

## Research on Methanol-Tolerant Catalysts for the Oxygen Reduction Reaction

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### ABSTRACT

Direct methanol fuel cells (DMFCs) allow obtaining electricity in a clean and efficient way, valuable to substitute traditional environmentally harmful technologies.

Portable power sources are one of the applications of passive DMFCs. One of the requirements in these devices is to use high alcohol concentration. The methanol permeation across the polymer electrolyte membrane (methanol crossover) causes a loss of fuel cell efficiency because the oxygen reduction reaction (ORR) and the methanol oxidation reaction (MOR) occur simultaneously at the cathode.

To develop methanol tolerant cathodes with suitable activity at low temperature, different PtM and PtMRu catalysts, with M = Co or Fe were prepared with the alloying method (**AM**), a variant of the impregnation method (**IM**) and the classic ethylene glycol method (**EG**).

The catalysts synthesized were PtCo/C, PtFe/C and PtFeRu/C and PtCoRu/C and they were studied to determine the role of the components in enhancing the ORR and discouraging the MOR, simultaneously.

The physical characterization of the synthesized materials was accomplished by TEM, XPS and EDS. According to the synthesis procedure, XPS spectra showed that the metal oxides amount on the catalyst varies. Small and well distributed particles for all the catalysts were shown by TEM.

The electrochemical characterization was accomplished by linear sweep and cyclic voltammetry in a three-electrode electrochemical cell with a glassy carbon rotating disk electrode covered with a thin catalytic layer as the working electrode.

**AM** and **IM** catalysts have better activity for the ORR. However, the enhanced activity of **AM** catalysts is lost when the ORR is studied in presence of methanol. Binary catalysts with a similar composition are resistant to methanol depending on their synthesis method. Ternary catalysts containing Ru showed higher methanol tolerance, regardless of the composition and synthesis method. The role of metal oxides is discussed.

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**Keywords:** Oxygen Reduction Reaction; Methanol Crossover; Direct Methanol Fuel Cells.



## **1. Introduction**

Direct methanol fuel cells (DMFCs) are attractive devices to obtain electricity in a clean and efficient way, potentially valuable to substitute traditional environmentally harmful technologies [1]. To make DMFC commercially interesting, it is yet necessary to improve the catalysts employed on both fuel cell electrodes. At the cathode, due to methanol permeation from the anode, a mixed potential is established because of the simultaneous occurrence of the oxygen reduction reaction ORR and the methanol oxidation reaction MOR [2].

To get cathodes resistant to methanol presence, different Pt-base catalysts have been prepared and analyzed. It has been claimed that supported Pt based catalysts containing Cr, Co, Fe are tolerant to methanol, justifying that enough Co or Cr or Fe atoms avoid methanol adsorption and oxidation [3, 4].

However, it is important to pay special attention not only to the catalyst composition but also to the employed method in their preparation, since a complex behavior can be obtained depending on both aspects [5].

In this work ORR catalysts with different compositions obtained by different methodologies are analyzed and the role of catalyst composition and synthesis preparation for the ORR in presence of methanol is discussed.

## **2. Experimental**

### **2.1. Catalysts Preparations**

In order to develop methanol tolerant cathodes with suitable activity at low temperature, we have prepared different PtM and PtMRu catalysts, with M = Co or Fe. Different synthesis methods were employed, namely: i) Alloying Method, **AM**, with a thermal treatment in a H<sub>2</sub>/N<sub>2</sub> reducing atmosphere, in line with [6] ii) a variant of the Impregnation Method, **IM**, employing NaBH<sub>4</sub> as reducing agent [5] iii) the classic Ethylene Glycol Method, **EG**, which uses the alcohol as solvent and reducing agent [7].

#### **A) AM catalysts**

In this method, the initial reactants were a given quantity of E-TEK Pt/Vulcan XC-72R, which was dispersed in water and ultrasonically stirred for 15 min. The initial acidic pH was shifted to 8 with NH<sub>4</sub>OH solution. At this point, the required amount of CoCl<sub>2</sub>, or FeCl<sub>3</sub> was put into the mixture and then, an HCl solution was added to reach a pH of 5.5. Stirring continued for 1 h and then the solid was isolated by filtering, rinsing with water repeatedly and finally drying at 70 °C in an oven for 12 h. After that, the powder was heat-treated at 900 °C in a H<sub>2</sub>/N<sub>2</sub> atmosphere for 1 h to form a binary catalyst. The synthesized electrocatalysts were labeled as PtCo/C **AM** and PtFe/C **AM**.

#### **B) IM catalyst**

Following [5], calculated amounts of H<sub>2</sub>PtCl<sub>6</sub>, FeCl<sub>3</sub> and RuCl<sub>3</sub> were each of them, dissolved in 5 ml of ethylene glycol. The solutions were ultrasonicated and purged with N<sub>2</sub> for 10 min. After that, a calculated amount of chemically treated carbon support (Vulcan XC-72R) was added to a given volume of ethylene glycol and ultrasonicated for 30 min, under N<sub>2</sub> flow, its pH was adjusted to 10 by adding NH<sub>4</sub>OH. Afterward, 0.2 ml of Pt precursor and 2 ml of a freshly prepared 0.1 M NaBH<sub>4</sub> solution were added to the carbon suspension under ultrasonication to form Pt seeds. Then, the remaining precursor solutions and a given amount of NaBH<sub>4</sub> solution were added to the mixture. Finally, the catalyst suspension was further ultrasonicated for 2 h under N<sub>2</sub> flow. The solid obtained after filtering the suspension, was thoroughly washed with abundant distilled water and dried in an oven overnight at 70 °C. The catalyst was denoted as PtFeRu/C **IM**.



*C) EG catalysts*

In the classic ethylene glycol method, ethylene glycol is the reducing agent and dissolving medium where the synthesis occurs. Summarizing, ethylene glycol solutions of each metal precursor,  $\text{H}_2\text{PtCl}_6$ ,  $\text{CoCl}_2$  and  $\text{RuCl}_3$ , in the required amount were added to a suspension of a calculated amount of functionalized carbon black support in ethylene glycol, under vigorous stirring. The mixture was stirred for 4 h under  $\text{N}_2$  bubbling. Once the stirring was finalized,  $\text{NaOH}$  in ethylene glycol solution was added to the mixture to adjust its pH to around 13. In order to achieve the complete reduction of the metallic precursors, the mixture was refluxed at  $197^\circ\text{C}$  for 2 h also under  $\text{N}_2$  bubbling. The solid was isolated by low pressure filtering, then thoroughly rinsed with water and dried at  $70^\circ\text{C}$  in an oven for 12 h. The synthesized electrocatalysts were labeled as  $\text{PtCo/C EG}$ ,  $\text{PtCoRu/C EG}$ .

Additionally the functionalization of the support was achieved after an oxidative treatment in 70%  $\text{HNO}_3$  solution at  $140^\circ\text{C}$  for 2 h following [8].

*2.2. Catalysts characterization*

All synthesized materials were studied in terms of composition and surface chemistry by using energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The distribution and size particles of the supported catalysts were analyzed by employing high resolution transmission electron microscopy (HRTEM).

The electrochemical characterization was accomplished employing a standard three-electrode electrochemical cell. We used as a working electrode a rotating disk electrode (RDE) of glassy carbon ( $0.071\text{ cm}^2$  geometric area) covered with a thin layer of catalyst powder, attached by a  $0.1\text{ }\mu\text{m}$  Nafion<sup>®</sup> thin film. A Pt foil of  $1\text{ cm}^2$  geometric area was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. In this work, we referred all potentials to that of the reversible hydrogen electrode (RHE). The supporting electrolyte was  $0.5\text{ M H}_2\text{SO}_4$  solution and the working solution was an  $\text{O}_2$  saturated  $0.5\text{ M H}_2\text{SO}_4$  solution with different  $\text{CH}_3\text{OH}$  concentrations. The electrochemical experiments were conducted at room temperature. In order to get a stable voltammetric profile, prior to ORR experiments, we cycled the potential of the working electrode at a rate of  $0.1\text{ Vs}^{-1}$  in a  $\text{N}_2$  purged  $0.5\text{ M H}_2\text{SO}_4$  solution.

**3. Results and discussion**

*3.1. Physicochemical characterization*

*A) XPS analysis*

The surface composition of the catalysts was determined measuring the Pt 4f (not shown) Co 2p, Fe 2p and Ru 3d photoelectron peaks. The Co 2p XPS spectra exhibit signals with binding energies at 778 eV assigned to Co (0) ( $778.3\text{ eV}$ ) and at 781 eV assigned to  $\text{Co(OH)}_2$  ( $781\text{ eV}$ ), Figure 1a.

The Fe 2p XPS spectra of the  $\text{PtFe/C AM}$  catalyst show a peak at ca 712 eV attributed to  $\text{Fe}_2\text{O}_3$  ( $710.9\text{ eV}$ ), Figure 1b.

In regard to Ru, the XPS spectra of  $\text{PtCoRu/C}$  catalysts have been analyzed in the region of the Ru 3d core-level peak, which partially overlaps with the C1s core-level peak. Despite the overlapping, the Ru signal at ca.  $281.5\text{ eV}$  can be assigned to  $\text{RuO}_2$  ( $281\text{ eV}$ ), Figure 1c.



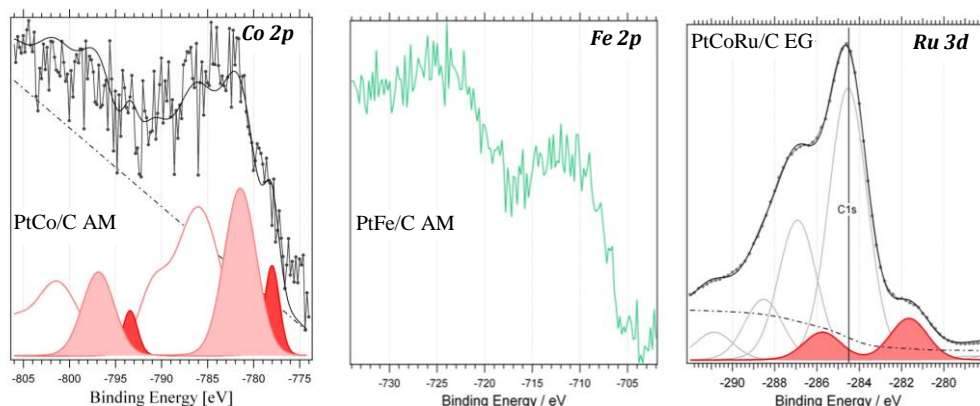


Figure 1- XPS spectra of (a) Co 2p from PtCo/C **AM**, (b) Fe 2p from PtFe/C **AM**, (c) Ru 3d from PtCoRu/C **EG**

### B) EDS analysis

In Table 1, the atomic ratio of the components in the prepared catalysts PtCo/C **AM** and **EG**, PtFe/C **AM** and PtCoRu/C **EG** and **AM** have been determined by EDS.

Table 1. EDS composition of the catalysts prepared by different methods

	Pt/Co at. ratio (EDS)	Pt/Ru at. ratio (EDS)	Pt/Fe at. ratio (EDS)	Catalyst label
EG	10.1			PtCo/C EG
AM	10.4			PtCo/C AM
EG	3.1	1.1		PtCoRu/C EG
AM			2.5	PtFe/C AM
IM		1.2	2.3	PtFeRu/C IM

### C) TEM images

High resolution transmission electron microscopy (HRTEM) showed for all catalysts, nanoparticles homogenously spread on the carbon support. In order to follow the change in the particle size as consequence of the heat-treatment in AM catalysts, we show in Figure 2a and b TEM images of PtFe/C before (*BHT*) and after (*AHT*) heat-treatment, the average particle size increases from 2.9 nm to 5.8 nm. In Figure 2c, for a ternary PtCoRu EG the average particle size is ca 2.5 nm.

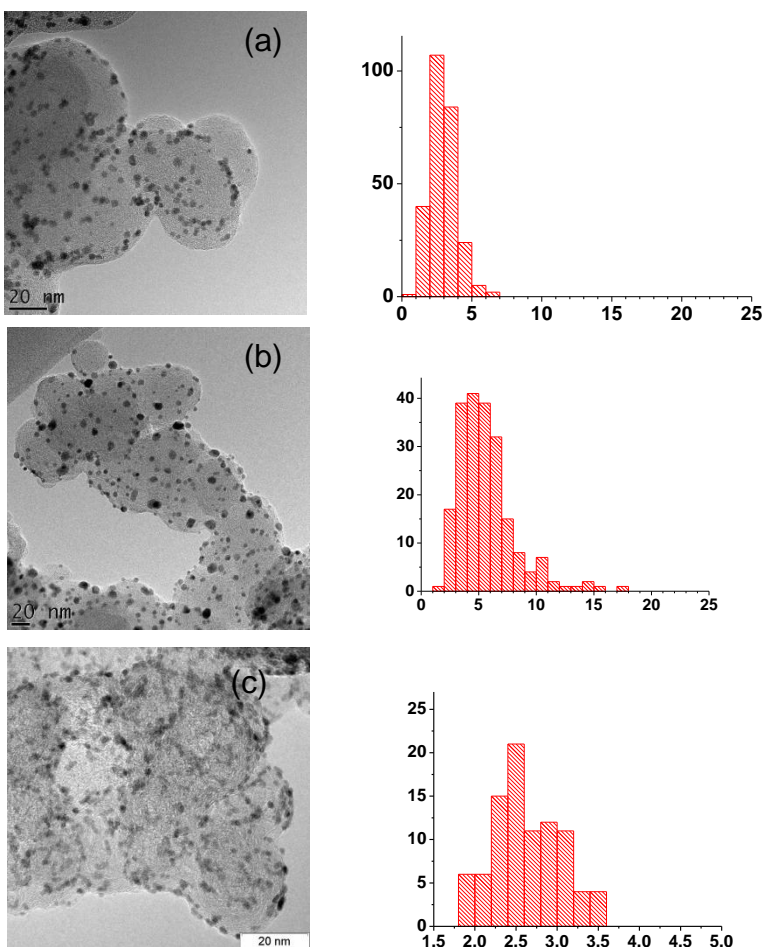


Figure 2- TEM images and particle size distribution of (a) PtFe/C **AM BHT**, (b) PtFe/C **AM AHT**, (c) PtCoRu/C **EG**

### 3.2. Electrochemical behavior

Typical polarization curves for ORR on PtCo/C **AM**, PtFe/C **AM** catalysts at a rotating disc rate  $\omega = 2000$  rpm without or with 0.1 M  $\text{CH}_3\text{OH}$  solution are shown in Figure 3. The polarization curves using Pt /C ETEK are added as reference for the ORR. It can be noticed that catalysts exposed to a reducing atmosphere at high temperatures, show a better catalytic activity for ORR. However these catalysts resulted less tolerant to methanol presence as shown in Figure 3 a and b.

PtFeRu/C and PtCoRu/C exhibit a similar methanol tolerance degree, although PtCoRu/C catalyst is less active for ORR, Figure 3 c and d.



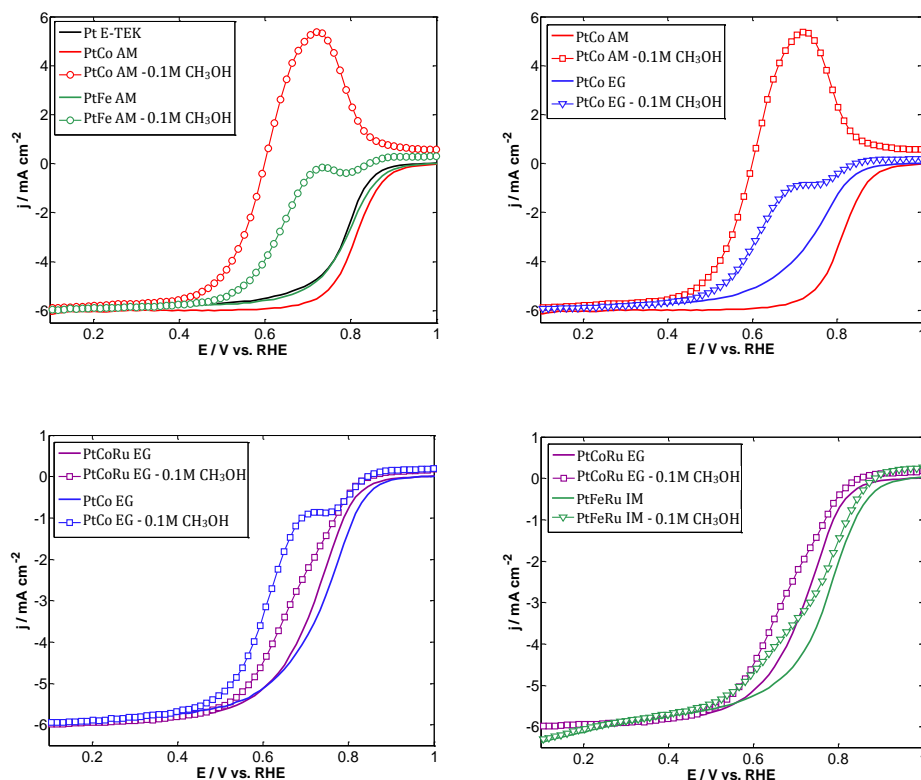


Figure 3- Polarization curves for ORR in  $O_2$  saturated  $0.5M H_2SO_4$  at  $v = 0.005V s^{-1}$  and  $\omega = 2000$  rpm without or with  $0.1M CH_3OH$  for (a) PtCo/C AM, PtFe/C AM and Pt/C ETEK, (b) PtCo/C AM and PtCo/C EG, (c) PtCoRu/C EG and PtCo/C EG, (d) PtCoRu/C EG and PtFeRu/C IM

### Summary and perspectives

- The methanol resistance of the bimetallic catalysts seems to be associated to the synthesis methodology. Consequently, EG catalysts are better.
- For those catalysts containing Ru, the tolerance to methanol regardless of the synthesis method. Thus, the PtCoRu/C EG and PtFeRu/C IM have similar tolerance degree.

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