

Preparation of Ni/Carbon Hybrids by Hydrothermal Carbonization and Thermal Treatment for Application as Supports for PtRu/C Electrocatalysts

M. M. Tusi^{a,b}, N. S. O. Polanco^b, M. Brandalise^b, V. A. Ribeiro^b, O. V. Correa^b, J. C. Villalba^c, F. J. Anaissi^c, A. O. Neto^b and E. V. Spinace^b

^a Universidade Regional Integrada do Alto Uruguai e das Missões - URI,
97700-000 Santiago - RS, Brazil

^b Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN-SP,
05508-900 São Paulo - SP, Brazil

^c Universidade Estadual do Centro-Oeste - UNICENTRO,
85040-080 Guarapuava - PR, Brazil

Ni/Carbon hybrids were prepared by hydrothermal carbonization at 200 °C for 48 h using glucose as carbon source, NiCl₂.6H₂O as oxidizing agent and catalyst of the carbonization process. The materials were prepared in the absence and in the presence of cetyltrimethylammonium bromide (CTAB) using an CTAB:glucose molar ratios of 1:10. The obtained carbonaceous materials were further treated at 900 °C under Argon and PtRu nanoparticles were deposited on these materials using an alcohol reduction process. The resulting PtRu/C electrocatalysts were characterized by EDX, thermogravimetrics analysis, X-ray diffraction and transmission electron microscopy and they were tested for methanol electro-oxidation using chronoamperometry. The PtRu/C electrocatalyst prepared using as support Ni/Carbon with CTAB showed superior performance for methanol electro-oxidation.

Introduction

Direct Methanol Fuel Cells (DMFC) are promising power sources for portable applications (1). In these devices the alcohol is fed directly without any previous chemical modification and this characteristic avoids the problems associated to the use of hydrogen (1). Carbon-supported PtRu nanoparticles (PtRu/C electrocatalysts) has been considered the best electrocatalyst for methanol electro-oxidation (1). Studies have shown that the use of carbon nanotubes and mesoporous carbon as support increase the performance of the PtRu/C electrocatalysts, however, the synthesis of these supports are normally complex or involve harsh conditions (2-4). Recently, the synthesis of metal/carbon nanoarchitectures by a one-step and mild hydrothermal carbonization was reported using starch or glucose and metals salts (5,6). It has been shown that the use of surfactants i.e. cetyltrimethylammonium bromide (CTAB) in the preparation of nanostructured materials resulted in interesting properties (7-9). In this work, Ni/Carbon hybrids were prepared by hydrothermal carbonization in the absence and in the presence of CTAB and the obtained materials were used as supports to prepare PtRu/C electrocatalysts (Pt:Ru atomic ratio of 50:50 and metal loading equal 20 wt%), which were tested for methanol electro-oxidation.

Experimental

Ni/Carbon hybrids (10 wt% of nickel loading) were prepared by hydrothermal carbonization (5,6) using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Synth), glucose (Aldrich) and cetyltrimethylammonium bromide (CTAB – Fluka). An aqueous solution of glucose and CTAB (CTAB:glucose molar ratio of 1:10) was mixed with an amount of nickel salt. The pH of resulting mixture was adjusted using tetrapropylammonium hydroxide (TPAOH, 20 wt% in water) solution at about 11. Then, the obtained solution was put into a 55 mL Teflon-lined stainless steel autoclave and submitted to hydrothermal treatment at 200 °C for 48 h. The obtained solid was filtered, washed with ethanol and water and dried at 70 °C for 2 h. Afterwards, the material was treated under argon atmosphere at 900 °C for 3 h. The carbonization yield (wt%) was determined by the quotient between the experimental yield and the theoretical yield (considering a initial mass of carbon source equal 5 g).

PtRu/C electrocatalysts (20 wt% metal loading and Pt:Ru atomic ratio of 50:50) were prepared by an alcohol-reduction process (10) using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich) as metal sources and ethylene glycol (Merck) as solvent and reducing agent. The reductions were carried-out by successive reduction (the metals were reduced separately in two successive steps: first step the Ru and second step the Pt). In a typical procedure, the metal sources were dissolved in ethylene glycol/water (75/25, v/v) and the carbon support was added. The resulting mixtures were sonicated for 5 min and submitted to reflux for 2 h under open atmosphere. The mixtures were filtered and the solids washed with water and dried at 70 °C for 2 h.

The PtRu metal loading (wt%) was determined by thermogravimetric analysis (TGA) using a Shimadzu D-50 instrument and platinum pans. Heating rate of 5 °C min^{-1} was employed under dry oxygen (30 mL min^{-1}) (11).

The Pt:Ru atomic ratios were obtained by EDX analysis using a scanning electron microscope Phillips XL30 with a 20 kV electron beam and equipped with EDAX DX-4 microanalyser.

The X-ray diffraction analyses were performed using a Rigaku diffractometer model Miniflex II using Cu $K\alpha$ radiation source ($\lambda = 0.15406$ nm). The diffractograms were recorded from $2\theta = 15^\circ$ to 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 of 200 nanoparticles from micrographs using Image Tool Software.

Results and Discussion

Ni/Carbon hybrids were prepared by hydrothermal carbonization of glucose at 200 °C using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as catalyst for the carbonization process in the absence and presence of CTAB (Table I). The carbonization yield of the Ni/Carbon hybrids was 73 wt% for the material prepared in the absence of CTAB and 71 wt% for the material prepared using CTAB:glucose molar ratio of 1:10.

TABLE I. Carbonization yield, weight loss, metal loading and crystallite average size of Ni/Carbon hybrids prepared in absence and presence of CTAB.

CTAB:glucose molar ratio	Carbonization yield (wt%)	Weight lost (wt%)	Nickel loading (wt%)	Crystallite average size (nm)
0	73	53	8	11
1:10	71	54	5	13

The weight loss after the thermal treatment at 900 °C was about 55 wt% for both Ni/Carbon hybrids. The nickel load of the materials after thermal treatment at 900 °C was 8 wt% for the material prepared in the absence of CTAB and 5 wt% for the material using CTAB:glucose molar ratio of 1:10.

The X-ray diffraction of Ni/Carbon hybrids as-synthesized and thermally treated at 900 °C are shown in Figure 1.

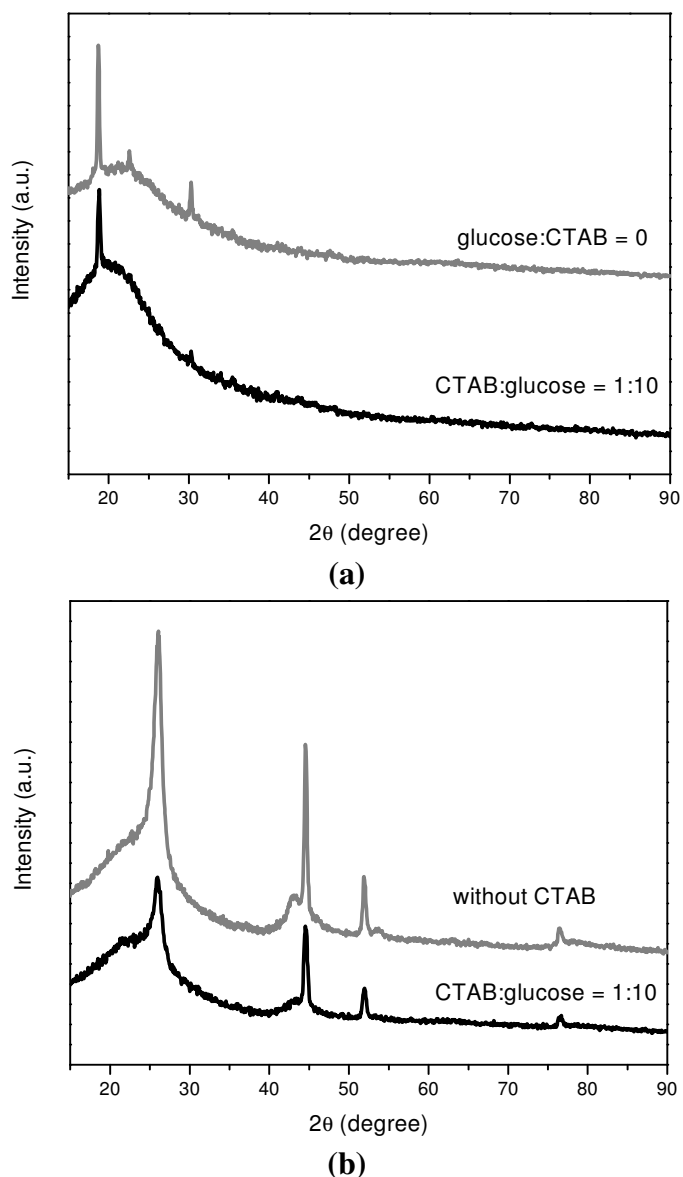


Figure 1. X-ray diffraction of Ni/Carbon hybrids (a) as-synthesized and (b) after thermal treatment at 900 °C.

The as-synthesized material showed a broad peak at about $2\theta = 23^\circ$ assigned to the amorphous carbon and three peaks at about $2\theta = 18^\circ$, 22° and 30° associated to β -NiOOH phase (12). After thermal treatment at 900°C three peaks were observed at $2\theta = 44^\circ$, 56° and 76° that were attributed to a face-centered cubic (fcc) structure of Ni (13). The broad peak at about $2\theta = 23^\circ$ was shifted to higher angle and four new peaks at about $2\theta = 26^\circ$, 43° , 54° and 78° were observed and associated to the (002), (100), (004) and (110) planes of graphitic framework (13), respectively. The average crystallite sizes calculated using the (220) reflections of Ni_{fcc} structure by Scherrer equation are in the range of 11-13 nm (Table 2).

TEM micrographs of Ni/Carbon hybrids obtained without CTAB (Figure 2a) and prepared with CTAB:glucose molar ratio of 1:10 (Figure 2b) by hydrothermal carbonization and after thermal treatment are shown in the Figure 2. In both materials it was observed the presence of amorphous carbon with graphitic domains. Sevilla et. al. (13) observed similar results by graphitization of porous carbon in the presence of metallic species.

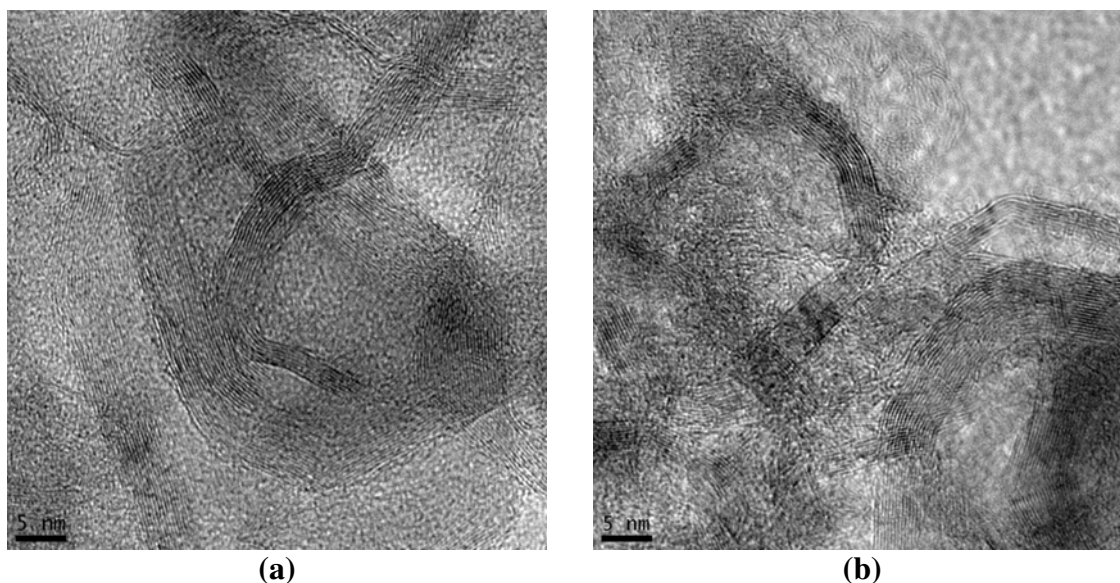


Figure 2. TEM images of Ni/Carbon hybrids after thermal treatment at 900°C .
(a) without CTAB and (b) CTAB:glucose = 1:10.

PtRu/C electrocatalysts were prepared by an alcohol-reduction process using Ni/Carbon as support (Table II).

TABLE II. Pt:Ru atomic ratio, metal loading, crystallite average size of PtRu/C electrocatalysts (50:50) and nominal metal loading of 20 wt% prepared by alcohol reduction process.

CTAB:glucose molar ratio	Pt:Ru atomic ratio EDX	Metal loading (%)	Crystallite average size (nm)
0	41:59	13	2
1:10	37:63	10	3

In the preparation of the PtRu/C electrocatalysts by successive reduction (first step - deposition of Ru), after the separation of the obtained Ru/C electrocatalysts by filtration, it was observed the presence of Ni⁺² species in the filtrates using dimethylglyoxime (14), however, at the end of the second step (deposition of Pt), no Ni⁺² species were detected in the filtrates. The EDX analysis of the obtained PtRu/C electrocatalysts showed that only

traces of Ni remain in the obtained materials. This suggest that in the first step of the preparation that Ni nanoparticles were oxidized to Ni^{+2} species, which were soluble in the reaction media, while Ru ions were reduced and supported on the carbon. The Pt:Ru atomic ratios obtained by EDX for both PtRu/C electrocatalysts were similar to the nominal ones, on the other hand, the obtained metal loading were only 50% of the nominal metal loading (Table 2) showing that not all of the nanoparticles formed were deposited on the carbon supports. This could be attributed to metal nanoparticles and the carbon supports having similar surface charges, which result in a repulsive force between them, making it difficult to deposit all metal nanoparticles on the carbon supports (15).

The Figure 3 presents the X-ray diffraction of PtRu/C electrocatalysts prepared by an alcohol reduction process using Ni/Carbon hybrids as supports.

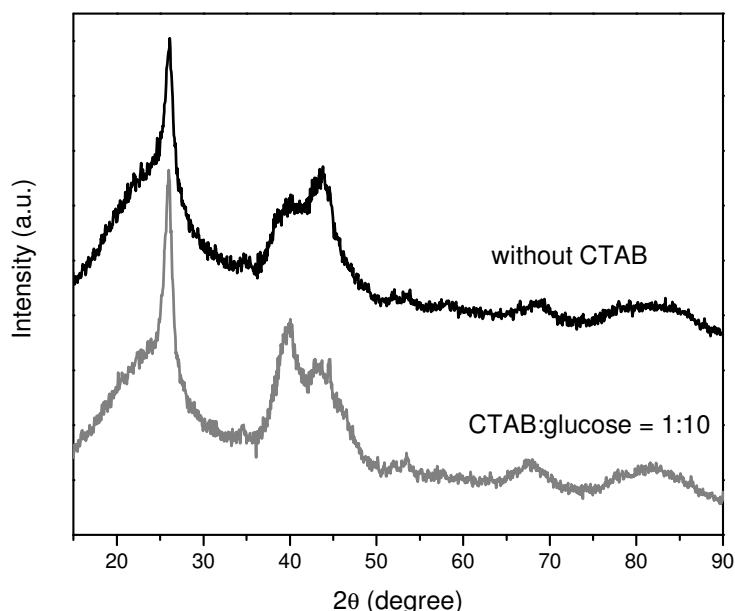


Figure 3. X-ray diffraction of PtRu/C electrocatalysts prepared by alcohol reduction method using Ni/Carbon hybrids as supports.

The X-ray diffractograms of PtRu/C electrocatalysts prepared using Ni/Carbon as supports showed a broad peak at about $2\theta = 23^\circ$ attributed to the amorphous carbon and four peaks at about $2\theta = 26^\circ, 43^\circ, 54^\circ$ and 78° assigned to the planes of the graphitic framework (13). Four peaks were observed at about $2\theta = 40^\circ, 47^\circ, 67^\circ$ and 82° associated to the (111), (200), (220) and (311) planes, respectively, of the face-centered cubic (fcc) structure of platinum and platinum alloys (1,10). It was also observed a peak at about $2\theta = 44^\circ$ which could be attributed a metallic ruthenium or materials rich in Ru with hexagonal structure (16). The (220) reflection of Pt_{fcc} structure were used to calculate the average crystallite size according to Scherrer equation and the calculated values are in the range of 2-3 nm (Table 2).

The Figure 4 show TEM micrographs and histograms of particle size distribution of PtRu/C electrocatalysts. For both electrocatalysts it was observed a good distribution of the nanoparticles on the carbon supports and the histograms showed a broad distribution of the nanoparticle sizes and average particle sizes of about 4 nm.

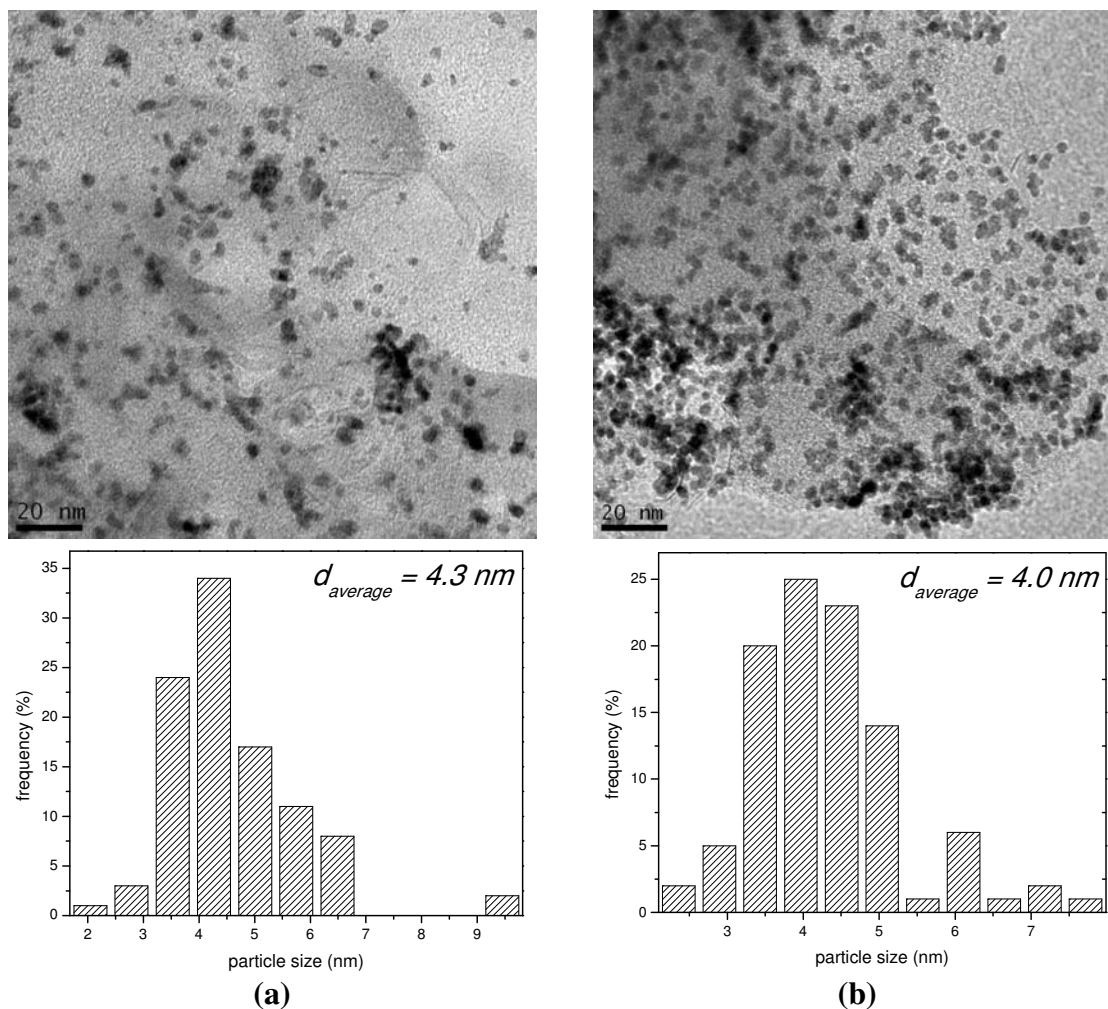


Figure 4. TEM micrographs and histograms of particle size distribution of PtRu/C electrocatalysts prepared by alcohol-reduction process using the Ni/Carbon hybrids: (a) without CTAB and (b) CTAB:glucose = 1:10.

The chronoamperometry experiments were carried out to examine the performance and stability of the PtRu/C electrocatalysts (Fig. 5). The PtRu/C electrocatalyst prepared using the Ni/C support with CTAB:glucose molar ratio of 1:10 showed superior performance for methanol electro-oxidation. The superior activity of the material prepared using CTAB probably could be attributed the formation of a carbon structure with increased surface area and/or pore volume. It has been showed that CTAB could act as structure-directing agent in the preparation of metal-carbon hybrids by hydrothermal carbonization (17,18) as well, modifying the morphology and pore size distribution of carbon xerogels (19).

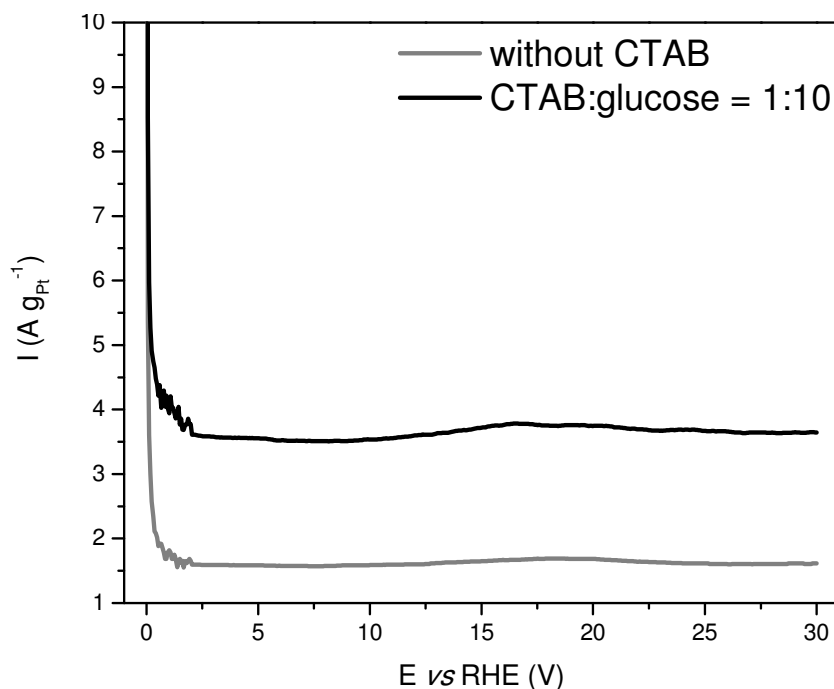


Figure 5. Current-time curves at 0.5 V in 0.5 mol L⁻¹ H₂SO₄ solution containing 1.0 mol L⁻¹ of methanol for PtRu/C electrocatalysts

Conclusions

The hydrothermal carbonization is a promising method to prepare carbonaceous materials for application as supports to prepare PtRu/C electrocatalysts. The X-ray diffraction of Ni/Carbon hybrids as-synthesized presented peaks associated to amorphous carbon and β -NiOOH while the material thermally treated at 900 °C presented peaks associated to nickel (fcc) phase and amorphous carbon with graphitic domains. The PtRu/C electrocatalyst prepared using as support Ni/Carbon with CTAB showed superior performance for methanol electro-oxidation. Further work is necessary to investigate the surface area and porosity of these materials to find better explanations.

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