Study on the influence of the thickness of nanostructured rhodium films toward electrooxidation of adsorbed carbon monoxide

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Abstract

Carbon-supported rhodium thin films with various thicknesses are grown by varying the number of laser pulses, N_p (from 5000 to 50,000) under 2 Torr of He background atmosphere using the pulsed laser deposition method. The thin films are characterized for their morphological features and structural properties. It is observed that smooth dense 2D nanosheets of Rh are obtained with 5000 N_p , whereas higher N_p yields to highly porous Rh films. X-ray photoelectron spectroscopy reveals that both metallic Rh and Rh^{3+} are present at the surface of the Rh films. Nevertheless, the amount of metallic Rh increased as the N_p increased. The influence of the thickness of the Rh films on the tolerance to CO, a poison that strongly adsorbs on the surface of catalysts in fuel cells reactions, was investigated through anodic stripping voltammetry. It is found that Rh film deposited with 50,000 N_p exhibits the highest electroactive surface area (27.90 cm^2 vs. 1.20 cm^2 of Pt), the lowest onset potential of CO electrooxidation (0.47 V vs. 0.60 V Pt), and a net charge corresponding to electrooxidation of the CO adlayer of $424 \mu\text{C cm}^{-2}$ (vs. $358 \mu\text{C cm}^{-2}$ of Pt). Such high tolerance to CO poisoning is explained on the basis of the elevated porosity and roughness of the Rh surface. Indeed, a roughness factor of 90.5 for Rh against about 3.8 for Pt grows under analogous deposition conditions of pressure and number of laser pulses.

Keywords Rhodium · Thin films · Pulsed laser deposition · Carbon monoxide · Electrooxidation

1 Introduction

Noble metal nanoparticles are of scientific interest and technological significance and have a wide range of potential applications in optoelectronics, sensors, catalysis, energy conversion/storage and biotechnology to medicine [1–5]. This is essentially attributed to their remarkable catalytic properties, which are radically different from that of their bulk form [6]. Rhodium is widely acknowledged as one of the most essential components in heterogeneous catalysis and often used in the fields of carbon monoxide (CO) oxidation [7], hydrocarbonylation [8], hydroformylation [9], hydrogenation [10], electroreduction of nitrates

[11], and CO elimination from exhaust stream [12]. Rh is also becoming cumulatively important in energy conversion systems such as direct ethanol fuel cells (DEFCs) [13–16], a promising green technology for transportation and portable electronic devices. However, CO poisoning is a critical problem in direct alcohol fuel cells, where CO is a reaction intermediate generated throughout the decomposition of ethanol [2–5]. To sustain their activity, catalysts must achieve the electrooxidation of CO alongside the fuel. Toward a rational design of new CO-tolerant catalysts, it is thus becoming important to understand how and where CO oxidation takes place on the highly inhomogeneous surface of a typical Rh catalyst.

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Miscellaneous methods have been employed for the synthesis of RhNPs. In 1978, Hirai and co-workers [17] first reported the synthesis of colloidal dispersion RhNPs by refluxing a mixed solvent of poly (vinyl alcohol) (PVA) and RhCl_3 at 79 °C under argon or air on a boiling water bath for 0.2–16 h. Nishida et al. [18] synthesized various sizes of RhNPs via microwave-assisted alcohol reduction in a closed vessel under 165 °C for 17 min. Grass et al. [19] used poly (vinylpyrrolidone) (PVP) as capping agent to stabilize monodisperse Rh through one-step polyol method at 140 °C under vacuum. Zettsu et al. [20] prepared branched Rh multipods in large quantities, and the reaction was continued up to 120 h. Ramírez-Meneses et al. [21] reported the synthesis of Rh nanoparticles through an organometallic approach starting from the tris(allyl) rhodium complex, $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$, as precursor and using an alcohol as both a solvent and a stabilizer, under mild reaction conditions (room temperature; 3 bar H_2). Park and co-workers [22] mentioned another approach by decomposing organometallic precursor to prepare spherical nanoparticles at 170 °C. However, the aforementioned wet-chemistry approaches are conducted under rigorous conditions by refluxing admixture of precursor (Rh salts), reductor polyol and stabilizer PVP or PVA at high temperature (60–190 °C) for 0.4–120 h, which is labor-intensive and time-consuming. Kundu et al. [23] reported a photochemical approach to obtain shape-selective RhNPs, where the reaction was performed under 6 h of UV-photoirradiation with alkaline 2,7-dihydroxynaphthalene (2,7-DHN) as reducing agent. Yet 2,7-DHN needs cautious treatment due to its acute toxicity and instability.

In the present work, we endeavor to take protocols for synthesizing Rh catalysts by the pulsed laser deposition (PLD) method and explore the relationships between the effect of number of laser pulses (N_{lp}) and by that the thickness, the structure, properties of Rh films and electrochemical performance toward the tolerance of CO poisoning. This is conducted through a combination of cyclic voltammetry (CV) in CO-free electrolyte and anodic stripping voltammetry (ASV) of CO adsorbed on Rh thin films surface.

2 Experimental section

2.1 Materials and methods

The current collector is an untreated carbon paper (CP, Toray from Electrochem) made of a 3D network of carbon fibers with a diameter between 7 and 10 μm . Targets Rh (99.8%) and Pt (99.99%) were purchased from Kurt J. Lesker Co. Sulfuric acid (96% purity) and ethanol (100% purity) were purchased from Agros Organics and

Commercial Alcohols Inc., respectively. The reactants were used as received without further purification.

2.2 Rhodium synthesis

Rh was deposited onto CP by PLD at room temperature by means of a pulsed KrF excimer laser ($\lambda = 248 \text{ nm}$, $\tau = 17 \text{ ns}$, $\nu = 50 \text{ Hz}$). The specific experimental parameters are listed in Table 1. Rh samples were synthesized in the presence of He background pressure with various N_{lp} setting to 5000, 10,000, 20,000 and 50,000, and they are denoted as Rh_5 , Rh_{10} , Rh_{20} and Rh_{50} , respectively. During deposition, the targets are moved continuously across the laser beam to obtain a uniform ablation over the entire surface of the target. Further information about PLD setup and its working principle are given elsewhere [24].

2.3 Materials characterization

The surface morphology of the as-prepared samples was examined by means of a scanning electron microscope (SEM, JEOL, JSM 6300 F apparatus) operated at an accelerating voltage of 10 kV in the secondary electron mode and a working distance of 10 mm. The measurements were taken in a working pressure of $8 \times 10^{-6} \text{ mbar}$.

The crystalline structure of all samples was determined by X-ray diffraction (XRD) using Bruker D8 Advance diffractometer equipped with a Cu K α source ($\lambda = 1.5406 \text{ \AA}$). The tube current was 40 mA with a tube voltage of 40 kV. All diffractograms were acquired in the Grazing Incidence Diffraction (GID) scan mode with a low incident angle of 2° and a 2θ angular step size of 0.04° with an acquisition time of 4 s per step in the range of 20°–90°.

The surface compositions of the samples were determined by X-ray photoelectron spectroscopy (XPS) measurements and were carried out via a VG Escalab 220i-XL set with an Al K α source (1486.6 eV). The anode was operated at 10 kV and 20 mA. The pass energy of the analyzer was fixed at 20 eV. The base pressure of the system was 10^{-9} mbar . All samples were analyzed with a spot size of

Table 1 Experimental parameters used during PLD-synthesis of Rh thin films

	Experimental parameters
Background gas helium	2 Torr
Working vacuum	$4 \times 10^{-5} \text{ Torr}$
Target	Rh
Substrate	CP
Laser fluence	7 J cm^{-2}
Distance between the target and the substrate	5 cm

250 × 1000 μm located approximately in the center of the sample. A survey spectrum ranging from 0 to 1000 eV was first acquired, and then higher resolution multiplex scan spectra (Rh 3d, O 1s, and C 1s core levels) were obtained. Quantification of the elements was performed with Casa XPS software version 2.3.12 (Casa Software Ltd.) by fitting the core level spectra after a Shirley background removal. The metallic components of the Rh 3d region were fitted using a Gaussian/Lorentzian asymmetrically modified line shape, also symmetrical Gaussian/Lorentzian were used to fit other components. The C 1s core level peak at 284.6 eV, resulting from hydrocarbon contaminants at the surface, was taken as an internal reference binding energy for charge correction.

2.4 Electrochemical measurements

The electrocatalytic characterization was evaluated by CV in Ar-saturated 0.5 M H₂SO₄ solutions in a three-compartment electrochemical cell containing an Ag/AgCl, 4 M NaCl reference electrode, a platinum coil as a counter electrode and the PLD-deposited Rh/CP samples as working electrodes. A Luggin capillary close to the working electrode served to minimize the ohmic drop. Before each test, dissolved oxygen was removed from the solution by bubbling argon for 30 min. Then the surfaces of the working electrodes were cleaned and completely activated by potential cycling to steady state in 0.5 M H₂SO₄ for 30 cycles at a sweep rate of 50 mV s⁻¹ between the range from -0.2 to 1.0 V (vs. Ag/AgCl). The electrochemical data acquisition

was conducted at room temperature (22 ± 0.5 °C) by a computer-controlled potentiostat–galvanostat (Autolab, PGSTAT 20, GPES). In this work, all the currents are normalized by the geometric area of the working electrode (0.308 cm²).

Carbon monoxide anodic stripping experiments were conducted as follows: first, after a 30 min-pure N₂ bubbling in the 0.5 M H₂SO₄ solution, the electrode surface was electrochemically cleaned and completely activated by potential cycling to steady state in 0.5 M H₂SO₄ for 30 cycles at a sweep rate of 50 mV s⁻¹ within the range from -0.20 to 1.03 V versus Ag/AgCl while keeping N₂ flowing. Then pure CO (99.5%) was purged into the above-mentioned solution at a polarized potential of 0 V versus Ag/AgCl for another 30 min to allow the complete adsorption of CO onto the Rh/CP catalyst. While keeping the electrode potential at the same value, the gas was switched to pure N₂ for 30 min to remove redundant CO dissolved in the solution. Finally, the CO anodic stripping voltammetry to electrooxidize the adsorbed CO was started at open-circuit potential with 50 mV s⁻¹.

3 Results and discussion

3.1 Structural characterization

Figure 1 shows SEM images of PLD-synthesized Rh films with increasing N_{lp} . When N_{lp} was 5000, a smooth dense 2D nanosheet (8 ± 1.6 nm thickness) was obtained.

Fig. 1 SEM images of Rh thin films grown by PLD with increasing number of laser pulses. Upper are top view and lower are cross-sectional images

Increasing N_{lp} to 10,000, the surface morphology became less flat but hilly, and the thickness augmented to 20 ± 2.4 nm. Doubling the N_{lp} to 20,000 led to a rougher layer with a thickness estimated to be 40 ± 1.9 nm. A dramatic change occurred when N_{lp} turned to 50,000, which yielded to a highly porous nanostructured layer ($\sim 200 \pm 1.3$ nm) of Rh deposit appearing as an ensemble of agglomerated particles.

Figure 2a reports the XRD diffraction patterns of Rh₅, Rh₁₀, Rh₂₀ and Rh₅₀ electrocatalysts with the XRD pattern of the CP substrate as reference. In the pattern of Rh₅₀, it exhibited diffraction peaks at ca. 40.8° , which can be indexed to (111) plane, characteristic of a face-centered cubic *fcc* structure (JCPDS PDF No. 05-0685). Nevertheless, the distinct diffraction peaks in the vicinity of $2\theta = 40.8^\circ$ can barely be seen in the electrocatalysts of Rh₅, Rh₁₀ and Rh₂₀ (Fig. 2b), implying bulk crystalline Rh was not generated during the deposition process and as also explained by Delpeuch et al. [25] that Rh nanoparticles had been highly dispersed or in amorphous nanoparticles. The most intensive diffraction peak Rh (111) was chosen to evaluate the lattice constant of Rh₅₀ electrode. The average crystallite size D was calculated by the Scherrer formula, whereas the lattice constant a and the interplanar space d_{hkl} were estimated by Bragg law, and the chemical surface area (CSA) of the catalyst was calculated using Eq. 1 [26].

$$CSA \text{ (m}^2\text{g}^{-1}\text{Rh)} = \frac{6000}{\rho D} \quad (1)$$

where ρ is the density of Rh (12.41 g cm^{-3}). The values of D and CSA for the Rh₅₀ electrode were 7.7 ± 0.2 nm and $62.6 \pm 1.4 \text{ m}^2 \text{ g}^{-1}$, respectively. A lattice constant a of $3.821 \text{ \AA}$ was obtained, which was in good agreement with previous calculations [27].

XPS was carried out to investigate the chemical state and electronic structure of the four Rh catalysts (Figure S1). Figure 3 shows typical high-resolution XPS spectra of (a) C 1s, (b) O 1s and (c) Rh 3d core level peaks. As shown in Fig. 3a, the C 1s spectra were deconvoluted into four components and ascribed to: (1) the non-oxygenated C–C (284.60 eV), (2) the hydroxyl carbon in C–OH (285.40 eV), (3) the O–C–O of epoxy groups (286.5 eV), and (4) the carbonyl C (C=O/C–OOH) (288.0 eV) [28]. The O 1s core level peaks (Fig. 3b) were resolved into two contributions located at 530.5 eV and 532.2 eV , which were attributed to lattice oxide Rh–O and C–O, respectively. The two pairs of overlapping doublets peaks (Fig. 3c) revealed that rhodium was in two different oxidation states. The relatively intensive doublet from the spin-orbital splitting (ca. 4.7 eV) of the $3d_{5/2}$ and $3d_{3/2}$ states, which presented at $307.4\text{--}307.5 \text{ eV}$ and $312.1\text{--}312.2 \text{ eV}$, respectively, corresponds to metallic Rh (Rh⁰), and the other less intensive doublet at $308.6\text{--}308.7 \text{ eV}$ and $313.3\text{--}313.4 \text{ eV}$ was due to rhodium oxide species Rh₂O₃ [29]. The partial oxidation of Rh occurred as a result of post-exposure in air. There

Fig. 2 **a** XRD patterns of PLD-grown Rh thin films on to carbon paper substrate. **b** Zoom in of the (111) diffraction peak

Fig. 3 Typical high-resolution XPS peaks of **a** C 1s **b** O 1s and **c** Rh 3d in PLD-grown Rh₂₀ thin films

Table 2 The surface concentration of Rh⁰ and Rh³⁺ species and the BE of Rh⁰ in Rh catalysts

Sample	Rh ⁰ (at%)	Rh ³⁺ (at%)	BE of Rh ⁰ 3d _{5/2} (eV)
Rh ₅	61.16	38.84	307.43
Rh ₁₀	64.62	35.38	307.35
Rh ₂₀	77.74	22.26	307.30
Rh ₅₀	83.65	16.35	307.26

is no clear trend for the oxygenated species at the carbon surface (C–O and C=O) groups (the at% sum of C–O, C=O and O–C=O in Rh₅, Rh₁₀ and Rh₂₀ and Rh₅₀ are 9.46, 9.18, 30.09, 24.69, respectively). The surface atomic concentrations of Rh⁰ and Rh³⁺ are displayed in Table 2. The estimation reveals that metallic Rh was the predominant species in all the Rh samples. One can further see that as the number of laser pulses increased, the amount of Rh⁰ at

the surface increased, while that of Rh³⁺ species decreased demonstrating that smaller particles are easily oxidized [30]. In addition to that, Rh 3d_{5/2} peak slightly shifts toward negative values of the binding energies (BE) as the number of laser pulses increased. Grass et al. [30] and Suarez-Martinez et al. [31] considered the increase in the Rh particle size caused the blueshift.

3.2 Electrochemical studies

3.2.1 CO-free electrolyte

Figure 4a shows CVs at the Rh₅, Rh₁₀, Rh₂₀ and Rh₅₀ electrocatalysts in the Ar-deaerated 0.5 M H₂SO₄ solution recorded within the potential range of $-0.2 \leq E \leq 1$ V using scan rate of 50 mV s⁻¹. As it can be seen, the four electrodes presented the typical CV profile of Rh with its characteristic potential regions: (1) H-region (-0.2 – 0.15 V), corresponding to the underpotential deposition of hydrogen H_{UPD}

Fig. 4 **a** Cyclic voltammograms at Rh/CP electrocatalysts in 0.5 M H₂SO₄ solution recorded with 50 mV s⁻¹ scan rate. Insert is the CV related to Pt/CP electrocatalyst. **b** logarithmic representation of Q_{H-des} , ECSA and R_F as function of N_{lp}

and (2) double layer (DL)-region (0–0.3 V). Wasberg and Horányi [32] pointed out that in DL range, both OH and H species are present simultaneously at low coverage on the surface of Rh electrode. (3) O-region (0.3–1.0 V) related to the formation of Rh surface oxides. Peuckert et al. [29] proposed that rhodium is oxidized to tetravalence according to the following reactions.

Oxidation

Reduction

Figure 4a further demonstrates that increasing N_{ip} of Rh from 5000 to 50,000, the hydrogen adsorption/desorption area increased remarkably. In addition, the oxophilicity character of the catalyst appeared to increase overall with increasing the N_{ip} of Rh. Indeed, the onset potential (defined here as the potential at which the current starts flowing) of formation of surface oxides $E_{\text{onset-ox}}$ shifted negatively, while the onset potential of formation of surface oxides reduction $E_{\text{onset-re}}$ shifted positively. It has to be clarified that the onset potential is not to be confused with the potential required obtaining a determined current density as frequently done when comparing the current activity among catalysts. In that case, the onset potential is determined by choosing an arbitrary criterion such as at a fixed current density or standardizing the CVs at the current density peak or by $ECSA$ and then takes a normalized current density value that would be equivalent to the reach of a certain percentage of the peak current density. In our analysis here, the onset potential is for the sake of discussing only the oxophilicity properties of the catalysts. Pt as a benchmark catalyst was deposited using 50,000 laser pulses, and its structural characterization is reported in Figure S2–S4. The inset of Fig. 4a displays the CV profile of Pt_{50} benchmark electrode ($\text{Pt } N_{\text{ip}} = 50,000$), which exhibits three well-defined peaks: the weakly bonded hydrogen H_{wr} , the strongly bonded hydrogen H_5 and a third anodic peak $\text{H}_{3\text{rd}}$, which were due to hydrogen adsorption on the plane of (111) and (110) facets [33], (100) facets [34] and UPD H_2 [35], respectively. Meanwhile, it is noteworthy that H desorption on Rh starts earlier than that of Pt. It may be because of the low H chemisorption energy on Rh compared with Pt [36]. Furthermore, the Pt_{50} electrode had a wide and thin DL region, whereas in the case of Rh_{50} electrode, the DL region, superimposed with surface oxide reduction peak, became narrow but bulky, consequently.

This can be attributed to the presence of $\text{Rh}(\text{OH})_x$ at the particle surface, increasing the electrode capacitance. The peak of formation of Rh surface oxides oxide/reduction appeared at lower potentials than that of Pt, implying Rh oxides were more stable therefore higher irreversibility of the process [37].

The true electrochemically active surface area ($ECSA$) and the roughness factor (R_F) of the electrocatalysts were estimated using the following equations [38]:

$$ECSA = \frac{Q_{\text{ox}}^H}{\theta_{\text{H,M}} \cdot Q_{\text{ox,ML,S}}^H} \quad (2)$$

$$R_F = ECSA/A_g \quad (3)$$

where Q_{ox}^H (mC) is the integrated charge of voltammetric areas corresponding to H_{des} on Rh (Pt) sites for a given cathodic vertex potential after correcting for the charge of the double layer. θ_{H} is the surface coverage with adsorbed hydrogen at that potential. $Q_{\text{ox,ML,S}}^H$ stands for charge of oxidizing a monolayer of hydrogen on Rh (Pt) per unit area. A_g represents the geometric area of the electrode. $\theta_{\text{H,Rh}} = 0.59$, $Q_{\text{ox,Rh}}^H = 221 \mu\text{C cm}^{-2}$, $\theta_{\text{H,Pt}} = 0.77$, $Q_{\text{ox,Pt}}^H = 210 \mu\text{C cm}^{-2}$, $A_g = 0.308 \text{ cm}^2$.

The Q_{ox}^H , $ECSA$ and R_F plotted in a logarithmic scale as function of N_{ip} of Rh are depicted in Fig. 4b. (Rh at $N_{\text{ip}} = 0$ corresponds to Pt_{50}). It is observed that the Q_{ox}^H , $ECSA$ and R_F increase with the increase in Rh N_{ip} . The Rh_{50} electrode had the highest Q_{ox}^H (3.6 mC), $ECSA$ (27.9 cm^2) and R_F (90.5). Two factors might account for the high performance of Rh_{50} electrode as compared with Pt electrode: (1) the number of nanoparticles (high porous surface). Since the density of Rh (12.4 g cm^{-3}) is almost half of Pt (21.4 g cm^{-3}), at equivalent particles size and metal loading, the number of Rh particles will be nearly two times higher than that of Pt. (2) Capability of hydrogen chemisorption. As mentioned before, Rh needs lower energy than Pt for hydrogen chemisorption, which is confirmed by the fact that the Rh_{50} catalyst exhibited a Q_{ox}^H almost 30 times higher than that of Pt_{50} .

3.2.2 CO-containing electrolyte

It is generally accepted that on pure Rh surface, the electrooxidation of the adsorbed CO follows the Langmuir–Hinshelwood (LH) mechanism [39]:

As illustrated in Fig. 5a, the CO electrooxidation CO_{ox} peak was only observed during the first anodic cycle suggesting

Fig. 5 **a** Typical CVs CO-stripping in 0.5 M H₂SO₄ recorded at 50 mV s⁻¹. **b** ASVs of CO at Rh/CP and Pt/CP electrocatalysts. As function of N_{ip} : **c** E_{onset} , E_{pa} and j_{pa} extracted from **b**, **d** Q_{net} , $Q_{\text{stripping}}$ and $\theta^{\text{sat}}_{\text{CO}}$

that all adsorbed CO was completely removed from the surface under such conditions (2nd cycle). The CO_{ox} peaks characteristics of the electrodes are summarized in Fig. 5b. As can be seen, the CO_{ox} peak of Rh electrodes is broad, which is mostly likely due to low CO mobility on Rh resulting in overlap of CO and Rh surface oxidation processes [40]. Conversely, in the case of Pt₅₀, the CO_{ox} peak was sharp and symmetrical, which was attributed to the fast CO mobility on Pt. Besides, it was observed that the CO_{ox} peak potential E_{pa} shifted to lower values as the N_{ip} of Rh increased in Fig. 5c. Besides, E_{pa} of Rh was lower than that of Pt, which indicates that CO_{ads} was easily removed from the surface of Rh than Pt [41]. $E_{\text{onset-CO}}$ is one of the main design parameters of electrocatalysts highly tolerant to CO poisoning or removal for liquid fuel cells. A similar trend was observed in the onset potential E_{onset} (measured at the potential at which the anodic current starts flowing) of CO electrooxidation when Rh N_{ip} increased. It declined in sequence from Pt₅₀ (0.6 V), Rh₅/CP (0.52 V), Rh₁₀ (0.48 V),

Rh₂₀ (0.47 V) to Rh₅₀ (0.46 V). Rhodium is an oxophilic metal and has the lower d -band center (-1.73 eV) than that of Pt (-2.25 eV) [42], meaning that Rh can provide oxygenic or OH species at potentials lower than that of Pt, which also concurs the observation in CO-free electrolyte (Fig. 4a). As a result, Rh electrodes have a lower onset potential E_{onset} of CO electrooxidation than that of Pt. Finally, the order of CO oxidation peak current density j_{pa} increased with the increase in N_{ip} , with Rh₅₀ displaying the highest peak current density (9.23 mA cm⁻²) that is eightfold greater than that of Rh₅ (1.22 mA cm⁻²). In addition, Rh₅₀ exhibited an E_{onset} of 130 mV negative than the one displayed by the state-of-the-art Pt catalyst. Such significant shift in the E_{onset} demonstrates that Rh₅₀ greatly facilitates the electrooxidation of CO at potentials lower than that of Pt.

In order to correct the contribution of anion adsorption during CO oxidation, the net charge of oxidation and desorption of the CO adlayer was estimated based on a strategy proposed by Gómez et al. [43, 44]:

$$Q_{\text{net}}^{\text{CO}} = Q_{\text{stripping}} - |Q_T| - \int_{E_T}^{E_+} \frac{j}{v} dE \quad (4)$$

where E_T is the potential that displacement has been performed, and E_+ is $Q_{\text{net}}^{\text{CO}}$ is the sought-after net charge density corresponding exclusively to the faradaic oxidation of the CO adlayer. $Q_{\text{stripping}}$ is the experimentally determined charge density obtained by integration of the CO-stripping voltammogram between E_T and E_+ . Q_T is the reduction charge density displaced by CO adsorption at a certain potential E_T in the double layer region. This charge is attributed to the adsorption of bisulfate at the adlayer. The last term equals the total charge density between the potential at which the displacement is performed and E_+ . This contribution corresponds to the double layer charging and Rh oxide formation.

The saturated coverage $\theta_{\text{CO}}^{\text{sat}}$ are obtained from the $Q_{\text{net}}^{\text{CO}}$ values from the following equation [44]:

$$\theta_{\text{CO}}^{\text{sat}} = Q_{\text{net}}^{\text{CO}} / n \cdot 221 \quad (5)$$

where n is the number of electrons exchanged per CO molecule during its oxidation ($n = 2$) and $221 \mu\text{C cm}^{-2}$ is the charge density for a process involving one electron per Rh surface site. The $Q_{\text{stripping}}$, the calculated $Q_{\text{net}}^{\text{CO}}$ (normalized to ECSA) and the corresponding CO coverage $\theta_{\text{CO}}^{\text{sat}}$ are depicted in Fig. 5d. It showed that Rh₅₀ electrode had the highest value of $424 \mu\text{C cm}^{-2}$ with a CO coverage $\theta_{\text{CO}}^{\text{sat}}$ of 0.95 (vs. Pt₅₀ $358 \mu\text{C cm}^{-2}$, 0.85).

4 Conclusions

The pulsed laser deposition PLD technique was employed for the first time to grow Rh films with different thicknesses by varying the number of laser pulses N_{lp} . SEM analysis revealed that Rh films deposited with low N_{lp} had a smooth surface topography. On the other hand, Rh films synthesized with higher N_{lp} were rougher. X-ray photoelectron spectroscopy showed all Rh films contained both metallic Rh and Rh³⁺ at their surfaces. Yet, the concentration of metallic Rh augmented as the N_{lp} increased. As to tolerance to CO poisoning, it is found that Rh film deposited with 50,000 N_{lp} demonstrates the utmost electroactive surface area of 27.90 cm^2 that is almost 23 times higher than that displayed by the benchmark Pt catalyst, an onset potential of CO electrooxidation of 130 mV negative than that at Pt, indicating faster kinetics at the former catalyst. In addition, Rh₅₀ electrode delivered a net charge density as high as $424 \mu\text{C cm}^{-2}$ with a surface saturated CO coverage of 0.95 demonstrating more active sites to CO coverage.

These insights provide important information for the design of highly tolerant electrocatalysts toward CO poisoning and emphasize the importance of considering the influence of the film thickness on the electrochemical performance of Rh when used as single catalyst or when combined with other elements in fuel cells reactions including H₂/O₂ and direct alcohol energy conversion systems.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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