

Electro-oxidation of methanol and ethanol using PtRu/C electrocatalysts prepared by spontaneous deposition of platinum on carbon-supported ruthenium nanoparticles

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Abstract

PtRu/C electrocatalysts were prepared by spontaneous deposition of Pt(II) and Pt(IV) ions on carbon-supported ruthenium nanoparticles, characterized by EDAX, TEM, cyclic voltammetry and tested for methanol and ethanol oxidation using the thin porous coating technique. The spontaneous deposition of Pt(II) ions was about two times more effective than Pt(IV) ions. The electrocatalysts were active for methanol and ethanol oxidation. For methanol oxidation good performance was obtained with high platinum coverage and for ethanol oxidation with low platinum coverage.

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1. Introduction

Fuel cells convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. The proton exchange membrane fuel cell (PEMFC) uses a proton conducting polymer membrane as an electrolyte and gas diffusion electrodes, where the noble metal catalyst is in contact with the ionic and electronic conductors. Platinum-based electrocatalysts are the best materials for the anodic oxidation of fuels and for the cathodic reduction of oxygen at low temperatures [1–5]. On the other hand, the high cost of the platinum limits its use. Thus, a great effort has been devoted to the development of fuel cell electrocatalysts with the aims of increasing their activity and reducing the noble metal content.

PtRu/C electrocatalysts have superior activity as an anode in direct methanol fuel cells (DMFC) and a CO-tolerant proton-exchange membrane fuel cell [6]. Recently, Adzic et al. [7–9] prepared PtRu/C electrocatalysts by the spontaneous deposition of platinum on carbon-supported ruthenium nanoparticles and tested then for the oxidation of H₂ with 100 ppm of CO. Although the electrocatalysts have

low platinum loadings they showed high activity and CO tolerance. The activities per gram of platinum were about three times those of the commercial electrocatalysts.

Ethanol is a renewable and attractive fuel for a direct alcohol fuel cell (DAFC) as it is much less toxic than methanol and can be produced in great quantities from biomass. In Brazil, ethanol has been produced, distributed, and used as a fuel for internal combustion engine cars for more than 20 years. Among different binary electrocatalysts tested in the direct oxidation of ethanol, Pt/Ru and Pt/Sn were the most active and the least poisoned ones [10].

In this work, the PtRu/C electrocatalysts, prepared by spontaneous deposition of platinum on carbon-supported ruthenium nanoparticles, were tested for methanol and ethanol oxidation using the thin porous coating electrode technique.

2. Experimental

In order to obtain electrocatalysts with 10 wt.% of ruthenium, carbon support (Vulcan XC-72R) was impregnated with a solution of RuCl₃·1.5H₂O (Aldrich) in water:ethanol (1:1 v/v) and dried at 343 K for 4 h. The obtained solids were heated from room temperature to 673 K at 1 K min⁻¹ under argon flow. When the desired temperature was reached, hydrogen gas was introduced and the sample was held at that

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temperature for 2 h. The sample was cooled to ambient temperature under hydrogen flow and was immersed in aqueous solutions of H_2PtCl_4 or H_2PtCl_6 (0.01 mol l^{-1}) under argon atmosphere. The mixture was stirred for 15 min and after this was filtered, washed thoroughly with water and dried at 343 K for 3 h.

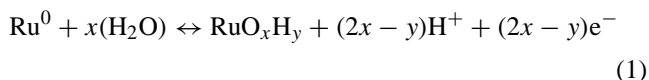
Transmission electron microscopy (TEM) was carried out using a Carl Zeiss CEM 902 apparatus with a Proscan high-speed slow-scan CCD camera and digitalized (1024×1024 pixels, 8 bits) using the AnalySis software. The particle size distributions were determined by measuring the nanoparticles from micrographs using Image Tool software.

The Pt/Ru atomic ratios were obtained by EDAX analysis using a scanning electron microscope Philips XL30 with a 20 keV electron beam and provided with EDAX DX-4 microanalyzer.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique. The working electrode was constructed using a PTFE cylinder with a cavity 0.15 mm deep and 0.36 cm^2 area. A known amount of the electrocatalysts were treated with a 2% PTFE suspension and transferred quantitatively to the cavity. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Electrochemical measurements (cyclic voltammetry) were made using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using the Microquimica software. Cyclic voltammetry was performed in a $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ solution saturated with N_2 . The evaluation of methanol and ethanol oxidation was performed at 25°C in three different concentrations of ethanol: 0.1, 0.5, and 1.0 mol l^{-1} . For comparative purposes a commercial carbon supported PtRu catalyst from E-TEK[®] (20 wt.%, Pt:Ru molar ratio 1:1, lot number 3028401) was used.

3. Results and discussion

Spontaneous deposition of platinum on carbon-supported ruthenium nanoparticles occurs after the sample reduced in hydrogen flow was immersed in the platinum-containing solution. The mechanism of spontaneous metal deposition on noble metal substrates is not clear yet, however, the oxidative dissolution of ruthenium can be excluded, because it occurs at a potential more positive than the equilibrium potential of $\text{Pt}/[\text{PtCl}_6]^{2-}$ [7]. It could be ascribed to a chemical reaction with adsorbed hydrogen or, as suggested by Adzic et al. [7–9], due to the interaction of platinum with surface Ru–OH species as shown in Eqs. (1) and (2).



The chemical compositions of the prepared PtRu/C electrocatalysts are shown in Table 1. It was observed that using

Table 1

Chemical compositions of the prepared PtRu/C electrocatalysts and commercial E-TEK electrocatalyst

Sample	Ru/C (Ru wt.%)	Platinum source	PtRu/C (wt.%)		Pt:Ru atomic ratio
			Pt	Ru	
Pt(II)Ru10	10	H_2PtCl_4	4.5	10	1:4
Pt(IV)Ru10	10	H_2PtCl_6	2.0	10	1:9
PtRu E-TEK	–	–	13.2	6.8	1:1

a solution of Pt(II) ions the quantity of deposited platinum is about two times greater than with Pt(IV) ions solution. This could be an indication that the mechanism proposed by Adzic et al. [7–9] is operative as two times more electrons are necessary to reduce Pt(IV) than Pt(II) ions. Considering the total amount of platinum ions present in the solutions only 13% of Pt(IV) ions and 30% of Pt(II) ions were deposited on the carbon-supported ruthenium nanoparticles in the used conditions. Adzic et al. [8] used different concentrations of Pt(IV) ions and times of deposition to obtain specific coverages. Our results show that the spontaneous deposition of platinum on carbon-supported ruthenium nanoparticles is also influenced by the oxidation state of the platinum ions.

The TEM micrograph taken before the deposition (Fig. 1) shows the ruthenium nanoparticles dispersed on the carbon support having an average particle size of $3.5 \pm 1.5 \text{ nm}$. For this range of particle size the ratio of surface atoms to total atoms is roughly between 0.15 (5.0 nm) and 0.45 (2.0 nm) [8,11]. Considering all ruthenium nanoparticles as having 3.5 nm the ratio of surface atoms to total atoms was about 0.25. Thus, the electrocatalyst prepared from the spontaneous deposition of Pt(II) ions to the carbon-supported ruthenium nanoparticles (Pt:Ru atomic ratio = 1:4) will have a Pt coverage of about 1. For the electrocatalyst prepared from Pt(IV) ions the Pt:Ru atomic ratio was 1:9 and the Pt coverage will be about 0.5.

The results of cyclic voltammetry experiments, in the absence of methanol or ethanol, are shown in Fig. 2. The electrocatalysts do not have a very defined hydrogen oxidation region (0–0.4 V), as observed for pure platinum, and the currents in the double layer region (0.4–0.8 V) are larger, which are characteristic of PtRu electrocatalysts [12,13]. The electrocatalyst Pt(IV)Ru10 presents higher current values in the double layer region than Pt(II)Ru10. This could be attributed to the presence of more ruthenium oxide species on the nanoparticles surface [12,13]. As discussed above, the Pt(IV)Ru10 electrocatalyst has approximately half of the ruthenium nanoparticles surface covered by platinum atoms compared to a complete monolayer of the Pt(II)Ru10 electrocatalyst. The presence of ruthenium species on the surface leads to the formation of ruthenium oxide species at potentials as low as 0.25 V. These species are very important to methanol and ethanol oxidation at low potentials.

The electro-oxidation of methanol and ethanol were studied varying the concentration from 0.1 to 1.0 mol l^{-1} . In the hydrogen region (0–0.4 V) the current values decrease with

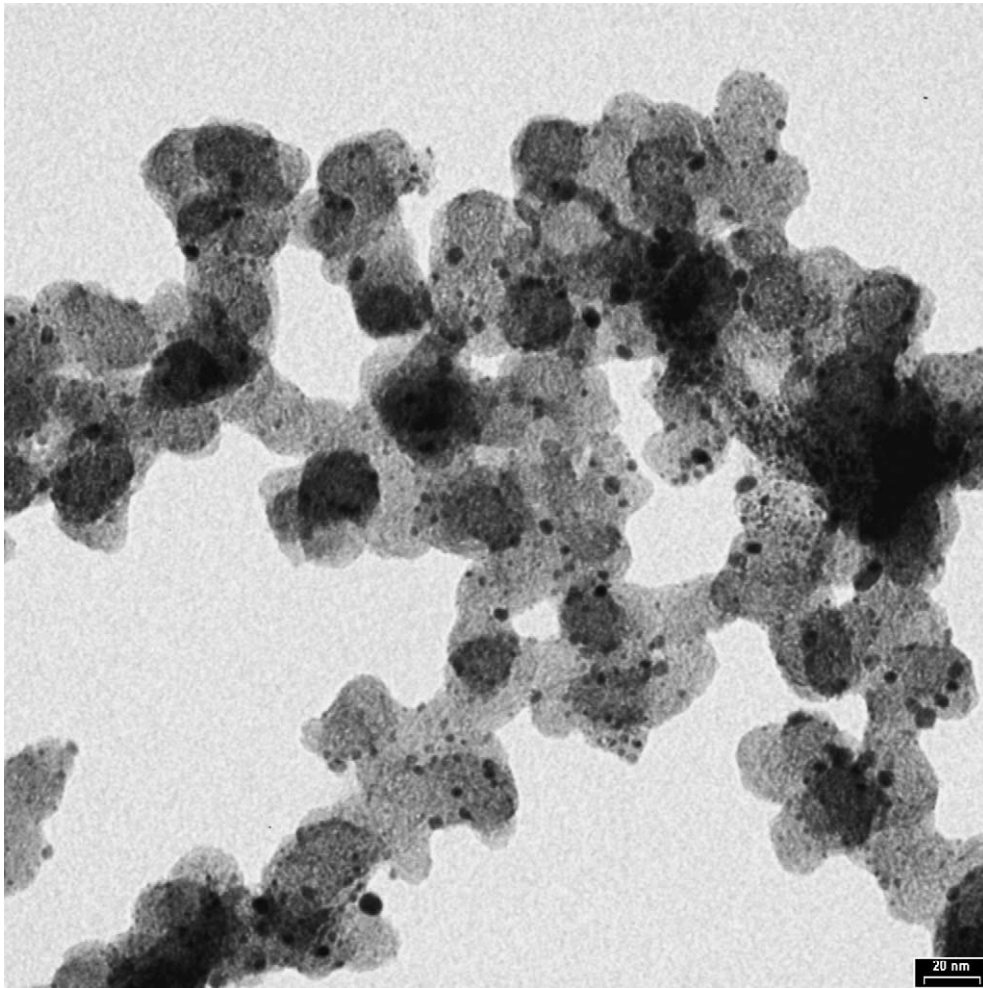


Fig. 1. TEM micrograph of carbon-supported ruthenium nanoparticles before spontaneous deposition of Pt ions.

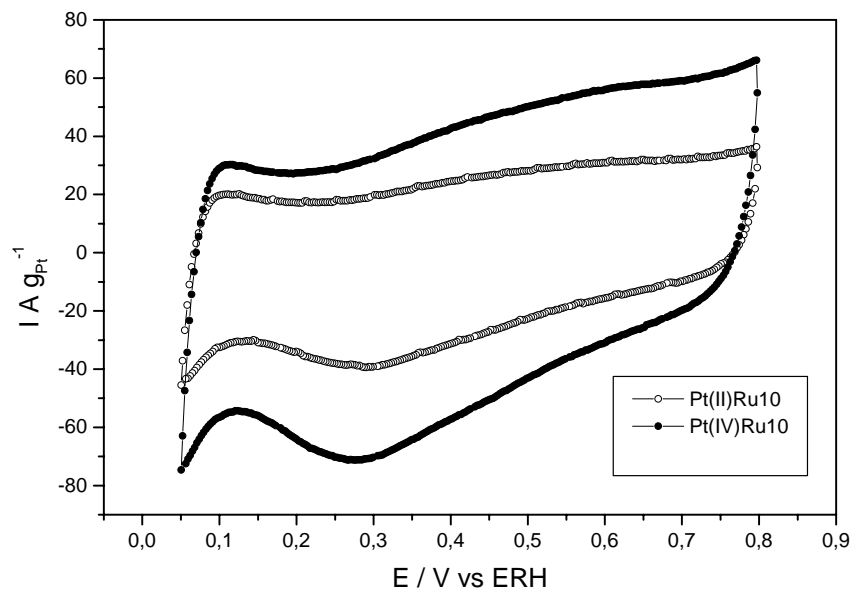


Fig. 2. Cyclic voltammetry of the electrocatalysts in 0.5 mol l⁻¹ H₂SO₄ with a sweep rate of 10 mV s⁻¹.

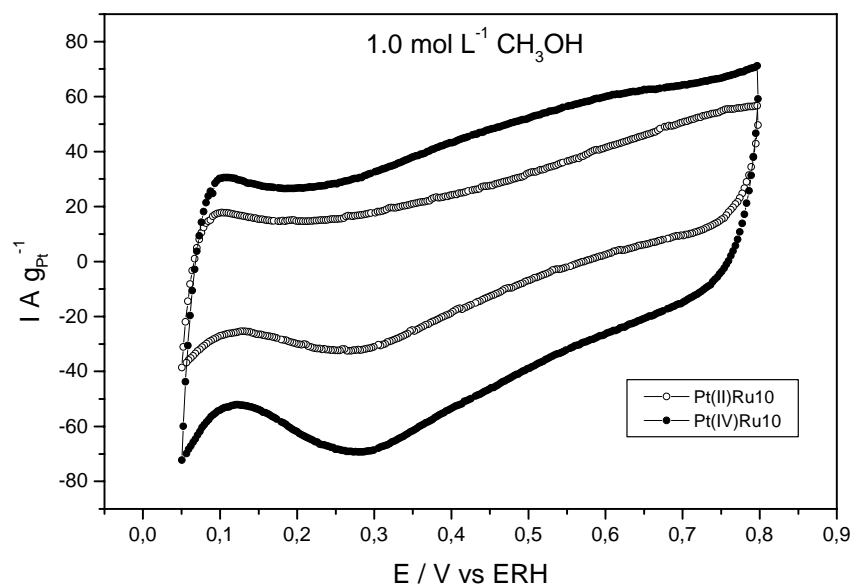


Fig. 3. Cyclic voltammetry of the electrocatalysts in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ containing 1.0 mol l^{-1} of methanol with a sweep rate of 10 mV s^{-1} .

the increase of methanol and ethanol concentration probably due to the increase of alcohol adsorption on the surface [13]. For potentials more positive than 0.4 V the current values increase with methanol and ethanol concentration (Figs. 3 and 4), even for 1.0 mol l^{-1} . Thus, the increase of current with methanol and ethanol concentration could be attributed to an enhancement of the oxidation of adsorbed intermediates promoted by oxygenated species formed on the ruthenium sites (bifunctional mechanism) [14–16]. For methanol and ethanol oxidation the Pt(IV)Ru10 electrocatalyst showed higher currents values than Pt(II)Ru10 electrocatalyst (Figs. 3 and 4). Probably this is due to the presence of more ruthenium oxide species on the nanoparticles surface of Pt(IV)Ru10 electrocatalyst. However, to obtain the real per-

formance of the electrocatalysts a subtraction of the background currents is necessary [17]. This is shown in Figs. 5 and 6 for methanol and ethanol oxidation, respectively. For the methanol oxidation (Fig. 5) Pt(II)Ru(10) electrocatalyst has similar performance (ampere per gram of platinum) of the commercial electrocatalyst from E-TEK, while the Pt(IV)Ru10 showed an inferior performance. Iwasita [16] considers that PtRu electrocatalysts having ruthenium content between 10 and 45% are the best catalysts for methanol oxidation at room temperature. Recently, Lamy et al. [10,18] described that the best electrocatalyst for methanol oxidation had low ruthenium content (Pt:Ru atomic ratio of 80:20). This was explained based on the number of Pt atoms necessary to activate the adsorption of methanol (three to five) and

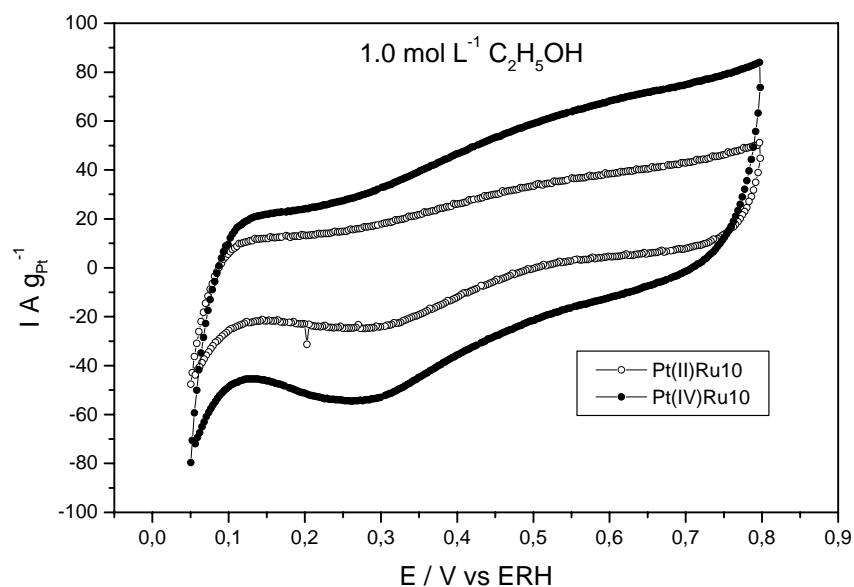


Fig. 4. Cyclic voltammetry of the electrocatalysts in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ containing 1.0 mol l^{-1} of ethanol with a sweep rate of 10 mV s^{-1} .

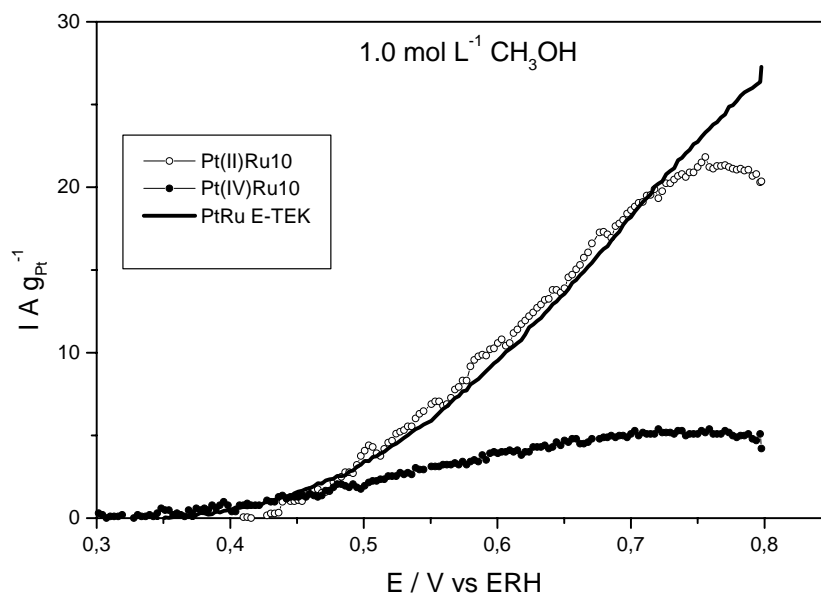


Fig. 5. Cyclic voltammetry of the electrocatalysts in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ containing 1.0 mol l^{-1} of methanol with a sweep rate of 10 mV s^{-1} , considering only the anodic sweep.

the number of ruthenium atoms to activate water (one atom usually). Thus, our results seem in agreement with these results as the Pt(II)Ru10 electrocatalyst has the nanoparticles surface more rich in platinum than the Pt(IV)Ru10 electrocatalyst. Similar results were also observed for methanol electro-oxidation using electrocatalysts prepared by spontaneous deposition of ruthenium on platinum nanoparticles. Wieckowski et al. [19] described that the catalyst activity maximizes at values of 0.4–0.5 ruthenium atoms per platinum surface atom and the catalyst was twice as active the commercial 50:50 Pt/Ru alloy catalyst from Johnson and

Matthey considering the current densities normalized to real surface area. Recently, Leger and co-workers [20] obtained the maximum electroactivity for methanol oxidation at room temperature using lower ruthenium coverage ($\sim 10\%$) and concluded that efficient DMFC electrocatalysts could be achieved by ruthenium deposition on platinum nanoparticles and the formation of a PtRu alloy was not a required condition for effective methanol oxidation.

For ethanol oxidation (Fig. 6) Pt(IV)Ru10 and Pt(II)Ru10 electrocatalysts presented superior performance compared to the E-TEK electrocatalyst and the ethanol oxidation starts

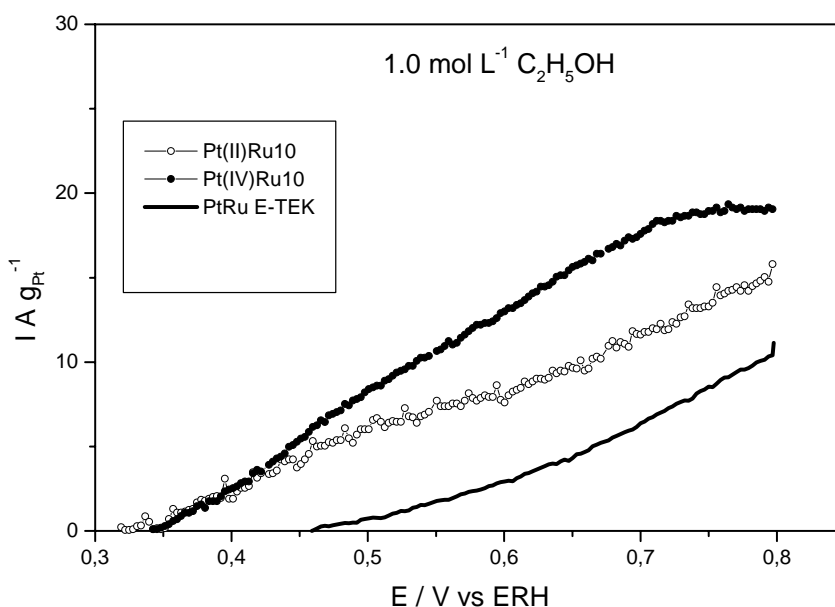


Fig. 6. Cyclic voltammetry of the electrocatalysts in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ containing 1.0 mol l^{-1} of ethanol with a sweep rate of 10 mV s^{-1} , considering only the anodic sweep.

at lower potentials (0.35 V). The Pt(IV)Ru₁₀ electrocatalyst showed the best performance which could be attributed to the presence of more ruthenium oxide species on the nanoparticles surface. Oliveira Neto et al. [17] observed that PtRu electrocatalysts, prepared by reduction with formic acid, the activity for ethanol oxidation increased with the content of ruthenium. Spinacé et al. [21] also observed that PtRu electrocatalysts submitted to an oxidative thermal treatment had better performance for ethanol oxidation. This was attributed to an increase of oxidized ruthenium species on the PtRu nanoparticles surface.

4. Conclusions

The spontaneous deposition of platinum ions on carbon-supported ruthenium nanoparticles was an effective method for making active PtRu/C electrocatalysts for methanol and ethanol oxidation. The quantity of Pt(II) ions spontaneously deposited was about two times greater than Pt(IV) ions. This method permits tuning the carbon-supported ruthenium nanoparticles surface to a selected coverage of platinum atoms. For methanol oxidation good performance was obtained with high platinum coverage and for ethanol oxidation with low platinum coverage.

Acknowledgements

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