

Preparation of PtRu/C Anode Electrocatalysts using NaBH₄ as Reducing Agent and OH⁻ ions as Stabilizing Agent

E.V. Spinacé, L. A. Indelicato do Vale, A. Oliveira Neto and M. Linardi

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

PtRu/C electrocatalysts were prepared using NaBH₄ as reducing agent and OH⁻ ions as stabilizing agent. The electrocatalysts were characterized by EDX, XRD, TEM and cyclic voltammetry. The electro-oxidation of methanol was studied by cyclic voltammetry using the thin porous coating. Active PtRu/C electrocatalysts for methanol oxidation could be prepared by a simple methodology.

Introduction

A Direct Alcohol Fuel Cell (DAFC) is a device in which the alcohol is fed directly into the fuel cell without any previous chemical modification and is oxidized at the anode, while oxygen is reduced to water at the cathode. Thus, DAFC are very attractive as power sources for mobile and portable applications because it is not necessary to convert the fuel into hydrogen in a reformer. However, alcohols are very difficult to electro-oxidize completely and up to now methanol has been considered the most promising organic fuel because it is more efficiently oxidized than other alcohols (1-4). PtRu/C electrocatalysts have good activity as anode in direct methanol fuel cell. The synthesis of highly dispersed supported platinum-ruthenium nanoparticles with high loadings still remains a challenge (5). The conventional methods for synthesis of PtRu/C electrocatalysts are impregnation and colloidal methods. The impregnation method usually leads to large average particle size and broad size distribution, while colloidal methods produce ultrafine particles homogeneously distributed on the support, but the synthesis are normally very complex (5). In this work, PtRu/C electrocatalysts were prepared using NaBH₄ as reducing agent and OH⁻ ions as stabilizing agent. The PtRu/C electrocatalysts were tested for methanol oxidation using cyclic voltammetry aiming fuel cell application.

Experimental

PtRu/C electrocatalysts (20 wt%) with Pt:Ru atomic ratio of 50:50 were prepared using H₂PtCl₆.6H₂O (Aldrich) and RuCl₃.xH₂O (Aldrich) as metal sources and Carbon Vulcan XC72R as support. Carbon support was suspended in an aqueous solution containing the Pt(IV) and Ru(III) ions and an aqueous solution of sodium borohydride was added dropwise with stirring at room temperature. The suspension was filtered to recover the solid product and it was washed with water and dried at 70°C for 2h. The electrocatalyst prepared in the presence of OH⁻ ions as stabilizing agent KOH was added in the reaction medium with OH⁻/PtRu molar ratio of 8. XRD analyses were performed using a Rigaku diffractometer model Multiflex with a Cu K_α radiation source. The mean

particle sizes were calculated using Scherrer equation (6). 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 (1024x1024 pixels, 8 bits) using the AnalySis software. The particle size distributions were determined by measuring the nanoparticles from micrographs using Image Tool Software. 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 microanalyser. Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique (7). The working electrode was constructed using PTFE cylinder with a cavity 0.15 mm deep and 0.36 cm² 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 with Microquimica software. Cyclic Voltammetry was performed in a 0.5 mol L⁻¹ H₂SO₄ solution saturated with N₂. The evaluation of ethanol oxidation was performed at 25°C using 1.0 mol L⁻¹ solution. For comparative purposes a commercial carbon supported PtRu catalyst from E-TEK (20 wt%, Pt:Ru molar ratio 50:50, Lot # 3028401) was used.

Results and Discussion

The EDX analysis showed that Pt:Ru atomic ratios of the prepared electrocatalysts were very similar to the nominal values. The X-ray diffractograms of PtRu/C electrocatalysts are shown in Figure 1. In all diffractograms a broad peak at about 25° was associated with the Vulcan XC72 support material. The PtRu/C electrocatalysts showed peaks at approximately $2\theta = 40^\circ$, 47° , 67° and 82° , which are associated with the (111), (200), (220) and (311) planes, respectively, of the fcc structure characteristic of platinum and platinum alloys. No peaks corresponding to a metallic ruthenium, materials rich in ruthenium with hexagonal structure or ruthenium oxide phase were observed (7,8).

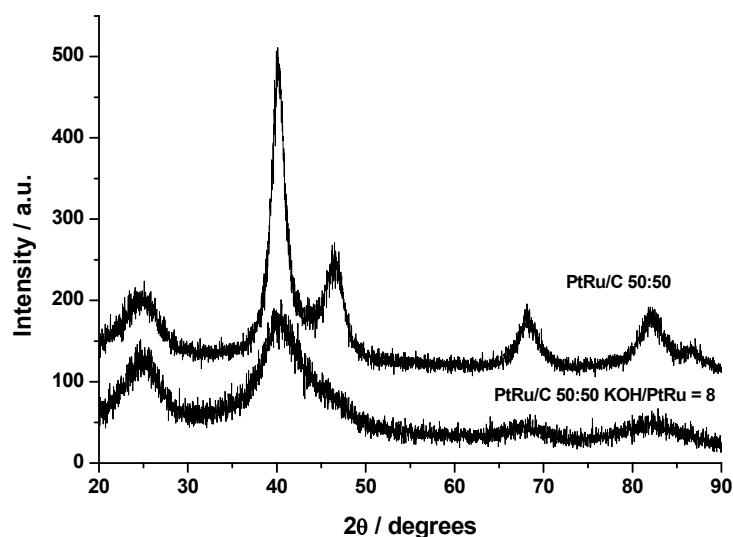
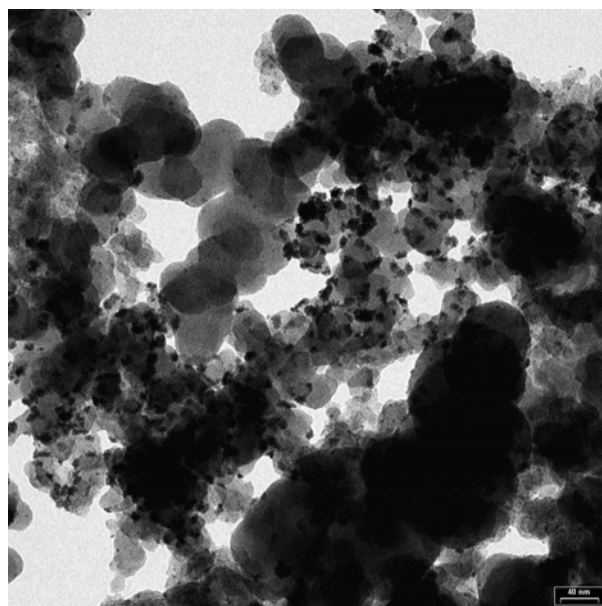
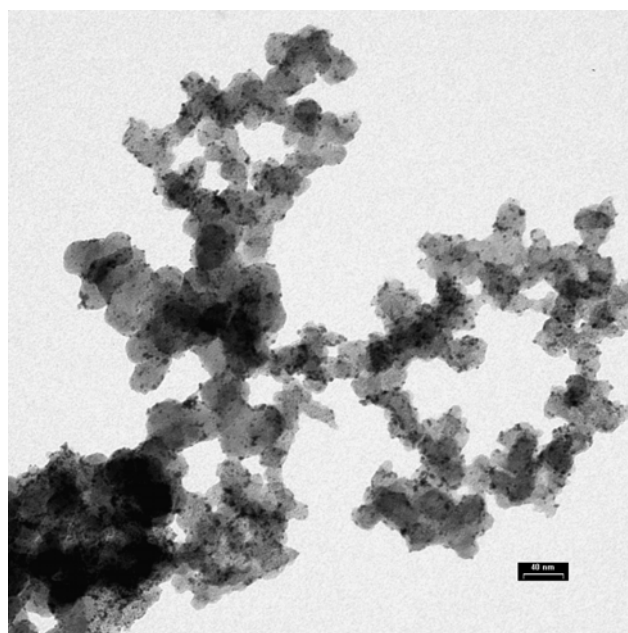


Figure 1. X-ray diffractograms of PtRu/C electrocatalysts.

The mean particle size calculated from XRD data of the PtRu/C electrocatalyst prepared in the absence of OH⁻ ions was 5 nm. For PtRu/C electrocatalyst prepared in the presence of OH⁻ ions the particle size decreased to 2.5 nm, which could be attributed to the electrostatic stabilization of PtRu nanoparticles by the adsorbed OH⁻ ions (9). TEM micrographs of PtRu/C electrocatalysts are shown in Figure 2. PtRu/C electrocatalyst prepared in absence of OH⁻ ions has not shown a good distribution of the nanoparticles on the carbon support with particle sizes in the range of 8 ± 3 nm. PtRu/C electrocatalyst prepared in the presence of OH⁻ ions showed a good distribution of the nanoparticles on the carbon support with particle sizes in the range of 3 ± 1 nm.



a)



b)

Figure 2. TEM micrographs **a)** PtRu/C electrocatalyst and **b)** PtRu/C electrocatalyst OH⁻/PtRu = 8. Scale bar corresponds to 40 nm.

The cyclic voltammograms of PtRu/C electrocatalysts were shown in Figure 3. Both electrocatalysts do not have a well-defined hydrogen adsorption-desorption region (0 – 0.4V), while the electrocatalyst prepared in the presence of OH⁻ ions showed high current values in the double layer region (0.4 – 0.8 V), which may be attributed to the presence of ruthenium oxide species that are very important to methanol oxidation at low potentials (10).

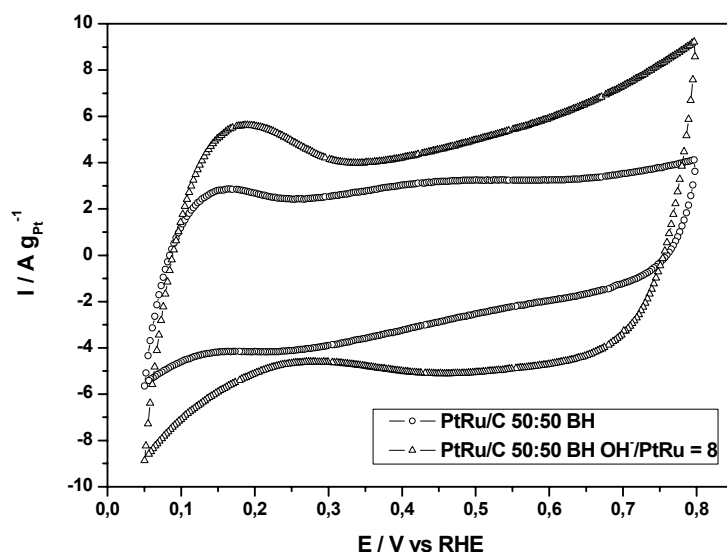


Figure 3. Cyclic voltammograms of PtRu/C electrocatalysts in 0.5 mol L⁻¹ H₂SO₄ with a sweep rate of 10 mV s⁻¹.

The PtRu/C electrocatalysts performances in methanol oxidation are shown in Figure 4.

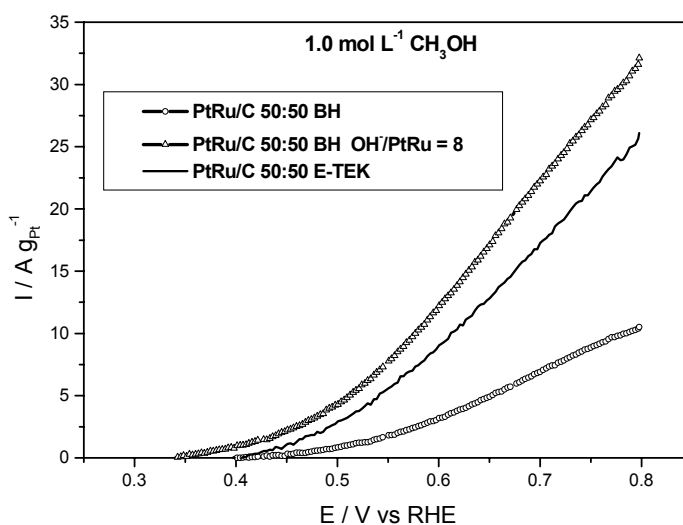


Figure 4. Cyclic voltammograms of PtRu/C electrocatalysts in 0.5 mol L⁻¹ H₂SO₄ and 1.0 mol L⁻¹ of methanol with a sweep rate of 10 mV s⁻¹, considering only the anodic sweep.

The anodic cyclic voltammetry responses were plotted after subtracting the background currents (11) and the currents values were normalized per gram of platinum, considering that methanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature (12). The electro-oxidation of methanol started at approximately 0.4 V for PtRu/C electrocatalyst prepared in the absence of OH⁻ ions while for PtRu/C electrocatalyst prepared in the presence of OH⁻ ions it started at 0.35 V, which could be attributed to the presence of ruthenium oxide species in this material. For methanol electro-oxidation PtRu/C electrocatalyst prepared in the absence of OH⁻ ions showed a inferior performance to that of a commercial PtRu/C electrocatalyst from E-TEK, while PtRu/C electrocatalyst prepared in the presence of OH⁻ ions showed a superior performance

Conclusions

Active PtRu/C electrocatalysts for methanol oxidation could be prepared by a simple methodology using NaBH₄ as reducing agent and OH⁻ ions as stabilizing agent. The X-ray diffractograms of the PtRu/C electrocatalysts showed the typical fcc structure of platinum and platinum alloys. PtRu/C electrocatalyst prepared in the presence of OH⁻ ions showed smaller particle sizes and better distribution on the carbon support than PtRu/C electrocatalyst prepared in the absence of OH⁻ ions. The electrochemical studies at ambient temperature showed that PtRu/C electrocatalyst prepared in the presence of OH⁻ ions was more active than the catalyst prepared in the absence of OH⁻ ions in the potential range of interest for direct methanol fuel cell (0.2-0.6V). Further work is necessary to investigate these electrocatalysts in gas diffusion electrodes for tests in single direct methanol fuel cell.

Acknowledgments

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References

1. H. Wendt, M. Götz and M. Linardi, *Quim. Nova*, **23**, 538 (2000).
2. E. V. Spinacé, A. Oliveira Neto, E. G. Franco, M. Linardi and E. R. Gonzalez, *Quim Nova*, **27**, 648 (2004).
3. C. Lamy, E.M. Belgsir and J-M. Léger, *J. Appl. Electrochem.*, **31**, 799 (2001).
4. T. Iwasita, *Electrochim. Acta*, **47**, 3663 (2002).
5. H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang and D.P. Wilkinson, *J. Power Sources*, **155**, 95 (2006).
6. V. Radmilovic, H.A. Gasteiger and P.N.Ross Jr, *J. Catal.*, **154**, 98 (1995).
7. F. Colmati, W.H. Lizacano-Valbuena, G.A Câmara, E.A. Ticianelli and E.R. Gonzalez, *J. Braz. Chem Soc.*, **13**, 474 (2002).
8. A.O.Neto, T.R.R. Vasconcelos, R.W.R.V. da Silva, M. Linardi and E.V. Spinacé, *J. Appl. Electrochem.*, **35**, 193 (2005).

9. Y. Wang, J. Zhang, X. Wang, J. Ren, B. Zuo and Y. Tang, *Top. Catal.*, **35**, 35 (2005).
10. R.B. Lima, V. Paganin, T. Iwasita and W. Vielstich, *Electrochim. Acta*, **49**, 85 (2003).
11. A.O. Neto, M.J. Giz, J. Perez, E.A. Ticianelli and E.R. Gonzalez, *J. Electrochem. Soc.*, **149**, A272 (2002).
12. H.A. Gasteiger, N. Markovic, P.N. Ross and E.J. Carins, *J. Electrochem. Soc.*, **141**, 1795 (1994).