

## Electrochemical oxidation of carbon in low temperature fuel cells: influence of the gas atmosphere

L. Dubau<sup>1</sup>, L. Castanheira<sup>1</sup>, M. Lopez-Haro<sup>2</sup>, P. Bayle-Guillemaud<sup>2</sup>, Frédéric Maillard<sup>1</sup><sup>1</sup> Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, LEPMI, UMR 5279 CNRS/Grenoble-INP/UdS/UJF, BP75, 38402 S<sup>1</sup> Martin d'Hères, France<sup>2</sup> CEA, SM/INAC/SP2M/LEMMA, Service de Physique des Matériaux et des Microstructures, 17, Rue des Martyrs, 38054 Grenoble, France[frederic.maillard@lepmi.grenoble-inp.fr](mailto:frederic.maillard@lepmi.grenoble-inp.fr)

Low temperature proton-exchange membrane fuel cells (PEMFC) use Pt nanoparticles supported on carbon to accelerate the rate of the electrochemical hydrogen oxidation and the oxygen reduction reaction. The carbon support provides electron conduction, large surface area to distribute to the best extent the metal nanoparticles and avoid their aggregation. Its structural properties and in particular its mesoporosity are also essential to ensure optimal mass-transport of the reactants and educts. However, these adequate properties change under PEMFC operating conditions, where carbon is prone to be oxidized. The corrosion of the carbon support causes formation of oxygen-containing carbon surface groups (water management issues), loss of porosity (increased mass-transport losses) and Pt nanoparticle detachment/aggregation (Pt surface area losses). However, the influences of the potential conditions and of the gas atmosphere remain unclear, and are the focus of the present study.

In this paper, X-ray Photoelectron Spectroscopy (XPS) measurements were used to monitor how the nature of the oxygen-containing surface groups vary under various potential conditions (800 potential cycles between  $0.05 < E < 0.50$  V or  $0.05 < E < 1.23$  V vs. RHE in 0.1 M HClO<sub>4</sub>), and in the presence of oxidizing/reducing molecules (O<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>3</sub>OH). We show that the presence of CO in the electrolyte promotes the reduction of the oxygen-containing carbon surface groups (Figure 1). Conversely, the presence of O<sub>2</sub> maintains a part of the oxygen-containing surface groups on the carbon support surface and Ar atmosphere promotes the oxidation of C-O containing groups (hydroxyl, epoxy and ether) into C=O (carbonyl and/or quinone-like), and O-C=O (carboxylic acid, lactone, anhydride). We also used identical location transmission electron microscopy (IL-TEM) to investigate how these molecules affect the stability of the supported Pt nanoparticles (1). In low potential cycling conditions ( $0.05 < E < 0.50$  V vs. RHE), the presence of CO in the liquid electrolyte promotes the migration/aggregation of the Pt crystallites (Figure 2), in agreement with our previous work (2). Minor changes were observed under Ar atmosphere, but the presence of O<sub>2</sub> causes carbon corrosion and Pt nanoparticle detachment. In high potential cycling conditions ( $0.05 < E < 1.23$  V vs. RHE), 3D Ostwald ripening dominates the morphological changes. To the best of our knowledge, this is the first report that the chemical nature of the gas atmosphere used in accelerated durability test impacts the Pt/C degradation mechanisms.

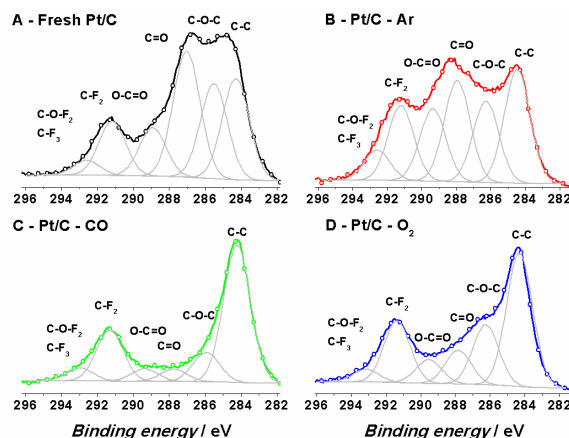


Figure 1. XPS C1s spectra measured on Pt/Vulcan XC 72 after 800 potential cycles between  $0.05 < E < 1.23$  V vs. RHE under various gas atmospheres. Electrolyte 0.1 M HClO<sub>4</sub>;  $\nu = 0.20$  V s<sup>-1</sup>,  $T = 20$  °C.

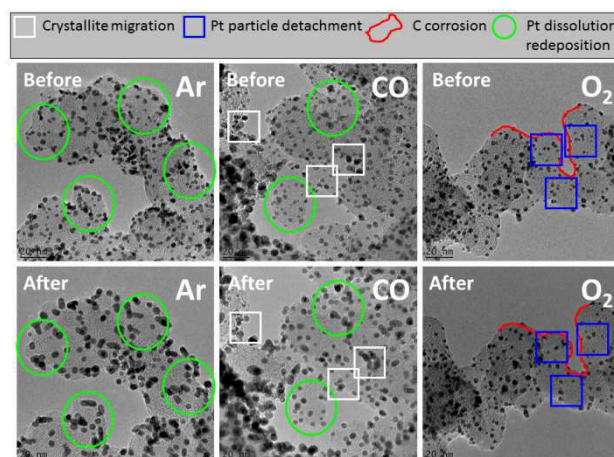


Figure 2. IL-TEM images of Pt/C catalysts before and after 800 potential cycles between 0.05 and 1.23 V vs. RHE in 0.1 M HClO<sub>4</sub> containing Ar, CO or O<sub>2</sub>. The white squares emphasize crystallite migration and further aggregation, the blue squares point particle detachment and the red lines underline zones where the carbon support was corroded.  $\nu = 0.200$  V s<sup>-1</sup>;  $T = 20$  °C.

## References

1. L. Dubau, L. Castanheira, Z. Zhao and F. Maillard, *Electrochim. Acta*, in preparation for *Electrochimica Acta*.
2. Z. Zhao, L. Dubau and F. Maillard, *J. Power Sources*, **217**, 449 (2012).