

Preparation of PtRu/Carbon hybrid structures by hydrothermal carbonization for methanol electro-oxidation

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Abstract – PtRu/Carbon hybrid structures were prepared using glucose as carbon source and reducing agent, and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ as metal sources. The obtained materials were characterized by EDX, SEM, TGA and CV and were tested for methanol electro-oxidation aiming fuel cell application.

Fuel Cells employing alcohols directly as fuel (Direct Alcohol Fuel Cell – DAFC) are extremely attractive as power sources for mobile and portable applications [1]. Methanol has been considered the most promising alcohol and carbon-supported PtRu nanoparticles (PtRu/C electrocatalyst) the best electrocatalyst [2]. The catalytic activity of PtRu/C electrocatalysts is strongly dependent on the method of preparation and it is one of the major topics studied in Direct Methanol Fuel Cell (DMFC) [2,3]. The use of carbon nanotubes and mesoporous carbons as support increase the performance of the PtRu/C electrocatalysts, however, the synthesis of these support are normally complex or involve harsh conditions [2]. Recently, the synthesis of metal/carbon nanoarchitectures by a one-step and mild hydrothermal carbonization process was reported using starch or glucose and noble metals salts [4,5]. In this work, we prepare PtRu/Carbon hybrid structures by hydrothermal carbonization and the obtained materials were tested for methanol electro-oxidation aiming fuel cell application.

PtRu/Carbon hybrid structures were prepared using glucose as carbon source and reducing agent, and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ as metal sources. An aqueous glucose solution was mixed with an amount of noble metal salts (glucose/PtRu molar ratio of 82 and Pt:Ru atomic ratio of 50:50) and then submitted to hydrothermal treatment in a Teflon lined autoclave at 150 and 200°C for 24 h. The obtained solids were filtered, washed with ethanol and water and dried at 70°C. Further, the solids were thermally treated at 900°C under argon. The PtRu/Carbon materials were characterized by EDX, XRD, SEM, TGA and CV and were tested for methanol electro-oxidation by cyclic voltammetry using the thin porous coating technique [3].

The yield for carbonization of glucose and Pt:Ru atomic ratio observed for materials as-synthesized were 45 wt% and Pt:Ru of 40:60 and 77 wt% and Pt:Ru of 50:50 for materials obtained at 150 and 200°C, respectively. The diffractograms of these samples showed the peaks characteristic of fcc structure of Pt and PtRu alloys [3]. SEM images showed a non-defined morphology for material prepared at 150°C while for material prepared at 200°C spheres were observed (Fig.1). The materials as-synthesized did not show any activity for methanol electro-oxidation probably due to an incompletely polymerization and carbonization of the glucose [4]. In order to obtain a graphitic structure, the materials were treated at 900°C and a decrease of 68 wt% and 64 wt% were observed for materials prepared at 150°C and 200°C, respectively. After thermal treatment at 900°C no changes were observed for Pt:Ru atomic ratio by EDX analysis and TGA analysis showed the presence of 17wt% (150°C) and 8wt% (200°C) of PtRu metals in these samples. The CV of these samples in 0.5 mol L⁻¹ of H₂SO₄ showed a characteristic profile of PtRu alloy [3]. The material prepared at 150°C and treated at 900°C was more active than the material prepared at 200°C and treated at 900°C (Fig.2) in the region of interest for DMFC (0.3-0.6V).

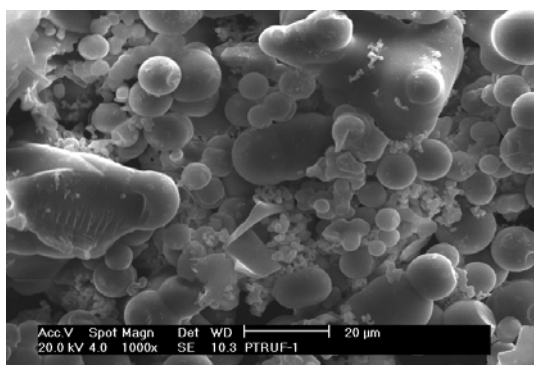


Fig. 1. SEM image of the sample prepared at 200°C and treated at 900°C under argon.

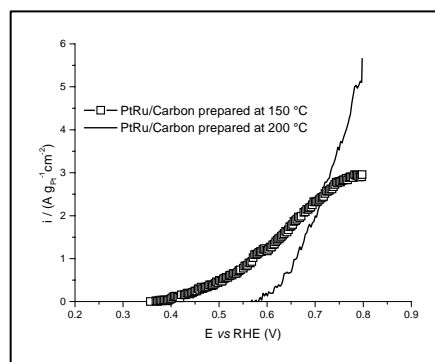


Fig. 2. CV of PtRu/Carbon materials in 0.5 mol L⁻¹ H₂SO₄ and 1.0 mol L⁻¹ methanol with sweep rate of 10mV s⁻¹, considering only the anodic sweep.

References

- [1] E.V. Spinacé, M. Linardi and A. Oliveira Neto, *Electrochem. Commun.* 365-369, 7 (2005).
- [2] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, *J. Power Sources* 95-110, 115 (2006).
- [3] E.V. Spinacé, A. Oliveira Neto, T.T.R. Vasconcelos and M. Linardi, *Journal Power Sources* 17 – 23, 137 (2004).
- [4] S.-H. Yu, X. Cui, L. Li, K. Li, B. Yu, M. Antonietti and H. Cölfen, *Advanced Materials* 1636-1640, 16 (2004).
- [5] H.-S. Qian, S.-H. Yu, L.-B. Luo, J.-Y. Gong, L.-F. Fei and X.-M. Liu, *Chemical Materials* 2102-2108, 18 (2006).