

# Low Load Pt Catalyst with Surface Functionalised Carbon Supports for PEM Fuel Cells: Half and Full Cell Assessments

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## Abstract

Current US DOE 2020 targets for electrocatalysts aim for a total platinum group metals (PGM) loading of  $0.125 \text{ mgcm}^{-2}$  on membrane-electrode assemblies. The catalysts are expected to endure an elevated number of load cycles in order to comply with the expected 5000 h stack lifetime. At the stated PGM low loading attributes of performance, power and durability, as well as costs, are simultaneously required. The present paper deals with performance assessment of new catalyst using Pt nanoparticles and a surface functionalized carbon support. Due to its relevance to fuel cell operation, the stability and durability were assessed in half cell mode, through the application of demanding aging cycling protocols (30000 cycles). Full fuel cell assessments were also conducted entailing power density curves and cell electrochemical impedance. Results denote significant improvements in cell performance as well as in catalyst stability, regarding a commercial catalyst tested in the same conditions, at Pt loadings of  $0.1 \text{ mgcm}^{-2}$ .

## 1. Introduction

Chemical modification of the carbon support surface, through functionalization with organic molecules, is one of the strategies intended to obtain a better dispersion of metal nanoparticles, good electrical conductivity, high thermal and chemical stability, promoting durability through the minimization of metal loss and in this way improve catalyst performance in PEMFCs [1]. In this work the interaction of the catalyst-support was tuned, through surface modification, using nitrogen and sulphonic groups. This is expected to enhance not only the catalytic properties but also the stability of catalyst nanoparticles, essential for improving performance, demonstrated in this work in half and full cell assessments.

## 2. Experimental

Vulcan XC-72 was functionalized using less studied aromatic with nitrogen and sulphonic groups and is referred to as C\_ABSA, which was prepared from C\_COCl [1]. To this end it was added an excess of 4-aminobenzenesulphonic acid to the dried C\_COCl. The mixture was refluxed in toluene. The Pt/C\_ABSA catalyst, with a nominal composition of 20 wt%, was prepared with  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  as a platinum precursor, using formic acid as reduction agent. Average loading of catalyst was  $\sim 0.2 \text{ mgcm}^{-2}$  and  $0.1 \text{ mgcm}^{-2}$  for half cell and full fuel cell respectively. Characterization of catalysts was done using SEM, TEM X-Ray diffraction as well as electrochemical techniques. Protocols used for aging are described in the next section. Half cell mode assessment was carried out using standard cyclic voltammetry. Full cell assessment was done using a fuel cell assembly with a  $2.5 \times 2.5 \text{ cm}^2$  MEA geometrical area and a Nafion XL ( $27.5 \text{ }\mu\text{m}$ ) membrane, operated using a purpose built fuel cell station. Air and sometimes  $\text{O}_2$  were used for cathode feeding. EIS measurements were implemented to compliment the study. Comparison was made with a commercial catalyst using the same loadings and experimental conditions.

### 3. Results and discussion

A TEM study of the catalysts, Pt/C\_ABSA and Pt/C\_COM, was carried out. Nanoparticles are shown to be well distributed on the carbon support and their mean crystallite size is of 4.1 nm while the mean value for Pt/C\_COM is of 2.5 nm. Values estimated from XRD data were in excellent agreement with those measured on TEM images. The ABSA loading on the functionalized carbon C\_ABSA, 1.06 mmol<sup>-1</sup>, was estimated by elemental analysis. The platinum contents of ~20 %, in both samples, were determined by ICP analysis and confirmed by EDS. Pt/C\_ABSA catalyst demonstrated easy activation in acid medium, voltammograms with well-defined features in the hydrogen region that can be rationalized on the basis of hydrogen electrochemistry at Pt (hkl) in the same solution. An enhanced Pt utilization was estimated to be 76% for Pt/C\_ABSA against 44% found for the commercial catalyst. Aging protocols were conducted up to 30000 cycles, for catalyst (0.4 to 0.8 V vs. Ag/AgCl) and catalyst/support (0.8 to 1.4 V vs. Ag/AgCl) assessments. ESCA recovery of the catalyst after 30000 cycles is reported, see figure 1a). A decrease in cell resistance and improvements in power density were evident in fuel cell assessments, see fig 1b) and 1c) for comparison of results regarding commercial catalyst.

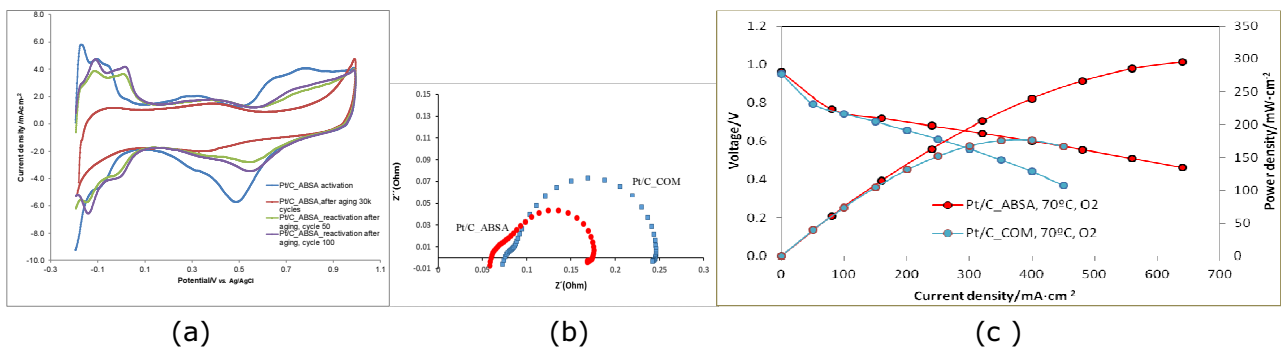


Fig. 1 Half cell: Pt/C\_ABSA voltammograms run in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 50 mVs<sup>-1</sup>, used to estimate catalyst ESCA after activation, 30000 cycles aging and recovery (a); Full cell: Pt/C\_ABSA and Pt/C\_COM catalyst, 70°C, oxygen cathode feeding: EIS impedance (b); Polarization and power density curves (c).

### Concluding Remarks

In both, half and fuel cell assessments, regarding stability and power density respectively, Pt/C\_ABSA catalyst shows superior behaviour that Pt/C\_COM catalyst when tested using the same loading. EIS measurements denoted a decrease in cell resistance for the catalyst with ABSA functionalized carbon in agreement with polarization behaviour, in fuel cell testing mode.

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### References

[1] A.Capelo, M.A. Esteves, A.I. de Sá, R.A. Silva, L. Canguero, A. Almeida, R. Vilar, C.M. Rangel, International Journal of Hydrogen Energy, 41, 12962-12975 (2016 ).