

01/12

Synthesis And Characterization Of Pt/C Catalysts By Colloidal And Deposition Methods For Fuel Cell Applications
Franco, E.G.(1,3,4); Oliveira Neto, A.(1); Spinacé, E.(1); Linardi, M.(1);
Martz, N.(2); Mazurek, M.(2); ~~Fueß, H.(2)~~

(1)IPEN/CNEN; (2)Technical University of Darmstadt;
(3)Universidade Bandeirante de São Paulo; (4)Centro de Ensino Superior de Barueri

→ FUESS, H.

The Aim Of This Work Is To Compare The Catalysts Produced By The Bönemann Method (Colloidal) And The Catalysts Produced By The Deposition Method. For Proton Exchange Membrane Fuel Cells Applications Both Methods Lead To A Good Electrochemical Behavior Of The Catalysts For The Oxidation Of Methanol. The Catalyst Structure Was Investigated By Transmission Electron Microscopy (TEM). Energy Dispersive Analyses (EDS) Were Used To Evaluate The Semi-Quantitative Composition Of The Catalysts And Electrochemical Behavior Was Analyzed By Cyclic Voltammetry (CV). **Key words:** Fuel Cell, Catalyst, Methanol, Electrocatalyst, Nanocrystal.

01/13

Filtro óptico de KBr +1% CuBr para a região em torno de 278nm.

Ruggiero, L.O.; Furlanete, K.
UNESP

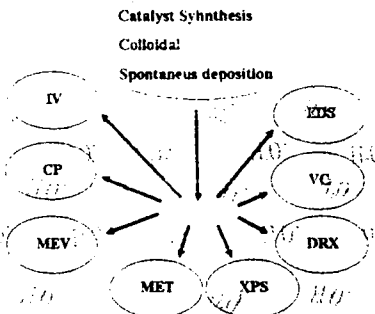
O processo de produção de materiais de halogenetos alcalinos dopados com CuBr, crescidos pela técnica de evaporação resistiva, tem dado origem a filmes policristalinos com qualidade óptica superior às dos monocristais. Esta alternativa de produção é capaz de minimizar o efeito das altas concentrações do dopante, possibilitando uma possível aplicação óptica destes materiais como filtros passa-banda na região do UV. Neste trabalho, nosso interesse é estudar as propriedades ópticas de filmes de KBr dopados com 1% de CuBr em espessuras de 1,6 e 0,6 μm e taxas de evaporação de 2,3nm/s e 5,6nm/s. Os resultados experimentais indicam que filmes menos espessos e crescidos com uma maior taxa de evaporação apresentam uma maior transparência da região do visível e infravermelho, uma banda mais intensa na região de 278nm, uma menor largura desta banda e uma maior cristalinidade dos grãos, ou seja, são filmes que apresentam maior qualidade óptica.

**PRODUÇÃO TÉCNICO CIENTÍFICA
DO IPEN
DEVOLVER NO BALCÃO DE
EMPRÉSTIMO**

9467

Objectives

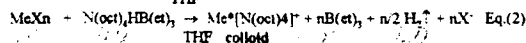
- 1) Synthesized electrocatalysts of the PtRu/C system by two different methods:
 - Colloidal Method
 - Spontaneous Deposition Method
- 2) Structural characterization of the catalysts:
 - EDX, TEM, MEV, XRD, XPS, IR
- 3) Electrochemical characterization:
 - CV, PC



Methods

Bönnemann's method

In order to obtain this nanocrystal a stable colloid should be prepared in an inert and dried atmosphere, according to the equations 1 and 2:

$$N(\text{Oct})_4\text{Br} + \text{KHB}(\text{et})_3 \rightarrow N(\text{Oct})_4\text{HB}(\text{et})_3 + \text{KBr} + \text{THF} \quad \text{Eq.(1)}$$


Thermal treatment

Reducing atmosphere as labeled as PtRu (B1). Heat the catalyst until 573 K in nitrogen, then change the gas for hydrogen for 1 h, change again the gas for nitrogen and turn off the heating.
Oxidizing/reducing atmosphere as PtRu (B2). Heat the catalyst until 573 K in nitrogen, then change the gas for oxygen during 20 minutes, change the gas for hydrogen during 1 h, and finally change again the gas for nitrogen and turn off the heating.

Spontaneous Deposition

Reported by Adzic et al.¹⁴ in order to minimize the amount of platinum used to synthesize the PtRu catalyst. In order to obtain an electrocatalyst with 20 wt% of ruthenium, carbon support (Vulcan XC-72R) was impregnated with a solution of $\text{K}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (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 temperature for 2 h. The sample was cooled to ambient temperature under hydrogen flow and was immersed in an aqueous solution of 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 343K for 3h. The catalyst synthesized by the spontaneous deposition is labeled as PtRu (SD).

Results and discussion

Table 1: Atomic ratio of the electrocatalysts obtained by EDX

Element	PtRu (B1)	PtRu (B2)	PtRu (SD)
Platinum	59	59	10
Ruthenium	41	41	90

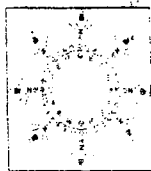


Figure 1: Stabilized Colloid



Figure 2: PtRu(B2) transmission electron microscopy

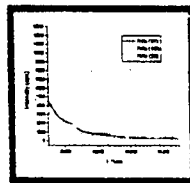


Figure 4: diffractograms of the catalysts



Figure 3: PtRu(SD) transmission electron microscopy

Catalysts composition

The catalysts compositions were checked by EDX and the results are presented in the Table 1. The compositions are in good agreement with the experimental procedure. The results for spontaneous deposition method shows that a small amount of platinum was deposited in the surface of the ruthenium supported-nanocrystals.

X-rays diffraction (XRD)

The diffractograms of the binary catalysts reveal platinum and ruthenium as the only crystalline phases showing reflections according to the ICDD data base, no evidence of other metallic phases or crystalline oxide species was found. The diffractograms can be observed in Figure 4. One can see that a huge difference remains between the results of the catalysts PtRu (B1) and PtRu (B2). As they were produced in the same batch, one can conclude that the only difference remains on the thermal treatment procedure. The average crystallite size seems to increase in the following order: PtRu (B1) < PtRu (B2) < PtRu (SD). This result is in good agreement with the high-resolution pictures of the catalysts (figures 2 and 3).

High-resolution transmission electron microscopy (HRTEM)

Nanocrystallites from catalyst PtRu (SD) and PtRu (B2) are displayed in Figure 2 and 3. The catalytic active particles are highly dispersed on the support grains for both samples. In comparison with the results for PtRu published by Schmidt et al.¹⁴ bigger crystallite sizes were found for the catalysts synthesized by Bönnemann method and thermal treated with oxidizing/reducing atmospheres. The same growth of the crystallite size happens to sample prepared by the spontaneous deposition method, but in a small scale. The first catalyst, PtRu (B1), has a small crystallite size with difficult resolution by XRD, the second one has the biggest crystallite size of all in good agreement with the FWHM for this catalyst and the third one presents medium size crystallites with agglomerates. PtRu (B1) catalyst has the same structure that PtRu (B2) except that the crystallite size is around 1.7 nm instead of 9.9 nm, probably due to the different thermal treatment. The nanocrystals are well dispersed on the carbon support similar as PtRu (B1).

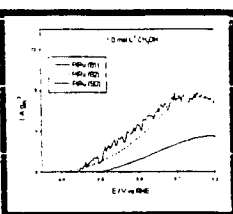


Figure 5: Cyclic voltammery of the catalysts

Cyclic voltammery (CV)

The catalysts were tested by cyclic voltammery to evaluate their electrochemical activity. The cyclic voltammery was performed with sulfuric acid (H_2SO_4 0.5 mol L⁻¹) as a support electrolyte recording the basic voltammogram of each catalyst. To compare the results the concentration of 1.0 mol L⁻¹ were chosen because this is the most usual concentration of fuel cell operation. A scan rate of 10 mV s^{-1} was used to perform the experiments and they are presented in Figure 5.
The catalyst produced by the spontaneous deposition method and the catalyst produced by the Bönnemann method and treated with oxygen atmosphere present similar behaviour according to cyclic voltammery, especially in the range of 0.4 V and 0.7 V, that is interesting for direct methanol fuel cell applications. The catalyst synthesized by the Bönnemann method and treated only with hydrogen atmosphere shows less electroactivity compared to the other ones.

Conclusions

Both methods are suitable for the production of electrocatalyst for fuel cell applications. The catalysts synthesized by the Bönnemann method present a good electrochemical activity and a structure based in well-dispersed nanocrystals on the carbon support that leads to a good electrochemical behavior for fuel cells applications. The catalysts synthesized by the spontaneous deposition method present also a good electrochemical activity while making the normalization by the amount of platinum in the catalyst. The structure of the catalyst is based on platinum atoms on carbon-supported ruthenium nanocrystals surface. The colloidal method (Bönnemann) should be performed in an inert atmosphere with non-hydrated chlorides of the metals involved becoming more expensive than the deposition method but colloidal method could produce ternary and quaternary systems of catalysts to improve their performance toward CO tolerance of the fuel.

1. Lamm, A.; Eick, E.M.; Franco, E.G. *J. Electrochem. Soc.* 1997, 144, 1071.
2. Springer, A. *J. Electrochem. Soc.* 1992, 139, 1465.
3. Gostiger, H.A.; Marzotto, N.; Ramm, P.; Gasteiger, H.A. *J. Electrochem. Soc.* 1994, 141, 1774.
4. Gostiger, H.A.; Marzotto, N.; Ramm, P.; Gasteiger, H.A. *J. Electrochem. Soc.* 1995, 142, 1945.
5. Bönnemann, H.; Gostiger, H.; Ramm, P.; Gasteiger, H.A.; Springer, A. *J. Electrochem. Soc.* 1996, 143, 1912.
6. Ruckenstein, L.; Gostiger, H.; Ramm, P.; Gasteiger, H.A. *J. Electrochem. Soc.* 1997, 144, 1912.
7. Drahokov, S.; Ruckenstein, L.; Gostiger, H.; Ramm, P.; Gasteiger, H.A. *J. Electrochem. Soc.* 1998, 145, 1912.
8. Ruckenstein, L.; Gostiger, H.; Ramm, P.; Gasteiger, H.A. *J. Electrochem. Soc.* 1999, 146, 1912.
9. Franco, E.G.; Oliveira Neto, A.; Spinacé, E.; Linardi, M.; Martz, N.P.; Mazurek, M.; Fueß, H.P. *J. Electrochem. Soc.* 2001, 148, 1912.
10. Franco, E.G.; Oliveira Neto, A.; Spinacé, E.; Linardi, M.; Martz, N.P.; Mazurek, M.; Fueß, H.P. *J. Electrochem. Soc.* 2002, 149, 1912.
11. Oliveira Neto, A.; Franco, E.G.; Spinacé, E.; Linardi, M.; Martz, N.P.; Mazurek, M.; Fueß, H.P. *J. Electrochem. Soc.* 2003, 150, 1912.
12. Franco, E.G.; Oliveira Neto, A.; Spinacé, E.; Linardi, M.; Martz, N.P.; Mazurek, M.; Fueß, H.P. *J. Electrochem. Soc.* 2004, 151, 1912.
13. Franco, E.G.; Oliveira Neto, A.; Spinacé, E.; Linardi, M.; Martz, N.P.; Mazurek, M.; Fueß, H.P. *J. Electrochem. Soc.* 2005, 152, 1912.
14. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 1994, 141, 1774.
15. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 1995, 142, 1945.
16. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 1996, 143, 1912.
17. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 1997, 144, 1912.
18. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 1998, 145, 1912.
19. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 1999, 146, 1912.
20. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 2000, 147, 1912.
21. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 2001, 148, 1912.
22. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 2002, 149, 1912.
23. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 2003, 150, 1912.
24. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 2004, 151, 1912.
25. Schmidt, T.J.; Gostiger, H.A.; Bönnemann, H.; Springer, A. *J. Electrochem. Soc.* 2005, 152, 1912.

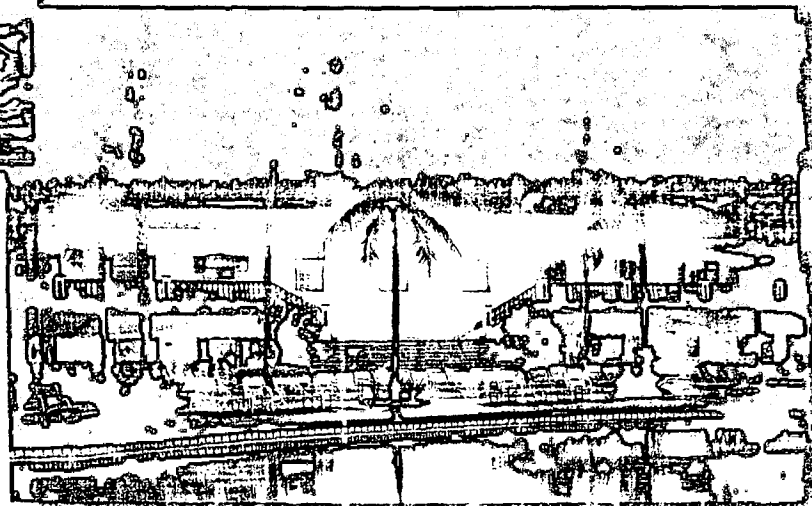
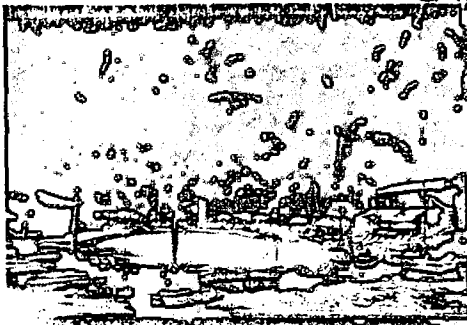
Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) e Financiadora de Estudos e Projetos (FINEP - CTPETRO) are gratefully acknowledged for the financial support and the Technical University of Darmstadt for the laboratory support.



PTECH 2003

FOURTH INTERNATIONAL LATIN-AMERICAN CONFERENCE ON POWDER TECHNOLOGY

NOVEMBER 19 TO 21, 2003 - GUARUJÁ - BRAZIL



ipen



SINTERCONSULT

IPEN/CNEN-SP
BIBLIOTECA
"TEREZINE ARANTES FERRAZ"

Formulário de envio de trabalhos produzidos pelos pesquisadores do IPEN para inclusão na
Produção Técnico Científica

AUTOR(ES) DO TRABALHO:

FRANCO, E.G.; OLIVEIRA NETO, A., SPINACÉ, E.V.; LINARDI, M.; MARTZ, N.;
MAZUREK, M.; FUEB, A.

LOTAÇÃO: CCTM

RAMAL:9192

TIPO DE REGISTRO:

art. / períod.:

Publ. IPEN

. resumo

cap. de livro

Art. conf

outros

(folheto, relatório, etc...)

TITULO DO TRABALHO:

Synthesis and Characterization of PtRu/C Catalyst by Colloidal and Deposition Methods
for Fuel Cell Applications

APRESENTADO EM: (informar os dados completos - no caso de artigos de conf., informar o título
da conferência, local, data, organizador, etc..)

4th International Latin-American Conference on Powder Technology, 19-21 Nov. 2003,
Guarujá, SP, Brasil

PALAVRAS CHAVES PARA IDENTIFICAR O TRABALHO:

Fuel cell, electrocatalyst, characterization methods, methanol

ASSINATURA:

Tanda

DATA: 12/02/2004

Alley
18 FEV 2004