

## Preparation of PtRu/C electrocatalysts by hydrothermal carbonization using different carbon sources

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### Abstract

PtRu/C electrocatalysts were prepared by hydrothermal carbonization using glucose, starch or cellulose as carbon sources and reducing agents and H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O and RuCl<sub>3</sub>.xH<sub>2</sub>O as metals source and catalysts of carbonization process. The obtained PtRu/C electrocatalysts were characterized by EDX, TGA, XRD and BET surface area and pore volume measurements. The electro-oxidation of methanol was studied by chronoamperometry. The PtRu/C electrocatalyst prepared using cellulose as carbon source showed the best performance for methanol electro-oxidation. The electrocatalytic activity of obtained materials seems to be related to the pore volume and mesoporous structure.

**Keywords:** PtRu/C electrocatalyst, hydrothermal carbonization, methanol, fuel cell

### 1. Introduction

Direct Methanol Fuel Cell (DMFC) is very attractive as energy source for portables, mobiles and stationary applications. PtRu/C electrocatalyst has been considered the best electrocatalyst and the catalytic activities depend on the preparation method [1]. Studies have been 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. Recently, the synthesis of metal/carbon nanoarchitectures by a one-step and mild hydrothermal carbonization process was reported using starch or glucose and metals salts [2]. We have studied the synthesis of PtRu/C electrocatalysts by hydrothermal carbonization and focused especially on the effects of different carbon sources on the electrocatalytic performance for methanol oxidation.

### 2. Experimental

#### 2.1. Preparation and characterization of PtRu/C electrocatalysts

PtRu/C electrocatalysts (5 wt% of metal loading; Pt:Ru atomic ratio of 50:50) were prepared using glucose, starch or cellulose as carbon sources and H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O and RuCl<sub>3</sub>.xH<sub>2</sub>O as metals sources. An aqueous solution of the carbon source was mixed with an amount of metals salts and then resulting mixture was submitted to

hydrothermal treatment in a Teflon lined autoclave at 200 °C for a period of 6 h. The obtained solids were filtered, washed with ethanol and water and dried at 70 °C. After this, the materials were thermally treated under argon atmosphere at 900 °C.

To calculate the carbonization yield (wt%) the mass of the as-synthesized material was divided by the mass of carbon atoms present in the molecule of the carbon source.

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

The Pt:Ru atomic ratios were obtained by Energy dispersive X-ray analysis (EDX) using a scanning electron microscope (SEM) Phillips XL30 with a 20 keV electron beam and equipped with EDAX DX-4 microanalyser.

X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu K $\alpha$  radiation source ( $\lambda = 0.15406$  nm).

The BET surface area and pore volume measurements were carried out by nitrogen adsorption at 77 K using a Micromeritics GEMINI V 2380 instrument.

## 2.2. Electro-oxidation of methanol

Chronoamperometry experiments were carried out to examine the electrochemical activity and stability of the electrocatalysts. An amount of 20 mg of the electrocatalyst was added to 50 mL of water containing 3 drops of a 6% polytetrafluoroethylene (PTFE) suspension. The resulting mixture was transferred to the cavity of the working electrode. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Chronoamperometry experiments were performed at room temperature with a Microquimica (model MQPG01) potentiostat/galvanostat using 1.0 mol L<sup>-1</sup> of methanol in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution saturated with N<sub>2</sub>.

## 3. Results and Discussion

PtRu/C electrocatalysts were prepared by hydrothermal carbonization process using different carbon sources (Table 1). In the reaction conditions, the carbohydrates and/or their products of degradation can act as reducing agent of Pt(IV) and Ru(III) ions, which acts as catalysts of the carbonization process [2]. The carbonization yields of the as-synthesized materials were in the range of 65-75 wt%. After thermal treatment at 900°C a weight loss of about 50-60 wt% was observed for all prepared materials and the Pt:Ru atomic ratios and the PtRu loadings were similar to the nominal values.

Table 1. Properties of PtRu/C electrocatalysts prepared by hydrothermal carbonization using different carbon sources

Carbon source	Carbonization yield (wt%)	Weight loss (wt%)	PtRu load (wt%)	Pt:Ru atomic ratio	Crystallite size (nm)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )
glucose	75	51	4.3	58:42	10	50	0.048
starch	71	51	4.8	51:49	10	117	0.084
cellulose	66	59	6.0	56:44	7	76	0.260

The BET surface area of the material prepared using glucose was 50 m<sup>2</sup> g<sup>-1</sup> and this value increase to 117 m<sup>2</sup> g<sup>-1</sup> when starch was used as carbon source. Using cellulose the value decrease to 76 m<sup>2</sup> g<sup>-1</sup>. However, the total pore volume of the material prepared

using cellulose ( $0.260 \text{ cm}^3 \text{ g}^{-1}$ ) was greater than the ones observed for starch ( $0.084 \text{ cm}^3 \text{ g}^{-1}$ ) and glucose ( $0.048 \text{ cm}^3 \text{ g}^{-1}$ ). Besides, the mesopore volume, calculated using BJH method, of the material prepared using cellulose ( $0.25 \text{ cm}^3 \text{ g}^{-1}$ ) showed that it was formed almost exclusively by mesopores while the materials prepared using glucose ( $0.01 \text{ cm}^3 \text{ g}^{-1}$ ) and starch ( $0.025 \text{ cm}^3 \text{ g}^{-1}$ ) have a low volume of mesopores.

The SEM micrographs of PtRu/C electrocatalysts after thermal treatment are shown in Figure 1.

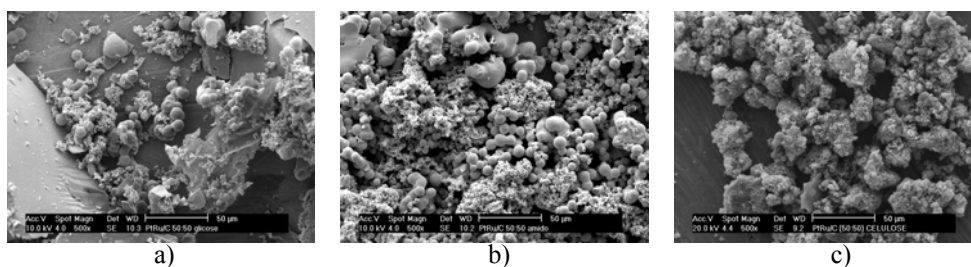


Figure 1. SEM micrographs of PtRu/C electrocatalysts a) glucose, b) starch and c) cellulose

The SEM micrograph of the PtRu/C electrocatalyst prepared using glucose (Fig. 1a) showed mainly a material with irregular morphology, however, some spherical shape were observed, while a spherical shape was predominant for the material prepared using starch (Fig. 1b). The use of cellulose as carbon source (Fig. 1c) leads to the formation of irregular agglomerates with porous structure.

The X-ray diffractograms of PtRu/Carbon materials after thermal treatment were shown in Figure 2.

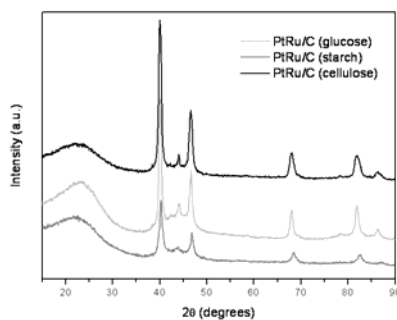


Figure 2. X-ray diffractograms of PtRu/C electrocatalysts prepared using different carbon sources after thermal treatment

The diffractograms of PtRu/C materials showed a broad peak at about  $2\theta = 23^\circ$  associated to the carbon material and five peaks at about  $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$  and  $87^\circ$  characteristic of the face-centered cubic (fcc) structure of Pt [1]. All samples also presented a peak at about  $2\theta = 44^\circ$  that was attributed to a separated hexagonal close-packed (hcp) phase of metallic ruthenium [1]. The (220) reflections of Pt (fcc)

crystalline structure were used to calculate the average crystallite size according to Scherrer formula and the calculated values were in the range of 7-10 nm (Table 1).

The chronoamperometric curves of PtRu/C electrocatalysts in 1 mol L<sup>-1</sup> methanol in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at 0.5 V for 30 min are shown in Figure 3. The current values were normalized by gram of Pt, considering that methanol adsorption and dehydrogenation occur only on Pt sites at room temperature [1].

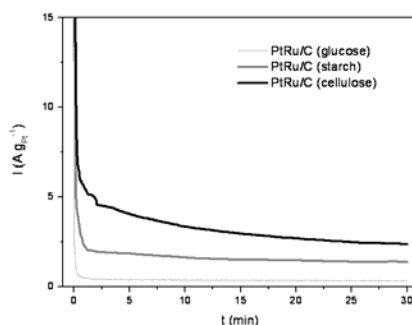


Figure 3 Current-time curves at 0.5 V for PtRu/C electrocatalysts in 1.0 mol L<sup>-1</sup> methanol in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>

The following order of activity for methanol electro-oxidation was observed for PtRu/C electrocatalysts prepared with different carbon sources: cellulose > starch > glucose. Some studies have been shown that mesoporous carbons are very active as supports of electrocatalysts for Proton Exchange Membrane Fuel Cell [3,4].

#### 4. Conclusions

The hydrothermal carbonization showed to be a promising method for producing active PtRu/C electrocatalysts for methanol electro-oxidation. The electrocatalytic activity seems to be related to the pore volume and mesoporous structure of the obtained materials.

#### References

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