

## SURICAT, A PROJECT DEDICATED TO STABLE PEMFC CATALYST SUPPORTS

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*Abstract - Durability of current membrane electrode assemblies (MEAs) used in proton-exchange membrane fuel cells (PEMFC) is limited by the corrosion of the high surface area carbon (HSAC) supports in real operating conditions. Among the different strategies used to tackle this problem, using metal oxides as catalyst supports reveals promising. Doped TiO<sub>2</sub> and doped SnO<sub>2</sub> nanofibers (NF) or aerogels (AG) with morphologies appropriate for efficient mass-transport along with improved electronic conductivity (once doped with Nb or Sb) have been prepared. Pt nanoparticles were then successfully deposited on their surface via different routes. First results obtained on MEAs based on Pt/doped SnO<sub>2</sub> NF showed increased stability compared to conventional Pt/C during accelerated stress tests (AST).*

*Index Terms - Metal oxides, catalyst support, PEMFC, durability.*

### I. INTRODUCTION

Proton Exchange Membrane Fuel Cell (PEMFC) are clean and efficient energy converters, producing electricity and heat by catalytic oxido-reduction of hydrogen and oxygen. The power range accessible from watts to megawatts provides access to a wide range of applications (transport, portable or stationary). However, they still suffer from limitations that hinder their widespread deployment and mass marketing; in

particular, the durability of catalyst supports (high surface area carbon blacks) in real PEMFC operating conditions remains critical.

The SURICAT project, funded by the French National Research Agency (ANR) and supported by Capenergies and Tenerrdis, aims at developing new cathode catalyst supports based on metal oxides (MOx). The synthesized supports should meet four basic criteria: i) be electron-conducting, ii) allow the deposition of metal catalyst nanoparticles with good electrocatalytic activity for the oxygen reduction reaction (ORR), iii) be corrosion resistant in accelerated aging tests as well as under real PEMFC operating conditions and iv) have a texture suited to the preparation of efficient MEAs. The research programme focused on two matrices, TiO<sub>2</sub> and SnO<sub>2</sub>, four dopants, Nb, Ta, V and Sb and two morphologies, nanofibers and aerogels.

Based on promising results, two metal oxides were selected, and doped with V, Nb, Ta or Sb. The metal oxides (MOx) were synthesized by various methods in order to evaluate the impact of i) the support on the spatial distribution of the catalyst and ii) the structure and morphology of the MOx support on the PEMFC performance. A selection process based on the four criteria (conductivity, electrocatalytic activity for the ORR,

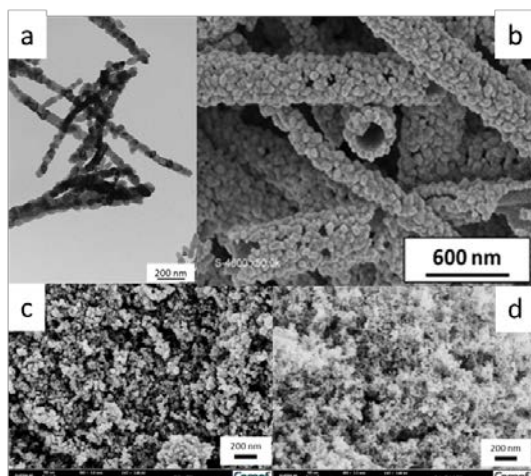
robustness and morphology) was used throughout the development chain (support matrix synthesis, deposition of electrocatalysts, and manufacture of catalytic layers) to select the best candidates.

The selected MOx were then used to prepare MEAs. Their electrochemical performance and their robustness were evaluated in single cell test bench. The performance of the best Pt/MOx electrocatalysts was compared to that of a conventional carbon-supported reference catalyst (Pt/C). Finally, the MOx support with higher performance (specific power and durability) will be implemented and evaluated in a small portable system.

## II. MAJOR RESULTS

### A. Support synthesis

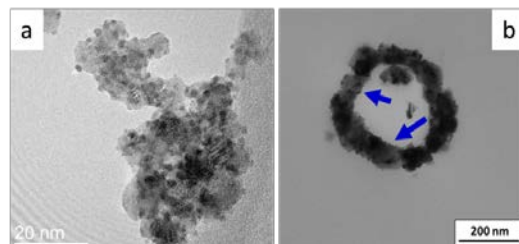
TiO<sub>2</sub>, SnO<sub>2</sub> and their doped counterparts were synthesized as nanofibers (NF) and aerogels (AG) following electrospinning and sol-gel routes, respectively (Figure 1). Initial results allowed to identify two formulations of interest for PEMFC applications: 1) titanium dioxide doped with niobium (Nb) to 10 at.% (Ti<sub>0.9</sub>Nb<sub>0.1</sub>O<sub>2</sub>) and 2) tin dioxide doped with antimony (Sb) to 10 at.% (Sn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>2</sub>). Doping with Sb increased the electronic conductivity of tin dioxide (SnO<sub>2</sub>) to 1 S/cm, *i.e.* a 5 to 6 orders of magnitude increase compared to undoped SnO<sub>2</sub>. The specific surface areas of the synthesized materials ranged from 20 m<sup>2</sup>/g (Ti<sub>0.9</sub>Nb<sub>0.1</sub>O<sub>2</sub>-NF) to 80 m<sup>2</sup>/g (Sn<sub>0.9</sub>Sb<sub>0.1</sub>O<sub>2</sub>-AG).



**Fig. 1.** Scanning electron microscopy images of TiO<sub>2</sub> (left) and SnO<sub>2</sub> (right) based materials (top: NF, bottom: AG)

### B. Pt deposition and electrochemical characterization

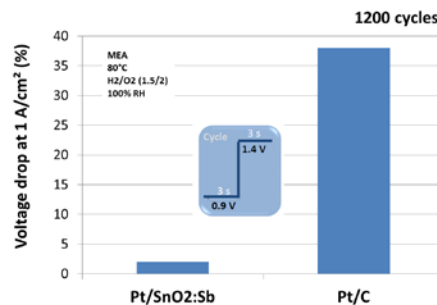
Different procedures were used to deposit Pt nanoparticles on the MOx surface. The synthesized Pt/MOx featured interesting catalytic activity for the ORR [1] and improved durability compared to conventional Pt/C [2].



**Fig. 2.** Transmission electron microscopy images of a: Pt/SnO<sub>2</sub>:Sb AG and b: Pt/SnO<sub>2</sub>:Nb NF

### C. Preliminary single cell test

Single cell tests and ASTs were made using TiO<sub>2</sub>:Nb and SnO<sub>2</sub>:Sb NF as supports [2]. The MEA cell voltages at  $j = 1$  A/cm<sup>2</sup> are respectively 0.4 and 0.5 V and max. power densities, 0.4 and 0.6 W/cm<sup>2</sup>. The durability of the synthesized Pt/MOx and the reference Pt/C was evaluated by performing 1,200 square potential cycles between 0.9 and 1.4 V *vs.* RHE with a holding time of 3 s at each potential, under H<sub>2</sub>/O<sub>2</sub> (1.5/2),  $T = 80$  °C and 100 % relative humidity. Interestingly, although Pt/SnO<sub>2</sub>:Sb and Pt/SnO<sub>2</sub>:Nb-based cathodes featured lower initial performance than Pt/C, the catalytic trend is inverted after the AST. Figure 3 shows that Pt/SnO<sub>2</sub>:Sb is much more stable than Pt/C (-0.025 V *vs.* 0.4 V at  $j = 1$  A/cm<sup>2</sup>).



**Fig. 3.** Comparison of MEA voltage drop at  $j = 1$  A/cm<sup>2</sup> for Pt/SnO<sub>2</sub>:Sb and Pt/C after the AST conducted in single cell

## III. CONCLUSION

TiO<sub>2</sub> and SnO<sub>2</sub>, as NF or AG, are potential alternative catalyst supports to HSAC supports used in PEMFC. With adequate morphology, once doped and after Pt deposition, they show high electronic conductivity enough and appropriate catalytic activity to replace C in PEMFC. Improved durability compared to Pt/C was also demonstrated on MEA.

## ACKNOWLEDGMENT

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