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J. Mater. Sci. Technol., 2013, 29(8), 747–751

JMST

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Ni/Carbon Hybrid Prepared by Hydrothermal Carbonization and Thermal Treatment as Support for PtRu Nanoparticles for Direct Methanol Fuel Cell

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[Manuscript received August 17, 2012, in revised form December 21, 2012, Available online 22 May 2013]

Ni/Carbon was prepared in two steps: initially cellulose as carbon source and $NiCl_2 \cdot 6H_2O$ as catalyst of the carbonization process were submitted to hydrothermal treatment at 200 °C and further to thermal treatment at 900 °C under argon atmosphere. The obtained material contains Ni nanoparticles with face-centered cubic (fcc) structure dispersed on amorphous carbon with graphitic domains. PtRu/C electrocatalysts (carbon-supported PtRu nanoparticles) were prepared by an alcohol-reduction process using Ni/Carbon as support. The materials were characterized by thermogravimetric analysis, energy-dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscopy and tested as anodes in single direct methanol fuel cell (DMFC). The performances of PtRu/C electrocatalysts using Ni/Carbon as support were superior to those obtained for PtRu/C using commercial carbon black Vulcan XC72 as support.

KEY WORDS: Cellulose; Hydrothermal carbonization; Alcohol-reduction process; PtRu/C electrocatalysts; Direct methanol fuel cell

1. Introduction

Due to the problems of production, storage and delivery associated to the hydrogen, the fuel cells employing alcohols as fuel have been considered promising power sources for portable applications[1–5]. Among the alcohols, the methanol has been considered the most promising, because it is more efficiently oxidized than other alcohols due to its low molecular complexity. The better results for the electro-oxidation of methanol have been reached using PtRu/C electrocatalyst (carbon-supported PtRu nanoparticles), whose activity is strongly dependent on the method of preparation and carbon support used[5–7].

Studies show that the use of different carbon supports like nanotubes[8], nanofibers[9], nanocoils[10], mesoporous carbons[11] and other carbons nanostructured[6,7] could improve the performance of PtRu/C electrocatalysts for methanol electro-oxidation. However, the synthesis of these supports generally involves complex steps and/or harsh conditions[10]. Recently, a direct route of synthesis of metal/carbon hybrids was reported involved with the hydrothermal carbonization of saccharides at low temperatures (<250 °C) yielding carbonaceous materials with interesting morphologies and porosity[2,12–16]. The carbonaceous materials produced by hydrothermal carbonization have potential for applications in fields such as environment, catalysis, energy storage, biology and sensors[16].

Kim et al.[14] prepared amorphous and graphitic spherical carbons from sucrose by hydrothermal carbonization and thermal treatment at 900 °C. To obtain graphitic spherical carbon, it was necessary to add $FeNO_3 \cdot 6H_2O$ in the hydrothermal carbonization step. Further, after thermal treatment, the Fe species were removed from the carbon. PtRu/C electrocatalysts were prepared by borohydride reduction using the resultant amorphous and graphitic spherical carbons as supports. The methanol oxidation study by cyclic voltammetry revealed that the PtRu/C electrocatalysts prepared using the amorphous spherical carbon as support had lower electroactivity than the PtRu/C electrocatalyst using carbon black Vulcan XC72. On the other hand, the PtRu/C electrocatalyst prepared using the graphitic spherical carbon as support exhibited 1.3 times higher catalytic performance than the

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http://dx.doi.org/10.1016/j.jmst.2013.05.004

PtRu/Vulcan. Sevilla et al.[15] prepared carbon spherules by hydrothermal carbonization of different saccharides. The obtained materials were impregnated with Ni(II) ions and they were treated at 900 °C under nitrogen atmosphere resulting in highly graphitic carbon nanocoils. After this, the nickel nanoparticles formed during the graphitization step were removed using acid and the amorphous carbon phase was also removed with an oxidizing mixture. The obtained materials were used as support of commercial PtRu nanoparticles and they were evaluated for methanol oxidation by electrochemical experiments. It was found that the carbon nanocoils supporting PtRu nanoparticles exhibited an activity greater than that of conventional carbon support Vulcan XC72.

In this work, Ni/Carbon hybrid was prepared by hydrothermal carbonization of cellulose and $NiCl_2 \cdot 6H_2O$ and by thermal treatment at 900 °C. The resulting Ni/Carbon material was used without further treatment as support to prepare PtRu/C electrocatalysts by alcohol-reduction process. The obtained PtRu/C electrocatalyst was characterized and tested as anode in single direct methanol fuel cell (DMFC).

2. Experimental

Ni/Carbon material (10 wt% of nickel loading) was prepared by hydrothermal carbonization[2,12−16] using $NiCl_2 \cdot 6H_2O$ (Synth), cellulose (Aldrich) and cetyltrimethylammonium bromide (CTAB, Fluka). An aqueous solution of cellulose and CTAB was mixed with an amount of nickel salt (cellulose:Ni molar ratio of 18.4 and CTAB:Ni molar ratio of 3). The pH of the mixture was adjusted using tetrapropylammonium hydroxide (TPAOH, 20 wt% in water) solution at about 11. Then, the obtained solution was putted 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. The material was then 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 an initial mass of carbon source of 5 g).

PtRu/C electrocatalysts (20 wt% metal loading and Pt:Ru atomic ratio of 50:50) were prepared by an alcohol-reduction process[17,18] using $H_2PtCl_6 \cdot 6H_2O$ (Aldrich) and $RuCl_3 \cdot xH_2O$ (Aldrich) as metal sources and ethylene glycol (Merck) as solvent and reducing agent. In a typical procedure, the metal sources were dissolved in ethylene glycol/water (75/25, v/v) and the carbon support was added. The mixtures were sonicated for 5 min and submitted to reflux for 2 h under open atmosphere. The mixtures were filtered and the solids were washed with water and dried at 70 °C for 2 h.

The Pt:Ru atomic ratios were obtained by energy-dispersed analysis of X-rays (EDX) using a scanning electron microscope (Phillips XL30) with a 20 kV electron beam equipped with EDX DX-4 microanaliser.

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})[2,19].

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Thermo Nicolet Nexus 4000 Advanced in the wavenumber range of 800−3700 cm^{-1}. 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 (KBr) at an approximate ratio of 1/500, the pellet mass being about 500 mg. The mixture was pressed and during pressing the system was evacuated with an oil pump.

The X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II with Cu$K\alpha$ radiation source ($\lambda = 0.15406$ nm). The diffractions were recorded from $2\theta = 20°$ 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 200 nanoparticles from micrographs using Image Tool Software.

The membrane electrode assemblies (MEA) were prepared by hot pressing a pretreated Nafion® 117 membrane placed between a PtRu/C anode (0.5 mg_{Pt} cm^{-2} catalyst loading) and a 20 wt% Pt/C E-TEK cathode (1 mg_{Pt} cm^{-2} catalyst loading) at 125 °C for 3 min under a pressure of 2205 (N cm^{-2}). It was used carbon cloth (ElectroChem) with 35 wt% of PTFE as gas diffusion layer. The direct ethanol fuel cell performances were determined in a single cell with an area of 5 cm^2. The temperature was set to 100 °C for the fuel cell and 85 °C for the oxygen humidifier. The fuel was a 2 mol L^{-1} methanol solution delivery at 2 mL min^{-1} and the oxygen flow was regulated at 500 mL min^{-1} and pressure of 0.2 MPa. Polarization curves were obtained by using an Electrocell electronic load.

3. Results and Discussion

Ni/Carbon material was prepared by hydrothermal carbonization of cellulose at 200 °C using $NiCl_2 \cdot 6H_2O$ as catalyst for the carbonization process. The as-synthesized Ni/Carbon material reached a carbonization yield of 55 wt% after thermal treatment at 900 °C and a weight loss of 62 wt% was observed. The Ni/Carbon material contained 6 wt% of Ni as determined by TGA analysis.

The FTIR spectra of the thermally treated Ni/Carbon and the commercial carbon black Vulcan XC72 are shown in Fig. 1. The FTIR spectrum of Vulcan XC72 showed the functional groups around 1000−1300 cm^{-1} attributed to C−OH stretching and OH bending vibrations at around 3400 cm^{-1}. It was also observed

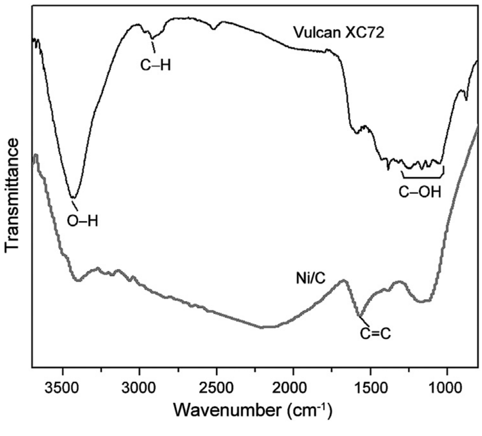

Fig. 1 FTIR spectra of Ni/Carbon support prepared by hydrothermal carbonization and thermal treatment and Vulcan XC72 support.

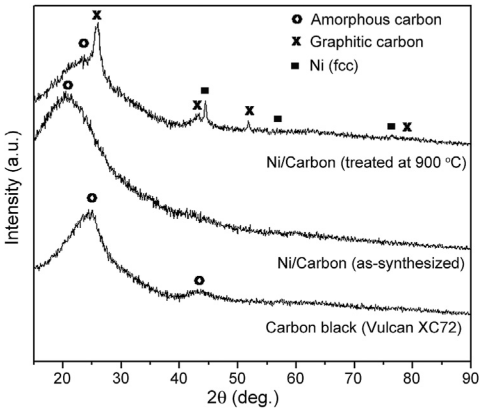

Fig. 2 XRD patterns of Ni/Carbon support prepared by hydrothermal carbonization and thermal treatment and Vulcan XC72 support.

that at around 2950 cm^{-1} υ_s(C−H) and υ_{as}(C−H), there are vibrations of methyl and methylene groups[13,20]. For Ni/Carbon material, it was observed that an increase of the band is at 1580 cm^{-1} associated to υ(C═C) of aromatic ring and a decrease of OH bending vibrations.

The XRD patterns of the Ni/Carbon (as-synthesized and after thermal treatment) are shown in Fig. 2. For comparison, the XRD patterns of carbon black Vulcan XC72 are also shown in Fig. 2. The as-synthesized Ni/Carbon material showed only a broad peak at about $2\theta = 23^\circ$ assigned to the amorphous carbon. After thermal treatment at 900 °C, three peaks are observed at around $2\theta = 44^\circ$, 56° and 76°, which were attributed to a face-centered cubic (fcc) structure of Ni[21]. Also, the broad peak at about $2\theta = 23^\circ$ 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[21], respectively. The XRD patterns of carbon Vulcan XC72 only showed broad peaks at about $2\theta = 25^\circ$ and 44° assigned to the amorphous carbon.

TEM micrographs of Ni/Carbon prepared by hydrothermal carbonization and thermal treatment are shown in Fig. 3(a and b). It is possible to observe the presence of Ni nanoparticles dispersed on amorphous carbon with graphitic domains (Fig. 3(a)). Similar results were observed by Sevilla and Fuertes[21] by graphitization of porous carbon in presence of metal species. Fig. 3(b) highlights the presence of graphitic domains in Ni/Carbon material.

Table 1 Pt:Ru atomic ratios, metal loading and average crystallite size of PtRu/C electrocatalysts (20 wt% PtRu loading and Pt:Ru atomic ratio of 50:50)

Support	Pt:Ru atomic ratio (EDX)	Pt:Ru:Ni atomic ratio (EDX)	Metal loading (wt%)	Crystallite size (nm)
Ni/Carbon	49:51	48:45:7	27	<2
Vulcan XC72	50:50	−	20	2

PtRu/C electrocatalysts were prepared by the alcohol-reduction process using Ni/Carbon and commercial carbon black Vulcan XC72 as supports (Table 1). In the preparation of the PtRu/C electrocatalyst using Ni/Carbon as support, the presence of Ni(II) species was observed in the filtrate using dimethylglyoxime[22] after the separation of the obtained PtRu/C electrocatalysts by filtration. This suggests that Ni(0) nanoparticles were oxidized to Ni(II) species while Pt(IV) and Ru(III) ions were reduced and supported on the carbon, which probably occurred by galvanic exchange reaction[23]. We have already observed that in the preparation of PtRuNi/C electrocatalysts by an alcohol-reduction process[18]. The reduction and incorporation of Ni(II) ions in the fcc-structure of Pt occurred if the pH of the reaction medium was above 9; however, in the used conditions, the pH of the reaction medium was in the range of 2−3.

Considering all Ni (6 wt%) remained in the obtained PtRu/C electrocatalyst, a Pt:Ru:Ni atomic ratio should be 31:31:38, however, the Pt:Ru:Ni atomic ratio obtained by EDX analysis was 48:45:7, showing that only a small quantity of Ni remained in obtained material (Table 1). It shows that the major part of Ni(0) nanoparticles were oxidized to the soluble Ni(II) species that remained in the reaction medium. This was also confirmed considering that the obtained Pt:Ru atomic ratio (49:51) was very similar to the nominal value (50:50). Moreover, considering that all Ni(0) nanoparticles (6 wt%: obtained by TGA analysis;

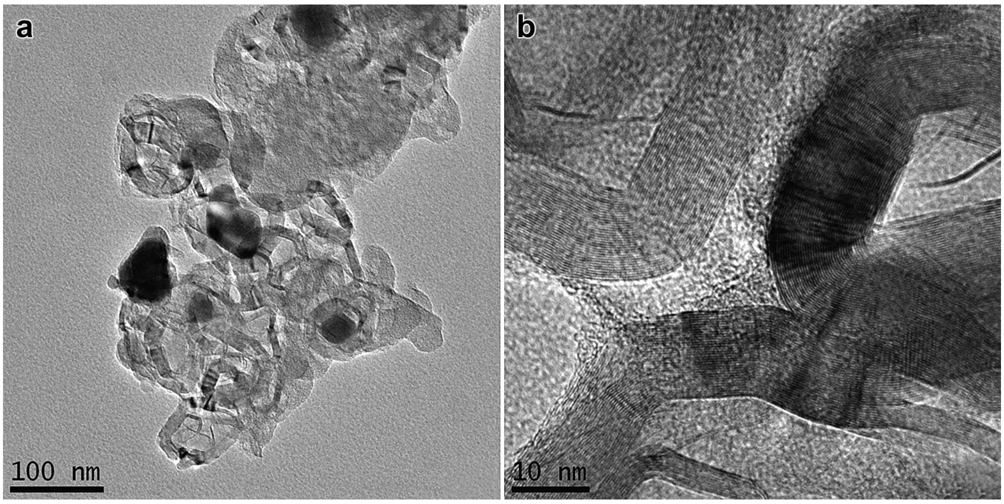

Fig. 3 TEM micrographs of Ni/Carbon support prepared by hydrothermal carbonization and thermal treatment: (a) overview, (b) graphitic domains.

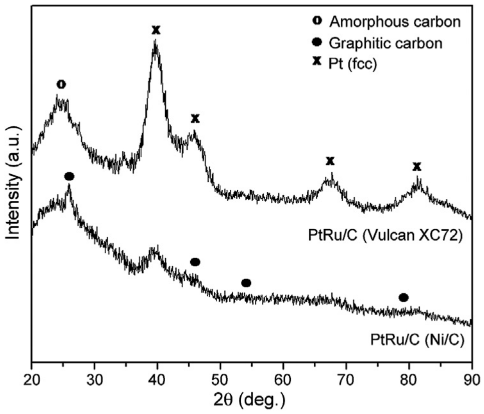

Fig. 4 XRD patterns of PtRu/C electrocatalysts prepared by alcohol-reduction process.

“0 wt%:”, nominal value used in the synthesis) were removed from Ni/Carbon support during the preparation of the PtRu/C electrocatalyst (20 wt% of PtRu and 80 wt% of Ni/Carbon support), the expected PtRu loading (wt%) would be in the range of 21 wt% (6 wt% of Ni) and 28.5 wt% (10 wt% of Ni), while the obtained value by TGA analysis was 27 wt% (Table 1). For the PtRu/C electrocatalyst prepared using commercial Vulcan XC72 as support, the obtained value was very similar to the nominal value (20 wt%).

The XRD patterns of PtRu/C electrocatalysts are shown in Fig. 4. PtRu/C electrocatalyst prepared using Vulcan XC72 as support showed a broad peak at about $2\theta = 25°$ attributed to the amorphous carbon phase and four peaks at about $2\theta = 40°$, 47°, 67° and 82° associated to the (111), (200), (220) and (311) planes, respectively, of the face-centered cubic (fcc) of platinum and platinum alloys[2,17,18]. The (220) reflection of Pt fcc-structure was used to calculate the average crystallite size according to Scherrer equation and the calculated value was around 2 nm (Table 1). The XRD patterns of PtRu/C electrocatalysts prepared using Ni/Carbon as support showed a broad peak at about $2\theta = 23°$ attributed to the amorphous carbon and four peaks at about $2\theta = 26°$, 43°, 54° and 78° assigned to the planes of the graphitic framework[21]. The peaks of Pt fcc-structure were also observed in the diffractogram, however, they were broader than the ones observed in the diffractogram of the PtRu/C electrocatalyst prepared using Vulcan XC72, indicating a small value (<2 nm) of average crystallite size. No peaks of Ni fcc-structure and/or ruthenium oxide phases were observed in the diffractogram[2,24,25].

TEM micrographs and histograms of particle size distribution of the PtRu/C electrocatalysts are shown in Fig. 5. For both electrocatalysts, a good distribution of the nanoparticles on the carbon supports was observed. The histograms showed a broad distribution of the nanoparticle sizes and average nanoparticle sizes of 3.6 nm and 4.4 nm for the PtRu/C electrocatalysts prepared using Ni/Carbon and Vulcan XC72, respectively.

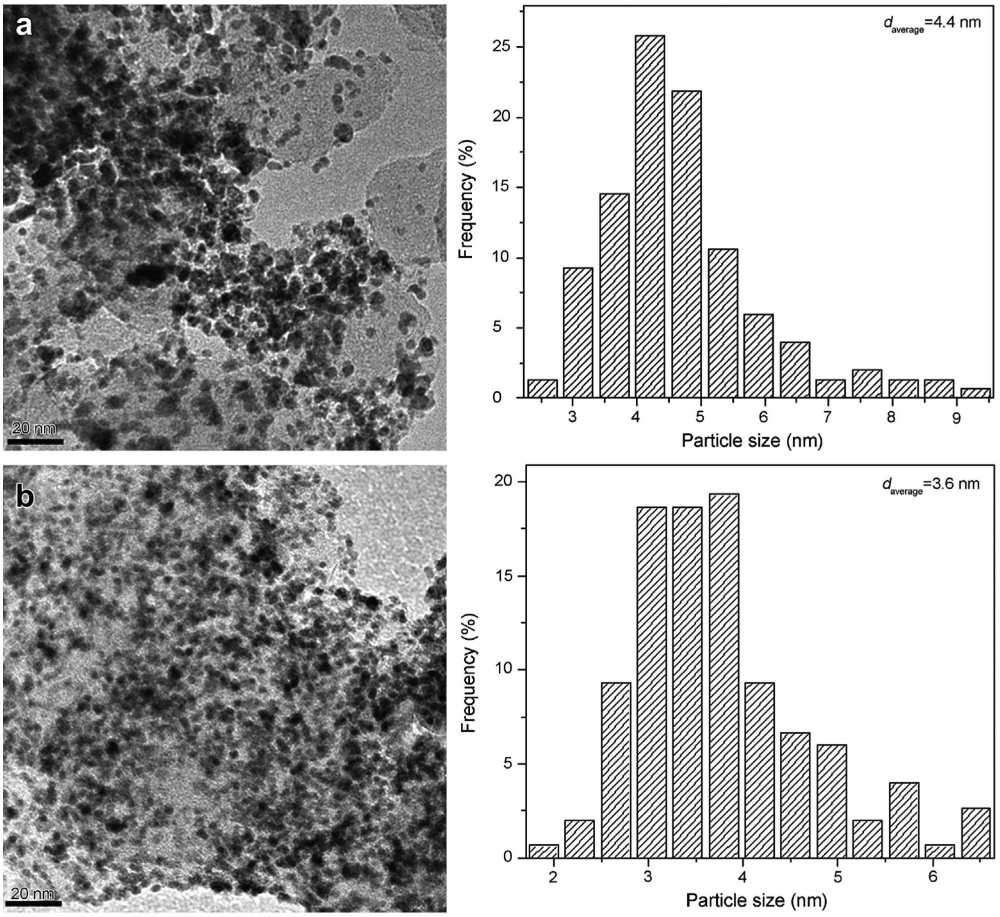

Fig. 5 TEM micrographs and histograms of particle size distribution of PtRu/C electrocatalysts prepared by alcohol-reduction process: (a) Vulcan XC72 as support, (b) Ni/Carbon as support.

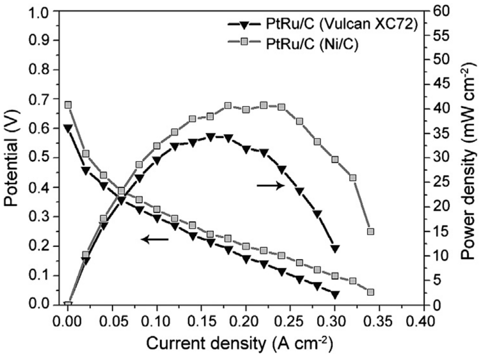

Fig. 6 *I−V* curves of a 5 cm^2 DMFC and the power density at 100 °C using PtRu/C electrocatalysts prepared by alcohol-reduction process in the anode (1 mg$_{Pt}$ cm^{-2} catalyst loading) and Pt/C E-TEK electrocatalyst in the cathode (1 mg$_{Pt}$ cm^{-2} catalyst loading), Nafion® 117 membrane, methanol (2.0 mol L^{-1}), oxygen pressure (0.2 MPa).

Fig. 6 shows the performances of single DMFC with PtRu/C electrocatalysts prepared using Ni/Carbon and Vulcan XC72 as anode. The open circuit voltage of the fuel cell containing PtRu/C electrocatalyst prepared using Vulcan XC72 was 0.60 V, while the corresponding value for PtRu/C electrocatalyst prepared using Ni/Carbon increases to 0.68 V. The maximum power density of PtRu/C electrocatalyst prepared using Ni/Carbon (41 mW cm^{-2}) was greater than that of PtRu/C electrocatalyst prepared using Vulcan XC72 (34 mW cm^{-2}).

The enhancement of the performance of the PtRu/C electrocatalysts for methanol electro-oxidation has been attributed to some characteristics of the carbon supports like a good combination of electrical conductivity from their graphitic structure[14,15] and an increased surface area and/or pore volume that could contribute to the access of the reagents minimizing the diffusional resistance[15,26]. In the present investigation we have used CTAB in the preparation of the Ni/Carbon. CTAB could act as structure-directing agent in the preparation of metal/carbon hybrids by hydrothermal carbonization[27,28] and modify the morphology and pore size distribution of carbon xerogels[29]. Thus, the good performance of Ni/Carbon as support for PtRu/C electrocatalyst could be a combination of its electrical and/or structural characteristics.

4. Conclusion

Ni/Carbon material prepared by hydrothermal carbonization and thermal treatment showed Ni nanoparticles with fcc-structure dispersed on amorphous carbon with graphitic domains. In the preparation of PtRu/C electrocatalyst by an alcohol-reduction process using Ni/Carbon as support, the Ni(0) nanoparticles were oxidized to Ni(II) species that are soluble in the reaction medium; while Pt(IV) and Ru(III) ions were reduced and supported on the carbon phase. The obtained PtRu/C anode electrocatalysts showed superior performance for DMFC compared to the PtRu/C electrocatalyst prepared with a conventional Vulcan XC72 carbon.

Acknowledgments

The authors thank CNPq, FAPESP and FINEP-MCT-ProH$_2$ for financial support. Laboratório de Microscopia do Centro de Ciências e Tecnologia de Materiais − CCTM/IPEN for TEM measurements and Dr. Marcelo Linardi for CCCH/IPEN facilities.

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