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ORIGINAL PAPER

PtRu/carbon hybrid materials prepared by hydrothermal carbonization as electrocatalysts for methanol electrooxidation

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Abstract PtRu/carbon hybrid materials were prepared by hydrothermal carbonization using starch as carbon source and reducing agent and $H_2PtCl_6.6H_2O$ and $RuCl_3.xH_2O$ as metal sources of the carbonization process. The materials were prepared in the following conditions: without pH adjustment, in the absence and in the presence of tetrapropylammonium chloride, and adjusting the pH using potassium hydroxide or tetrapropylammonium hydroxide. The as-synthesized materials were further treated under argon atmosphere at 900 °C and characterized by energy dispersive X-ray spectroscopy, thermogravimetric analysis, BET isotherm, Fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscope, and cyclic voltammetry. The electrooxidation of methanol was studied by chronoamperometry. The addition of tetrapropylammonium ion promoted an increase in surface area and total pore volume while the alkaline medium favored smaller particle sizes. The material prepared using tetrapropylammonium hydroxide showed the best electroactivity for methanol electrooxidation compared to others obtained materials.

Keywords Hydrothermal carbonization · Tetrapropylammonium ion · PtRu/carbon hybrids · Methanol electrooxidation · Direct methanol fuel cells

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Introduction

Researches and experts alert for possible problems associated with the scarcity of energy and pollution due to fossil fuel combustion. Thus, scientists search for new power sources, and fuel cells have been considered pretty interesting [1, 2]. Fuel cells are electrochemical devices that convert chemical energy of a fuel directly into electrical energy with high efficiency and low emission of pollutants [3, 4]. Despite the higher current densities obtained by the use of hydrogen, this fuel presents problems of production, storage, and delivery [5–7].

In this context, fuel cells directly employing alcohols as fuel (direct alcohol fuel cells (DAFC)) are attractive power sources for portable, mobile, and stationary applications [8–12]. These devices work by oxidizing the alcohol (it feeds without any previous chemistry modification or purification) in the anode and reduce oxygen (usually from air) in the cathode. The direct feeding of the alcohol, combined with the fact that alcohols are liquid and they have a well-developed infrastructure for production, storage, and delivery, avoids problems related to the use of hydrogen [9, 11].

Methanol has been considered the most promising fuel for DAFC because it is more efficiently oxidized than other alcohols due to the low complexity of its molecular structure. PtRu/carbon (PtRu/C) electrocatalyst (carbon-supported PtRu nanoparticles) has been considered the best electrocatalyst for methanol electrooxidation. However, the catalytic activity of the PtRu/C electrocatalysts is strongly dependent on the composition, particle size, structure and morphology, which are influenced by the preparation methods [11–13].

Recent studies indicate that the use of mesoporous carbons [14–17] or nanostructured carbons, i.e., nanotubes

[18, 19], nanofibers [20, 21], and others nanoarchitectures [22–24] as support increases the performance of the electrocatalysts used for alcohol electrooxidation. On the other hand, it is known that the syntheses of these materials normally involve complex steps or harsh temperature and/or pressure conditions [20, 23, 25]. Recently, the synthesis of metal/carbon nanoarchitectures by a one-step and mild hydrothermal carbonization was reported using starch or glucose and metals salts [26–28].

Studies [29–31] have shown the importance of pH adjustment of the reactant medium of electrocatalyst preparation in the decrease of particle size, better dispersion of nanoparticles on support and, consequently, in the improvement of electroactivity of the catalysts.

Tonanon [32] evaluated the influence of the surfactant on the porous properties of carbon cryogels prepared by sol-gel polycondensation of resorcinol and formaldehyde. The results showed that different types of surfactants greatly influence the morphologies and porous properties of carbon gels. Carbon cryogels prepared by using the cationic surfactant trimethylstearylammonium chloride (C18) presented larger mesopore size and broader mesopore size distribution compared with carbon cryogels prepared by using other surfactants.

In this work, it was studied that the synthesis of PtRu/carbon hybrid materials by hydrothermal carbonization of starch in different conditions of pH (alkaline and acid medium) and in the absence and presence of tetrapropylammonium ion (TPA^+). The obtained materials were evaluated as electrocatalysts for methanol electrooxidation.

Experimental

PtRu/carbon (Pt/Ru atomic ratio of 50:50 and metallic load of 5 wt.%) were prepared by hydrothermal carbonization using $H_2PtCl_6.6H_2O$ (Aldrich), $RuCl_3.xH_2O$ (Aldrich), and starch (Aldrich). Initially, the noble metals were dissolved in 13 mL of an aqueous solution of starch (starch/noble metals molar ratio of 91). After this, the following conditions were used: without pH adjustment and without addition of tetrapropylammonium chloride (TPACl), without pH adjustment but with addition of TPACl, and adjusting the pH around 11–12 using potassium hydroxide (KOH) or tetrapropylammonium hydroxide (TPAOH). Then, the obtained solutions were submitted to hydrothermal treatment at 200 °C for 6 h in a 150 mL capacity Teflon-lined stainless steel autoclave. The obtained solids were filtered, washed with ethanol and water, and dried at 70 °C for 2 h. Finally, the materials were thermally treated under argon atmosphere at 900 °C for 3 h.

The Pt/Ru atomic ratios were obtained by energy dispersive X-ray spectroscopy (EDX) analysis using a scanning electron microscope Philips XL30 working a 20-keV electron beam and equipped with EDAX DX4 microanalyser.

The PtRu metal loading (weight percent) was determined by thermogravimetric analysis using a Shimadzu D-50 instrument and platinum pans. Heating rate of 5 °C/min was employed under dry oxygen (30 mL min^{-1}) [33, 34].

The BET surface area and pore volume measurements were carried out by nitrogen adsorption at 77 K using a Micromeritics GEMINI V 2380 instrument. Before BET measurements, the samples were degassed at 150 °C for 1 h to remove previously adsorbed gases.

The Fourier transform infrared spectroscopy spectra (FTIR) were recorded on a Thermo Nicolet Nexus 4000 Advanced in the 800–3,700 cm^{-1} wavenumber range. The spectra were recorded with 64 scans at 4 cm^{-1} resolution. In the preparation of pellets, specimens of the PtRu/carbon hybrid materials were first powdered in an agate mortar and then mixed with potassium bromide at an approximate ratio of 1/500, the pellet mass being about 500 mg. The resulting mixture was pressed, and during pressing, the system was evacuated with an oil pump.

The X-ray diffraction analyses were performed using a Rigaku diffractometer model Miniflex II using Cu Kα radiation source (l=0.15406 nm). The diffractograms were recorded in the range of 2θ between 20° and 90° with a step size of 0.05° and a scan time of 2 s per step.

Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 electron microscope operated at 200 kV. The particle size distributions were determined by measuring 200 nanoparticles from micrographs using an Image Tool Software.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [3, 9, 13, 29]. An amount of 20 mg of the catalyst was added to a solution of 50 mL of water containing three drops of a 6% solution polytetrafluoroethylene suspension. The resulting mixture was treated in an ultrasound bath for 10 min, filtered, and transferred to the cavity of the working electrode. It was used as a reference hydrogen electrode, as reference electrode, and a platinum plate as counter electrode. Electrochemical measurements were made using a Microquímica (model MQPG 01, Brazil) potentiostat/galvanostat coupled to a PC and using the Microquímica software. Cyclic voltammetry was performed in a 0.5 mol L^{-1} H_2SO_4 solution saturated with N_2. Chronoamperometry was performed in 0.5 mol L^{-1} H_2SO_4 containing 1.0 mol L^{-1} methanol with a controlled potential of 500 mV for 30 min.

Results and discussion

PtRu/carbon hybrids were prepared in different conditions by hydrothermal carbonization (Table 1). In the reaction

Table 1 pH of reaction medium, Pt/Ru atomic ratio, carbonization yield, weight lost after thermal treatment, PtRu metal load of PtRu/carbon hybrids

	pH of reaction medium	Pt/Ru atomic ratio EDX	Carbonization yield (wt.%)	Weight lost (wt.%)	Metal load (wt.%)
–	2.0	47:53	52	53	6
TPACl	1.7	66:34	48	57	8
KOH	12.3	66:34	88	53	6
TPAOH	11.5	51:49	71	51	5

conditions, the starch hydrolyses to glucose units that act as reducing agents of the Pt(IV) and Ru(III) ions and the resulting metal nanoparticles act as catalysts of the carbonization process [26]. During the synthesis of hybrids, the pH of the medium was in the range of 1–3 without adjustment of the pH, and it was in the range of 11–12 after the adjustment using KOH or TPAOH. The carbonization yields of the as-synthesized PtRu/carbon hybrids were in the range of 52–88 wt.%. The as-synthesized materials did not show catalytic activity for methanol electrooxidation probably due to the carbonaceous structure having low electrical conductivity [35, 36]. After thermal treatment at 900 °C, a weight loss in the range of 51–57 wt.% was observed, and the obtained materials became active for methanol electrooxidation. The Pt/Ru atomic ratios of the obtained materials determined by EDX analysis after thermal treatment at 900 °C were similar to the nominal ones. The obtained PtRu loadings (weight percent) were around 5 wt.%, which were similar to the nominal value.

Figure 1 presents FTIR spectra of PtRu/carbon hybrids after thermal treatment. FTIR spectra reveal the presence of a functional group's characteristics of carbons obtained by hydrothermal carbonization as hydroxyl, carbonyl and carboxyl groups, and aliphatic double bounds [37–41]. The band (1) at about 3,400 cm^{-1} can be ascribed to υ(O–H) vibrations in the hydroxyl groups; (2) at 2,900 cm^{-1}, to υ_{as}(C–H) and υ_{s}(C–H) of methyl and methylene groups; (3) the band at 1,720 cm^{-1} can be attributed to υ(C=O) vibrations of the carboxyl groups; (4) the band at 1,650 cm^{-1} could result from the υ(C=C) vibrations; however, Lua and Guo [42] associate it to the υ(C=O) vibrations in quinones (graphite can display absorption bands in the υ(C=O) and the aromatic υ(C=C) vibrations regions) [41]; (5) the band at about 1,460 cm^{-1} can be ascribed to $\delta_{as}(CH_3, CH_2)$ vibrations; (6) at 1,375 cm^{-1}, it is monitored the $\delta_{s}(CH_3\ CH_2)$ vibrations; and (7) at about 1,100–1,050 cm^{-1}, it is observed υ(C–O) vibrations in primary alcohols. Therefore, spectra of all samples were very similar showing that the materials have the same oxygenated functional groups on theirs surface.

The X-ray diffraction analyses of PtRu/carbon materials prepared by hydrothermal carbonization after treatment at 900 °C are shown in Fig. 2. The diffractograms of PtRu/carbon materials showed a broad peak at about 2θ=23° associated to the carbon material and five peaks at about 2θ= 40°, 47°, 67°, 82°, and 87° that are associated to the (111), (200), (220), (311), and (222) planes, respectively, of the fcc structure of platinum and platinum alloys [43–45]. All

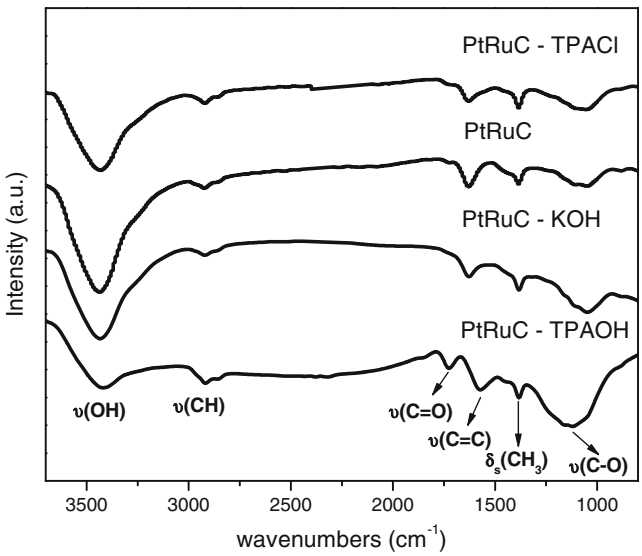

Fig. 1 FTIR spectra of PtRu/carbon hybrid materials prepared by hydrothermal carbonization and thermal treatment

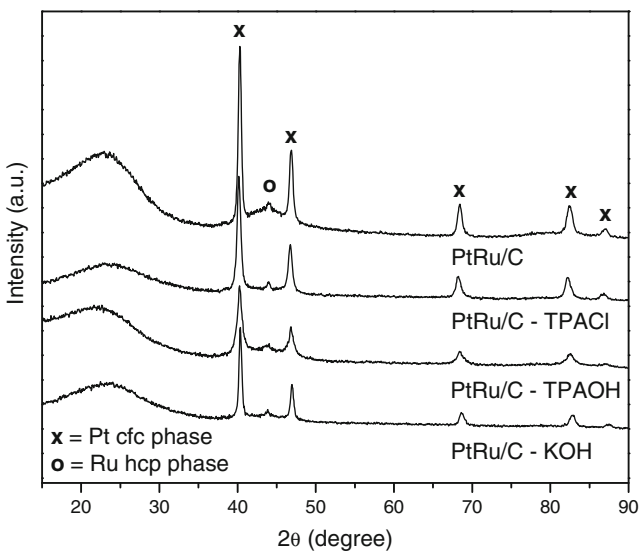

Fig. 2 X-ray diffractograms of PtRu/carbon hybrid materials prepared by hydrothermal carbonization and thermal treatment

Table 2 Average crystallite size, alloy degree, surface area, mesopore volume, and total pore volume obtained by BET isotherm analyses of PtRu/carbon hybrids

	Crystallite size[a,b] (nm)	Alloy degree[a,b] (%)	Surface área[a] ($m^2\ g^{-1}$)	Mesopore volume[a] ($cm^3\ g^{-1}$)	Total pore volume[a] ($cm^3\ g^{-1}$)
–	15	51	20	0.0317	0.032
TPACl	13	35	233	0.0899	0.169
KOH	14	66	28	0.0199	0.028
TPAOH	12	47	117	0.0382	0.084

[a] After thermal treatment

[b] Calculated by Scherrer equation

[c] Calculated by Vegard's law

samples also presented a peak at about 2θ=44° attributed to a separated hexagonal close-packed phase of metallic ruthenium [43–47].

Average crystallite size and alloy degree was calculated from X-ray diffractograms, and surface area, mesopores volume, and total pore volume were obtained from BET isotherms (Table 2). The average crystallite size estimated by the Scherrer equation were in the range of 12–15 nm, and the alloy degree, calculated by Vegard's law, was in the range of 45–65%. Apparently, there are no patterns of variation in alloy degrees in the function of pH, but lower values of this parameter were found for materials prepared in the presence of the TPA^+ ion indicating that, possibly, this surfactant decreases the alloy formation between platinum and ruthenium and, consequently, increases the ruthenium segregated phase.

The superficial area, mesopore volume, and total pore volume values indicate that the materials prepared in the absence of TPA^+ ions have lower values for these parameters compared with materials prepared in the presence of TPA^+ ions. Therefore, the addition of TPA^+ ions leads to an increase of surface area and pore structure in the obtained materials. These data are in agreement with data observed by Tonanon [32] that studied the influence of surfactants in carbon cryogels prepared by sol-gel polycondensation of resorcinol and formaldehyde. It was found that cationic surfactants increase the porosity of such materials.

SEM micrographs of PtRu/carbon hybrid materials after thermal treatment are shown in Fig. 3. The micrographs reveal that all PtRu/carbon hybrids presented predominance of spherical morphology with the presence of some irregular shapes independent of the use of tetrapropylammonium ion or the pH of the reaction medium. The spherical morphology has been frequently observed in the synthesis of carbonaceous materials and metal/carbon hybrids by hydrothermal carbonization [26, 27, 38, 39]. The growth of spherical carbonaceous particles by hydrothermal carbonization of glucose, in the absence of metals, follows the LaMer model, where seeds or nuclei of carbon

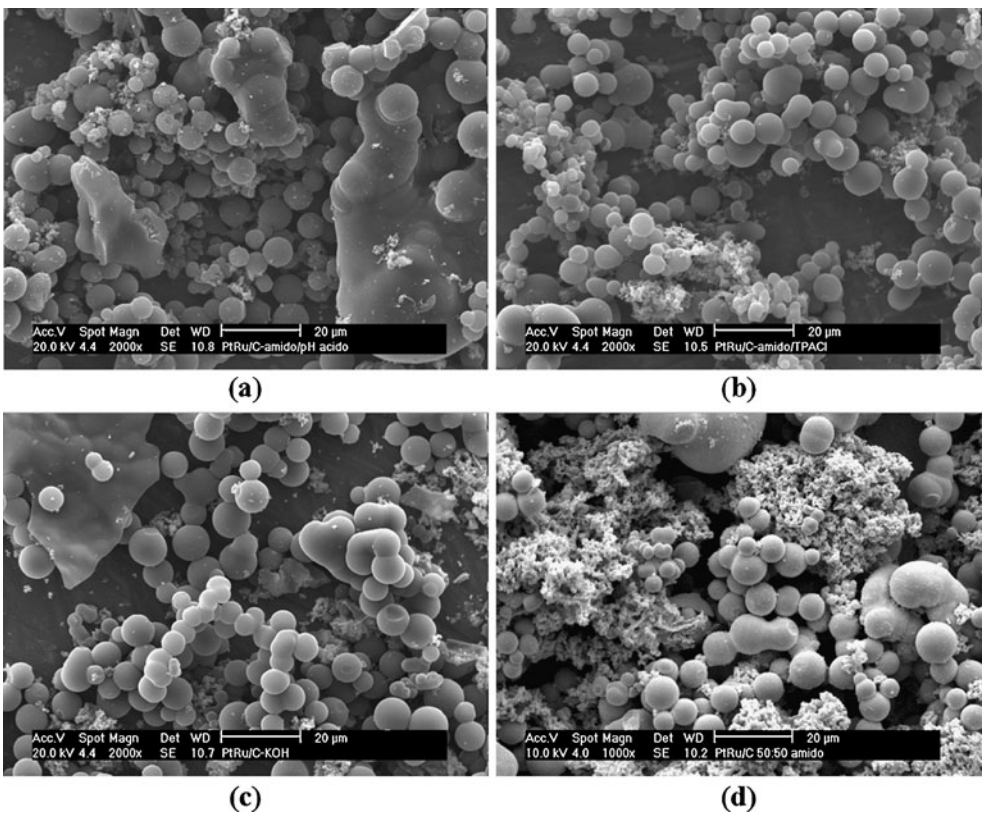

Fig. 3 SEM micrographs of PtRu/carbon hybrid materials after thermal treatment prepared: **a** without additive, **b** with TPACl, **c** with KOH, and **d** with TPAOH

are formed during the hydrothermal treatment and they grow uniformly by diffusion of solutes to the particle surface [39, 48]. The irregular forms appear during the carbonization in the presence of metals suggesting a modified mechanism (not yet completely understood) due to the catalytic action of metallic species [48]. Probably, the catalytic actions of metallic species are involved in the process of polymerization and carbonization resulting in particles with irregular shape [48].

TEM micrographs of PtRu/carbon hybrid materials prepared with the addition of TPACl, KOH, and TPAOH are presented in Fig. 4. The micrographs show the metal nanoparticles reasonably dispersed on the carbon support. The histograms presented a monomodal distribution of particle sizes. The average particle sizes calculated from micrographs were 13.9 nm for PtRu/C-TPACl, 8.8 nm for PtRu/C-KOH, and 8.2 nm for PtRu/C-TPAOH. Therefore, the alkaline medium favors the formation of smaller metal nanoparticles compared with the synthesis carried out in acid medium. It was described that at high pH value, the hydrogen bonding between the metal nanoparticles and –OH groups of the glucose molecule is strong enough to prevent the metal nanoparticle growth [49, 50].

Electrochemical experiments showed that PtRu/carbon hybrids as-synthesized do not present catalytic activity for methanol electrooxidation probably due to the fact that the carbonaceous material does not have good electrical conductivity and/or contains organic residues (material not

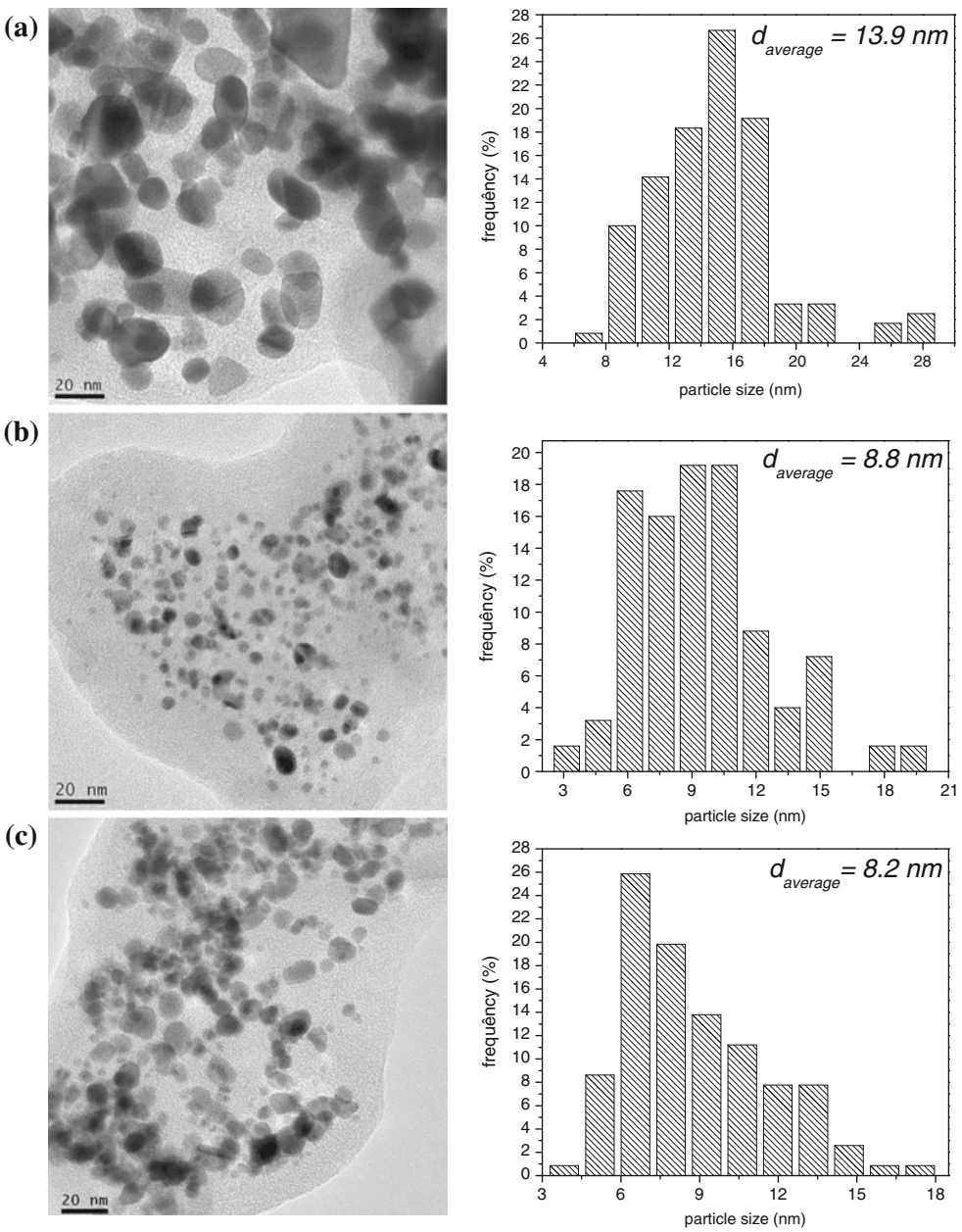

Fig. 4 TEM micrographs and histograms of the particle size distribuition of PtRu/carbon hybrid materials prepared with **a** TPACl, **b** KOH, and **c** TPAOH

completely carbonized) that could block the active metallic sites. After thermal treatment occurs, an organization of the carbonaceous structure of these hybrids [35] results in the improvement of the electrical conductivity of these materials thus making them active for methanol electrooxidation.

Figure 5 presents the cyclic voltammograms in H_2SO_4 solution of the PtRu/carbon hybrid materials thermally treated. For all materials, the cyclic voltammograms do not have a well-defined hydrogen adsorption–desorption region (0–0.4 V) and an increase of current values in the double layer region (0.4–0.8 V), suggesting the presence of oxide species on the nanoparticle surface. Such behaviors are characteristic of materials with a Pt/Ru atomic ratio of 50:50 [13]. The inhibition of hydrogen adsorption–desorption is possibly due to the incorporation of ruthenium to the platinum structure, and the increase of current values in the double layer region is due the capacitive currents and redox process of ruthenium oxides [50, 51]. These increases in currents can be attributed to the transition between the oxidation states of Ru(III) and Ru(IV). Due to the existence of different oxidation states in the range of potentials, ruthenium oxides are capable of adsorbing large amounts of OH species during the adsorption process [51].

The current–time curves obtained by chronoamperometry at 0.5 V for PtRu/carbon hybrid materials thermally treated in 0.5 mol L^{-1} H_2SO_4 containing 1.0 mol L^{-1} of methanol are shown in Fig. 6. The final current values, i.e., the order of electroactivity of the PtRu/carbon materials for methanol electrooxidation after 30 min at 0.5 V were: PtRu/C (TPAOH)>PtRu/C (TPACl)=PtRu/C (KOH)>PtRu/C. Apparently, the electroactivity of the materials prepared by hydrothermal carbonization is dependent of two properties: particle size and pore structure. Despite having larger pore

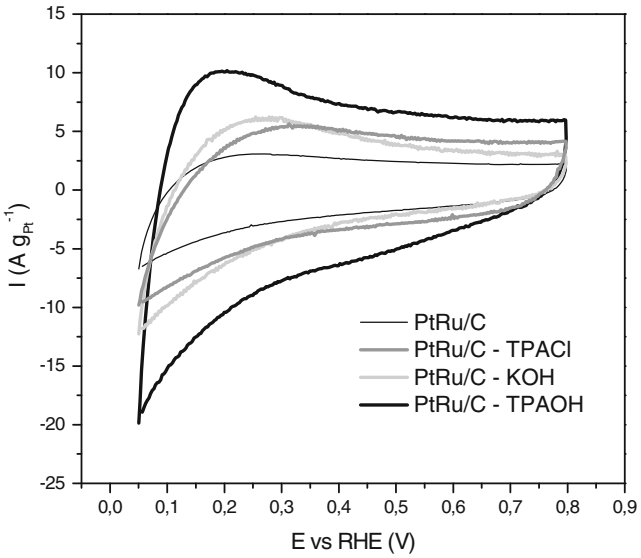

Fig. 5 Cyclic voltammograms of PtRu/carbon hybrid materials in 0.5 mol L^{-1} H_2SO_4 solution and scan rate of 10 mV s^{-1}

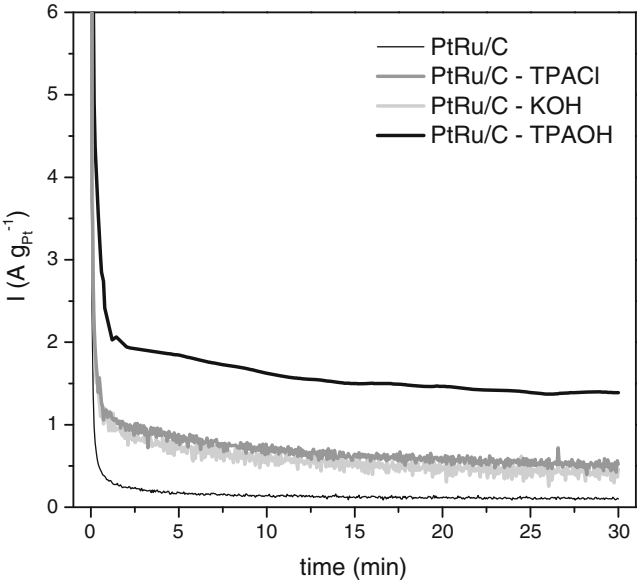

Fig. 6 Current–time curves at 0.5 V in 0.5 mol L^{-1} H_2SO_4+ 1.0 mol L^{-1} of methanol for PtRu/carbon hybrid materials

volume, the material PtRu/C (TPACl) has the larger particle size. PtRu/C (KOH) and PtRu/C (TPAOH) have similar particle sizes, but surface areas and total pore volumes are very different; the material prepared using TPAOH has the higher values of these parameters. Thus, a compromise between metal particle size and pore structure is essential to obtain a good catalytic activity for methanol electrooxidation. Materials with smaller particle sizes are normally more active due to the larger number of surface atoms [52]. Also, the electronic properties of the metal, the coordination number of the atoms, and the interaction nanoparticle support are affected by the particle size and can favor the catalytic properties of the materials [15, 53]. The pores' structure (mainly the presence of mesopores) influences the catalytic activity due the easier transport of reactants to the active sites [15, 54].

Conclusion

PtRu/carbon hybrid materials could be prepared by hydrothermal carbonization; however, the materials as-synthesized did not show activity for methanol electrooxidation probably due to the carbonaceous structure having low electrical conductivity and/or organic residues that block the active sites. After thermal treatment with argon at 900 °C, the materials become active for methanol electrooxidation, and the activity of these materials could be related to their pore structure and metal particle sizes, which are influenced by the synthesis conditions. The PtRu/carbon hybrid material prepared using TPAOH showed the best electroactivity for methanol electrooxidation. In addition, the study of parameters such as different metal precursors, weight percent of metals,

new carbon sources, and the use of different additives (surfactants) should be investigated in order to improve the catalytic activities of the obtained materials.

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