

Hydrogen peroxide, Non-Precious Metal Catalysts and radical species

V. Goellner, M. Zaton, J. Rozière, F. Jaouen
 Institut Charles Gerhardt /Agréats, Interfaces et
 Matériaux pour l'Energie – UMR 5253
 Montpellier, France

Introduction

While Proton Exchange Membrane Fuel Cells (PEMFCs) are already entering the portable sector and the market of materials handling vehicles, the long term economic growth of this technology remains subject to further advances in electrocatalysis and to the cost of precious metal catalysts. Today, platinum is used at both the anode and cathode, although in much greater amounts in the latter due to the slower Oxygen Reduction Reaction (ORR). Recent advances in non-precious metal catalysts for the ORR and synthesized from a transition metal (Fe, Co), a nitrogen and a carbon precursor are encouraging [1-2]. However, much remains to be done to convert the try, especially regarding their durability.

The present work will report on one possible degradation mechanism of non-precious metal catalysts in practical PEMFCs, namely the reaction between H_2O_2 and Fe or Co ions found as active or inactive species for the ORR in Fe- or Co/N/C catalysts. H_2O_2 is produced in minor quantities (1-10%) during the ORR on either Pt/C or Fe(Co)/N/C-catalysts [3]. In contrast to Pt/C, Fe(Co)/N/C are very poor electrocatalysts for the H_2O_2 electro-reduction to water, but react chemically at a slow rate to disproportionate H_2O_2 [3]. This reaction is however likely to result in the formation of highly-oxidizing radical species through a mechanism similar to the Fenton reaction.

Experimental

Fe- and Co/N/C-catalysts were synthesized from the metal salts, phenanthroline and a Zn-based metal organic framework in a 1/20/80 weight ratio [1]. Wet impregnation, drying and planetary ballmilling were performed, followed by a pyrolysis in Ar at 1050°C and subsequent acid-washing (labeled Metal-A-AW). Ex-situ Fenton's test involved 200 mg of catalyst and 100 mL of a 3 wt % H_2O_2 solution (i.e. ca 0.5 mol $H_2O_2/g_{catalyst}$). The Fenton solution was heated at 80°C under reflux for 24 h, with a 25 cm² NR212 Nafion™ membrane in it. In order to detach fluoride species adsorbed on or trapped in the catalyst, the solution was sonicated at maximum power before filtration. The fluoride concentration was then measured by an ion-selective electrode (Orion Star™ series meter). PEMFC measurements were recorded at 80°C, 100% RH and using H_2 and O_2 gases. The cathode contained 4 mg_{catalyst} cm⁻².

Results

Figure 1 shows the fluoride concentrations measured after a Fenton test on the Fe/N/C- and Co/N/C-catalysts. Significant levels of fluoride above that of deionized water could be measured on the Fe/N/C-catalyst. The Co/N/C catalyst might also result in F-release, but larger amounts of H_2O_2 should be used to detect this. These preliminary results demonstrate the production during the chemical disproportionation of H_2O_2 on Fe-A-AW of radical species, which then attacked the membrane immersed in solution. In order to test whether this phenomenon also occurred during PEMFC operation, we collected the exhaust water from both the anode and cathode sides and measured the fluoride

concentration. Figure 2a shows the current density in PEMFC measured over 50 h for the Fe- and Co-based catalysts while Fig. 2b shows the fluoride concentrations in the collected exhaust water. Here, fluoride release could be detected for the Co-based catalyst. The larger fluoride concentration measured with the Fe-based catalyst might explain its faster degradation. Quantitatively, 4000 ppb [F] in the present PEMFC test corresponds to ca 1.7 μg fluor cm⁻² hr⁻¹ (0.1 L collected water and 4.84 cm² MEA surface). This is a significant release, much higher than that observed with Pt-based catalysts especially at 100% RH [4]. Whether the presence of radical species decreases the catalyst activity, ionomer conductivity or mass transport properties of the cathode is unknown at this stage. It might also be a combination of these factors.

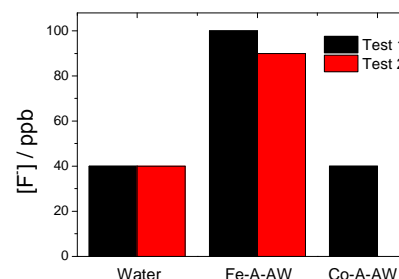


Figure 1. Fluoride concentration measured after Fenton test for the Fe- and Co-based catalyst and baseline (deionized water).

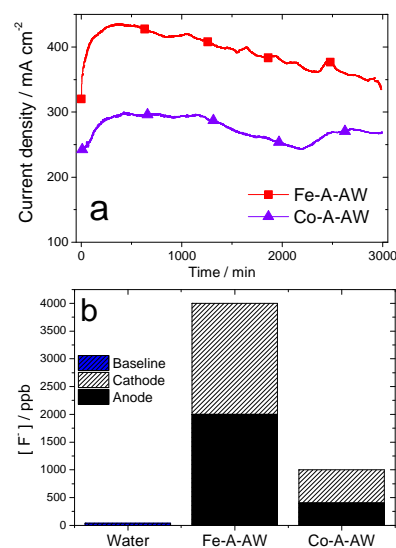


Figure 2. a) Current density at 0.5 V vs. time and b) fluoride concentration in exhaust water after 50 h with Fe-A-AW or Co-A-AW as cathode catalysts.

Conclusions

Large amounts of fluoride are released when Fe or Co/N/C catalysts are placed at the cathode side of a PEMFC. A Fenton like reaction is suspected. This reaction must be minimized in the future, using radical scavengers or minimizing the H_2O_2 side product.

References

- [1] E. Proietti, F. Jaouen, M. Lefèvre, N. Larouche, J. Herranz, J. Tian, J.P. Dodelet, *Nature Comm.* 2 (2011) 416
- [2] G. Wu, K.L. More, C.M. Johnston, P. Zelenay, *Science* 332 (2011) 443
- [3] F. Jaouen, J.P. Dodelet, *J. Phys. Chem. C* 113 (2009) 15422
- [4] J. Healy, C. Haydn, T. Xie, K. Olson, R. Waldo, M. Brundage, H. Gasteiger, J. Abbott, *Fuel Cells* 5 (2005) 302.