sequence of Au(111) < Au(110) < Au(100) [2,3]. In alkaline solution, Au(100) has much higher activity than the other low-index surfaces and it supports the further reduc-

ABSTRACT

The electrochemical reduction of oxygen was studied on Au/C catalysts (20 and 30 wt%) in 0.5 M H_2SO_4 and 0.1 M KOH solutions using the rotating disk electrode (RDE) method. The thickness of the Au/C–Nafion layers was varied between 1.5 and 10 μ m. The specific activity of Au was independent of catalyst loading in both solutions, indicating that the transport of reactants through the catalyst layer does not limit the process of oxygen reduction under these conditions. The mass activity of 20 wt% Au/C catalysts was higher due to smaller particle size. The number of electrons involved in the reaction and the Tafel slopes were found; the values of these parameters are similar to that of bulk polycrystalline gold and indicate that the mechanism of O₂ reduction is not affected by carbon support or the catalyst configuration.

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tion of peroxide to OH⁻ in a limited potential region at low overpotentials [30-37]. By varying the conditions of Au electrodeposition, electrodes of different morphology can be prepared, and their electrocatalytic activity also varies [10,14-16]. There are also other methods for preparing the AuNPs of well-defined morphology, for example, gold nanorods with only (111) and (110) surface domains [6,7,9] and cubic Au nanoparticles with high amount of (100) sites [8,9] have been synthesised in water-in-oil microemulsion in the presence of different additives. Au nanoparticles electrodeposited on an organic template partially inhibit the 4e⁻ O₂ reduction pathway compared with bulk Au electrodes [18]. The oxygen reduction reaction in alkaline solution can serve as an indirect means for characterising the crystallographic orientation of such structures [6–9,14–16]. In some cases, the nanostructured Au electrodes have shown increased electrocatalytic activity as compared to bulk Au [13,17,20,21,38,39], but the origin of this effect remains unclear. Recently, the increase of kinetic current density of O₂ reduction with decreasing AuNP size in alkaline solution was noted [40]. In acid solutions, however, the specific activity of vacuum-deposited Au films decreased as the size of AuNPs decreased below ~3 nm [25]. The Au-coated nanoparticles of other metals (Fe, Co, Ni and Pb) exhibited higher oxygen reduction activity in acid solutions than bulk Au [41].

For practical electrocatalysts, optimisation of the catalyst layer thickness is crucial. It is desirable to keep the catalyst loading as low as possible without performance loss. The RDE method is convenient for studying the carbon-supported Pt electrocatalysts in the form of "ink" electrodes and the reproducibility of the measurements is satisfactory [42]. Several reports deal with thickness

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effects of Pt/C catalysts for oxygen reduction [43–46]. However, if the catalyst film on the electrode is rather thick, then O₂ is reduced on all catalyst particles only at low current densities, while at higher overpotentials, just the outermost layer of the film is active [42]. The studies of the electrodes with catalyst gradient confirm that the catalyst particles near the solution interface are utilized more efficiently [47]. The macro-homogeneous model has been used for describing the behaviour of the compact catalyst layer on RDE [43], whereas for gas diffusion electrodes, the agglomerate model gives better results [44]. This model takes into account gas diffusion, ohmic drops and interfacial kinetics within the thin layer and allows calculating the kinetic parameters [43]. Attachment of the catalyst powder on the electrode via a very thin Nafion film minimizes the effect of oxygen diffusion and the mathematical modelling is not necessary [48].

Jiang and Yi have found that the activity of the Pt/C films increases with increasing the catalyst film thickness. As an explanation to this effect they proposed increased utilization efficiency of the catalyst that is caused by the enhanced diffusion of adsorbed reagent species on Pt particles for thicker films, where the particle–particle distance is shorter [45]. They concluded that a film thickness of $2-4 \,\mu$ m is required for reasonable activity [45].

There are only a few reports dealing with oxygen reduction on practical Au/C catalysts. Zhong et al. have prepared Au and AuPt nanoparticles with diameter (d) of 3–5 nm supported on carbon black and studied the reduction of oxygen in acid and alkaline solution. They found that both 2e⁻ and 4e⁻ reduction of oxygen takes place on Au/C catalysts [49,50]. Similarly, the value of the number of electrons transferred per O₂ molecule n = 3.5-4 was determined by Lobyntseva et al. in alkaline solution [51]. In their study, polyte-trafluoroethylene was used as a binder in preparing Au/C catalyst layers. Bron studied the reduction of oxygen in acid media on Au/C catalysts and concluded that the surface specific activity does not depend on the Au particle size or on the type of the supporting carbon black [52]. The electrocatalytic properties of AuNPs modified carbon nanotubes in acid solution have also been studied [53,54].

The objective of the present work was to study the effect of the thickness of Au/C catalyst layer on the kinetics of oxygen reduction in acid and alkaline solutions. Thin layer rotating disk electrode method was used for electrochemical testing of the catalysts. To our knowledge, this is the first work in which the dependence of O_2 reduction activity on the Au/C catalyst layer thickness has been systematically investigated.

2. Experimental

2.1. Electrode preparation

Au/C catalysts (20 and 30 wt% Au nanoparticles supported on Vulcan XC-72R carbon black) were supplied by Johnson Matthey. The catalysts were prepared by a proprietary process involving the base hydrolysis of an aqueous solution of hydrogen tetrachloroauric acid (HAuCl₄). Carbon powder (Vulcan XC-72R, product of Cabot Corporation, Inc.) was used for comparison. The specific surface area of the carbon powder used was 250 m² g⁻¹ according to the producer. Catalyst suspensions were prepared by mixing 4.7 mg of catalyst powder, 20 µl of 5 wt% solution of Nafion (Aldrich) and a known volume of ethanol, followed by sonication for 15 min. Glassy carbon (GC) electrodes with a geometric area of 0.196 cm² were prepared by mounting GC disks (GC-20SS, Tokai Carbon) into Teflon holders. The surface of the GC electrodes was polished to a mirror finish with 1.0 µm alumina slurry (Buehler) and after that the electrodes were sonicated in Milli-Q (Millipore) water for 5 min. A 5 µl aliquot of the catalyst suspension was dropped onto the GC disk using a micropipette. The resulting Au loading

on the electrodes was varied from 5.6 to $57 \,\mu g \, cm^{-2}$, which corresponds to approximate thickness of the catalyst layer from 1.5 to 10 μ m. The electrodes were left to dry overnight at room temperature.

2.2. Electrochemical measurements

Oxygen reduction was studied in 0.5 M H_2SO_4 and in 0.1 M KOH employing a rotating disk electrode (RDE). The solutions were prepared from 96% H_2SO_4 (Suprapur, Merck) or potassium hydroxide pellets (pro analysis, Merck) and Milli-Q (Millipore) water; these were saturated with pure O_2 (99.999%, AGA) or deaerated with Ar gas (99.999%, AGA).

An EDI101 rotator and a CTV101 speed control unit (Radiometer, Copenhagen) were used for the RDE experiments. A saturated calomel electrode (SCE) was employed as a reference and all the potentials are referred to this electrode. The experiments were carried out in a three-electrode glass cell. Pt wire served as a counter electrode and the counter electrode compartment was separated from the main cell compartment by a glass frit. 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. All experiments were carried out at room temperature $(23 \pm 1 \,^{\circ}C)$.

2.3. Characterisation of the Au/C catalysts structure and morphology

Transmission electron microscopy (TEM) measurements were performed on a Tecnai F20 instrument at 200 kV accelerating voltage. Images were acquired in scanning transmission electron microscopy (STEM) mode using a high angle annular dark field (HAADF) detector. For preparation of the TEM specimens, a small portion of catalyst powder was dispersed directly onto perforated carbon film copper grid.

X-ray diffraction (XRD) data was acquired with a Bruker AXS D8 diffractometer using Ni-filtered Cu K α radiation at the tube voltage of 40 kV and 40 mA current. A Lynxeye PSD detector was employed at the 2θ scan range of 10–130° and 0.02° step size. The average grain size of the Au nanoparticles was calculated using Rietveld analysis.

3. Results and discussion

3.1. Surface characterisation of the Au/C catalysts

The representative TEM micrographs for two Au/C catalysts employed are presented in Fig. 1. The particle size analysis was conducted on 264 and 123 particles for 20 and 30 wt% catalysts, respectively. A rather wide size distribution with the maximum frequency at about 10 nm for 20 wt% catalyst and 14 nm for 30 wt% catalyst was obtained. The average particle size was 11.0 ± 1.7 nm for 20 wt% catalyst and 14.0 ± 1.7 nm for 30 wt% catalyst.

For comparison, the XRD method was used for the estimation of Au particle size. The XRD pattern of Au/C catalysts is shown in Fig. 2. Four major peaks with 2θ values of 38.2° , 44.4° , 64.6° and 77.6° corresponding to the $(1\ 1\ 1), (2\ 0\ 0), (2\ 2\ 0)$ and $(3\ 1\ 1)$ planes of the bulk Au, respectively, were observed, which can be assigned to the Au face-centered cubic structure. The broad peak at about 25° is due to the graphitic regions of carbon support. The Rietveld analysis was carried out to calculate the crystallite size of Au particles and the average values of d = 16.8 nm and d = 26.3 nm were obtained for 20 and 30 wt% Au/C, respectively. These values are larger than those obtained from TEM images. This is most probably due to the



Fig. 1. High angle annular dark field TEM images (a and b) and Au particle size distribution (c and d) of Au/C catalysts. (a and c) 20 wt% catalyst, (b and d) 30 wt% catalyst.

wide size distribution of Au particles, as the small number of large Au particles contains a significant fraction of all gold and therefore have a higher contribution to the XRD response.

3.2. Cyclic voltammetry (CV)

Prior to O₂ reduction measurements, the thin layer Au/C electrodes were electrochemically pre-treated and characterised by cyclic voltammetry in Ar-saturated 0.5 M H₂SO₄ by scanning the potential for 20 cycles between -0.3 and 1.45 V at a scan rate of 100 mV s⁻¹. The stable CV curves obtained are presented in Fig. 3. The anodic peak at E > 1.1 V corresponds to the formation of Au surface oxides and the cathodic peak at ca 0.89 V to the reduction of these oxides [55]. The large background current is mainly due to the supporting carbon black and it increases proportionally to the catalyst loading. The current increase at E > 1.3 V is apparently caused by the oxidation of carbon surface. The pair of peaks centered at ca 0.3 V is related to the oxidation and reduction of some functional groups on the carbon surface and it has been suggested that these may be quinone-type species [56]. These peaks increase during the first potential cycles as a result of the oxidation of the carbon surface.

The electroactive surface area of gold (A_r) was determined from the stable cyclic voltammograms by charge integration under the





Fig. 2. XRD pattern for (a) 20 wt% Au/C catalyst and (b) 30 wt% Au/C catalyst.



Fig. 3. Cyclic voltammograms for (a) 20 wt% Au/C catalyst and (b) 30 wt% Au/C catalyst in Ar-saturated 0.5 M H₂SO₄. Catalyst layer thickness: (1) 10 μ m; (2) 6 μ m; (3) 3 μ m and (4) 1.5 μ m. ν = 100 mV s⁻¹.

3.3. Oxygen reduction in 0.5 M H₂SO₄

Both gold and carbon are rather inactive catalysts for oxygen reduction in acid solution. For all Au/C electrodes studied, singlewave oxygen reduction polarisation curves with no well-defined current plateau were obtained using the rotating disk electrode method, and a typical set of current–potential curves registered at various electrode rotation rates for a 20 wt% catalyst is given in Fig. 4. The Koutecky–Levich (K–L) equation was employed for analysing the RDE data [57]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = -\frac{1}{nFkC_{O_2}^b} - \frac{1}{0.62nFD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}^b\omega^{1/2}}$$
(1)

where *j* is the measured current density, j_k and j_d are the kinetic and diffusion-limited current densities, respectively, *n* is the number of electrons transferred per O₂ molecule, *k* is the rate constant for O₂ reduction, *F* is the Faraday constant (96 485 C mol⁻¹), ω is the rotation rate, $C_{O_2}^b$ is the concentration of oxygen in the bulk $(1.13 \times 10^{-6} \text{ mol cm}^{-3} [58])$, D_{O_2} is the diffusion coefficient of oxygen $(1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$ [58] and ν is the kinematic viscosity of the solution $(0.01 \text{ cm}^2 \text{ s}^{-1})$ [59]. The corresponding K–L plots are presented in the inset of Fig. 4. From the slopes of the K–L plots, the number of electrons transferred per O₂ molecule (*n*) was found. The values of *n* were close to 2 at the foot of the polarisation curve and therefore, H₂O₂ is the final reduction product at these potentials. *n* gradually increases at more negative potentials, as a result of further reduction of H₂O₂. At *E* = -0.3 V the *n* value slightly depends on the catalyst loading, increasing from ca 2.5 to 3 with increasing the



Fig. 4. RDE voltammetry curves for O₂ reduction on 10 μ m Au/C (20 wt%) in O₂-saturated 0.5 M H₂SO₄. $\nu = 10$ mV s⁻¹. Inset shows the Koutecky–Levich plots for O₂ reduction derived from the RDE data at various potentials: (\blacklozenge) 0 V; (\blacklozenge) –0.05 V; (\blacksquare) –0.1 V; (\checkmark) –0.2 V and (\blacktriangle) –0.3 V.

catalyst layer thickness. This is in accordance to previous results obtained for Au thin films [26,27] and Au/C catalysts [52].

The electrocatalytic activity of Au/C electrodes towards oxygen reduction was almost proportionally increasing with increasing the catalyst loading and the half-wave potential $(E_{1/2})$ shifted positively (Table 1). The *j*–*E* curves for 20 wt% Au/C electrodes of different Au loadings are presented in Fig. 5. The specific activity (SA) of the electrodes was calculated from

$$SA = \frac{l_k}{A_r}$$
(2)

where I_k is the kinetic current and A_r is the real surface area of gold; the SA values at E = 0 V vs. SCE are given in Table 1 and in Fig. 6. At this potential, the supporting carbon powder is inactive towards oxygen reduction (Fig. 5) and the reduction occurs only at Au particles. It is evident that there is no large dependence of the SA value on the catalyst loading. In addition, the specific activities of 20 wt% Au/C and 30 wt% Au/C catalysts are not significantly different. The mass activities (MA) were determined from

$$MA = \frac{l_k}{m_{Au}}$$
(3)

where I_k is the kinetic current and m_{Au} is the mass of gold in the catalyst layer, calculated theoretically from the mass of the catalyst applied onto the electrode. The mass activity was smaller for 30 wt%



Fig. 5. RDE voltammetry curves for O₂ reduction on 20 wt% Au/C catalyst in O₂-saturated 0.5 M H₂SO₄. Catalyst layer thickness: (\blacksquare) 1.5 µm; (\blacktriangle) 3 µm; (\blacklozenge) 6 µm and (\blacklozenge) 10 µm. (×) 3 µm layer of carbon powder; (\checkmark) bulk Au. ω = 1900 rpm; ν = 10 mV s⁻¹.

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Kinetic parameters of oxygen reduction on Au/C catalysts in 0.5 M H ₂ SO ₄ at ω = 1900 rpm.	
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Catalyst	Au/C layer thickness (μm)	Au loading ($\mu gcm^{-2})$	$A_r({\rm cm}^2)$	Tafel slope (V dec ⁻¹)	$E_{1/2}$ (V)	SA at 0 V (mA $cm^{-2})$	MA at $0 V (A g^{-1})$
20% Au/C	1.5	5.8	0.026	-0.157	-0.24	1.2	27
	3	11.5	0.047	-0.152	-0.16	1.5	30
	6	23	0.097	-0.154	-0.14	1.3	28
	10	38	0.16	-0.165	-0.08	1.9	41
30% Au/C	1.5	8.6	0.014	-0.169	-	1.2	9.6
	3	17.3	0.036	-0.151	-0.19	1.5	16
	6	34.5	0.068	-0.151	-0.14	1.6	15
	10	57	0.21	-0.181	-0.07	1.9	35
Bulk Au	-	-	0.64	-0.107	0.01	1.1	-

Au/C catalysts, as a result of the larger particle size of this catalyst. The values of mass activity are given in Table 1 and presented in Fig. 6.

The mass-transfer corrected Tafel plots were constructed from the RDE data (Fig. 7). For bulk gold, Tafel slope values close to -120 mV dec^{-1} have previously been found, which indicates that the transfer of the first electron is the rate-limiting step [26,27]. For Au/C catalysts, however, these values seem to be higher, -160 mV dec^{-1} on average. This is higher than that obtained by Bron for electrodes coated with Au/C catalyst layers with the thickness of 7.6 µm [52].



Fig. 6. Dependences of the specific activity and mass activity of oxygen reduction for Au/C catalysts on catalyst layer thickness (*h*) in 0.5 M H₂SO₄ at 0 V vs. SCE. (\blacktriangle) 20 wt% Au/C, SA; (\blacktriangledown) 30 wt% Au/C, SA; (\blacksquare) 20 wt% Au/C, MA; (\bigcirc) 30 wt% Au/C, MA.



Fig. 7. Mass-transfer corrected Tafel plots for O₂ reduction on 20 wt% Au/C catalyst (closed symbols); on 30 wt% Au/C (open symbols) and on bulk Au (\mathbf{V}) in O₂-saturated 0.5 M H₂SO₄. Catalyst layer thickness: (\mathbf{H} , \Box) 1.5 µm; (\mathbf{A} , \triangle) 3 µm; ($\mathbf{\Phi}$, \bigcirc) 6 µm and ($\mathbf{\Phi}$, \Diamond) 10 µm. ω = 1900 rpm.

3.4. Oxygen reduction in 0.1 M KOH

In alkaline solution, gold is a rather active catalyst for oxygen reduction, especially the Au(100) crystal face [2,3]. The representative i-E curves at various electrode rotation rates are presented in Fig. 8. Two-wave polarisation curves similar to these were registered for all electrodes. It has been previously shown that at the potentials of the first wave, HO_2^{-} is predominantly formed, while at more negative potentials, complete reduction to OH- occurs. In some cases, a current maximum has been observed at low overpotentials. The extensive studies on Au single crystals have revealed that this is caused by the exceptionally high electrocatalytic activity of Au(100) plane, which catalyses the $4e^{-}$ reduction of O₂ to OH⁻ in a certain potential range at low overpotentials [3]. Comparison of the *i*-*E* curves of the electrodes of different catalyst loading in Fig. 9 reveals that the activity of the electrodes increases with increasing the loading and the half-wave potential shifts to positive direction. For the thickest layers, a current maximum appears at ca -0.4 V, this behaviour is similar to that of bulk polycrystalline gold (Fig. 9).

The Koutecky–Levich plots derived from the data in Fig. 8 are shown in the inset of Fig. 8. The number of electrons transferred (*n*) was calculated using Eq. (1) and the values given for 0.1 M KOH: $C_{O_2}^b = 1.2 \times 10^{-6} \text{ mol cm}^{-3}$ [60], $D_{O_2} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [60] and $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$ [59]. At the potentials near to the current maximum, the value of *n* was close to 3 for the bulk gold and the thicker layers and ca 2.5 for the thinner layers. The *n* value decreased until 2 at more negative potentials, indicating that the peroxide is the final reduction product. At the potentials *E* < -0.6 V the further reduction of peroxide begins on all electrodes and the value of *n* increases again up to about four at the most negative potentials.



Fig. 8. RDE voltammetry curves for O_2 reduction on 3 µm Au/C (20 wt%) in O_2 -saturated 0.1 M KOH. $\nu = 10$ mV s⁻¹. Inset: Koutecky–Levich plots for O_2 reduction on 3 µm Au/C (20 wt%) in O_2 -saturated 0.1 M KOH at various potentials: (\blacklozenge) -0.3 V; (\blacklozenge) -0.4 V; (\blacktriangledown) -0.6 V; (\blacksquare) -0.8 V and (\blacktriangle) -1.2 V.



Fig. 9. RDE voltammetry curves for O₂ reduction on 20 wt% Au/C catalyst in O₂-saturated 0.1 M KOH. Catalyst layer thickness: (**■**) 1.5 μ m; (**▲**) 3 μ m; (**●**) 6 μ m; (**♦**) 10 μ m. (**×**) 3 μ m layer of carbon powder; (**▼**) bulk Au. ω = 1900 rpm; ν = 10 mV s⁻¹.



Fig. 10. RDE voltammetry curves for peroxide reduction and oxidation on $10 \,\mu$ m Au/C catalyst ($20 \,wt\%$) in 0.1 M KOH containing $1.2 \,m$ M of HO₂⁻. ν = $10 \,m$ V s⁻¹.

The reduction and oxidation of peroxide was studied in Arsaturated 0.1 M KOH containing 1.2 mM of HO₂⁻ (Fig. 10). A small pre-peak at ca -0.25 V further confirms that the existence of the current peak of O₂ reduction is related to the reduction or catalytic decomposition of HO₂⁻. There are various explanations to the fact that this process is limited to a certain potential range and occurs only on Au(100) domains. It has been related to a strong chemisorption of OH⁻ on Au(100) single crystal planes at these potential, which enables the dissociative adsorption of O₂ [30,36,37], or to a specific interaction of HO₂⁻ with Au(100) [34]. DFT calculations and experimental results have suggested that in alkaline solution, the disproportionation of peroxide is enhanced on



Fig. 11. Dependences of the specific activity and mass activity of oxygen reduction for Au/C catalysts on catalyst layer thickness (*h*) in 0.1 M KOH at -0.2 V vs. SCE. (\blacktriangle) 20 wt% Au/C, SA; (\blacktriangledown) 30 wt% Au/C, SA; (\blacksquare) 20 wt% Au/C, MA; (\spadesuit) 30 wt% Au/C, MA.

Au(100) relative to the other low-index crystal faces [61]. The disproportionation of peroxide and "recycling" of oxygen released was considered to be responsible for n > 2 at pre-wave potentials also in earlier investigations of O₂ reduction on gold electrodes in alkaline solutions [24,62]. At the potentials of E < -0.4 V the reduction of peroxide is retarded, until the onset of the second reduction wave at about $E \approx -0.7$ V. At -1.2 V, the number of electrons involved in the reduction process is close to 2, as determined from Eq. (1) and using the value of $D_{HO_2^-} = 8.75 \times 10^{-6}$ cm² s⁻¹ [63]. At the potentials E > -0.15 V, the oxidation of HO₂⁻ commences.

It should be noted that the supporting carbon powder also shows considerable activity towards oxygen reduction in alkaline solution (Fig. 9). However, at E = -0.2 V the reduction current on the support is still negligible and therefore it is possible to calculate the specific activity of gold at this potential. The SA values are similar for 20 and 30 wt% Au/C catalysts of all thickness and slightly higher than that of bulk gold (Table 2, Fig. 11). As expected, the MA is lower for 30 wt% catalyst because of larger particle size. The activity of the Au/C catalysts used in this study was much higher than that of smaller Au nanoparticles (3 and 7 nm) prepared by reverse micelle encapsulation [40]. In that study, the SA value of 3.5 mA cm^{-2} was obtained at -0.6 V vs. Ag/AgCl for more active 3 nm particles, but for our catalysts, this value was reached at a much more positive potential (ca -0.25 V vs. SCE). It indicates the superior electrocatalytic properties of the Au/C catalysts used in the present work.

The mass-transfer corrected Tafel plots were constructed from the RDE data (Fig. 12) and the slope values close to -120 mV dec^{-1} were found between -0.2 and -0.3 V (Table 2). These values are common for polycrystalline Au electrodes and indicate that the first electron transfer is the rate-limiting step for O₂ reduction on gold in alkaline solution [27,64].

Kinetic parameters of oxygen reduction on Au/C catalysts in 0.1 M KOH at ω = 1900 rpm.

Catalyst	Au/C layer thickness (μm)	Au loading ($\mu g cm^{-2}$)	A_r (cm ²)	Tafel slope (V dec ⁻¹)	$E_{1/2}(V)$	SA at -0.2 V (mA cm ⁻²)	MA at $-0.2 V (A g^{-1})$
20% Au/C	1.5	5.8	0.030	-0.100	-0.30	1.5	37
	3	11.5	0.047	-0.111	-0.31	1.2	25
	6	23	0.074	-0.135	-0.28	1.7	27.5
	10	38	0.20	-0.091	-0.22	1.9	48
30% Au/C	1.5	8.6	0.010	-0.090	-0.34	1.2	7.4
	3	17.3	0.036	-0.115	-0.31	1.6	17
	6	34.5	0.077	-0.109	-0.27	1.6	18
	10	57	0.21	-0.114	-0.24	1.8	33
Bulk Au	-	-	0.64	-0.093	-0.21	1.0	-



Fig. 12. Mass-transfer corrected Tafel plots for O₂ reduction on 20 wt% Au/C catalyst (closed symbols); on 30 wt% Au/C (open symbols) and on bulk Au (\mathbf{V}) in O₂-saturated 0.1 M KOH. Catalyst layer thickness: (\mathbf{I} , \Box) 1.5 µm; (\mathbf{A} , \triangle) 3 µm; ($\mathbf{\Phi}$, \bigcirc) 6 µm and ($\mathbf{\phi}$, \Diamond) 10 µm. ω = 1900 rpm.

The fact that the SA values are independent of catalyst layer thickness in both solutions indicates that at least at low overpotentials, where the SA was determined, the transport of reactants through the catalyst layer does not limit the oxygen reduction and the reduction occurs also on Au particles that are located in the inner layers, close to the GC substrate. The Tafel slopes are parallel even at more negative potentials in the mixed kinetic-diffusion limitation region, suggesting that the limitation also does not occur at these potentials. The specific activities are similar for 20 and 30 wt% Au/C catalysts, as expected for Au nanoparticles of larger size.

4. Conclusions

On the basis of the results obtained, it can be concluded that the oxygen reduction activity of carbon-supported Au nanoparticles is similar to the activity of bulk Au, both in acid and alkaline solution. The specific activity is almost constant for the catalyst layers with the thickness between 1.5 and 10 μ m, indicating effective diffusion of O₂ within the layer. The mass activity of the catalysts is higher for 20 wt% Au/C catalyst because of smaller particle size. The O₂ reduction mechanism on Au/C catalysts is similar to that of polycrystalline Au.

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