NITROGEN-DOPED CARBON SUPPORTS FOR PEM FUEL CELL Fe-BASED ELECTROCATALYSTS

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The activity of Fe-based catalysts for O_2 electroreduction in H_2SO_4 solution at pH=1 and in polymer electrolyte membrane (PEM) fuel cells depends on the nitrogen content of the catalyst. A higher catalytic activity is obtained for catalysts with larger nitrogen contents [1]. These catalysts are prepared by adsorbing 0.2 wt% Fe, using iron (II) acetate as the Fe precursor, onto a carbon support and then, heat-treating this material at 900°C in NH_3 : H_2 : Ar (2:1:1) atmosphere. In this study, Norit was used as the carbon support and different attempts were undertaken to improve the N content of the carbon support prior to the iron acetate adsorption.

Obtaining oxygenated functionalities at the surface of the carbon support and then transforming them into nitrogen-containing functionalities by a heat-treatment in NH_3 containing atmosphere should results in an improvement of the N content. Norit was therefore oxidized : (i) in air at various temperatures and (ii) in acid solutions of different concentrations at various temperatures, using sulfuric, perchloric and nitric acids. The subsequent heat-treatment was performed at various temperatures in NH_3 : H_2 : Ar (2:1:1) atmosphere. The best results were obtained with a reflux of Norit in concentrated HNO_3 for a period of time not exceeding one hour (Fig. 1). Catalysts prepared using these modified carbon supports contain up to 4 at% N and display the highest catalytic activity.

Fuel cells made with these catalysts at the cathode are characterized by polarization curves very close to the one obtained with commercial 10 wt% Pt/C ELAT and measured in the same experimental conditions. When these polarization curves are expressed in terms of mass activity (current density per mg metal), Fe-based catalysts even surpass the performance of Pt catalyst in our measurements but are still short of the mass activity reported for the state-of-the-art Pt catalysts (Fig. 2).

XPS analysis was used to obtain the nitrogen surface concentration and to also characterize the nitrogen speciation. Experiments were first performed on Norit carbon supports alone after oxidation in concentrated HNO_3 and also on the catalysts prepared with these oxidized supports. Hence, the evolution of the surface concentration of the various nitrogen species, obtained after reflux in HNO_3 and after heat-treatment of these materials in NH_3 containing atmosphere, was determined in relation with the heat-treatment temperatures.

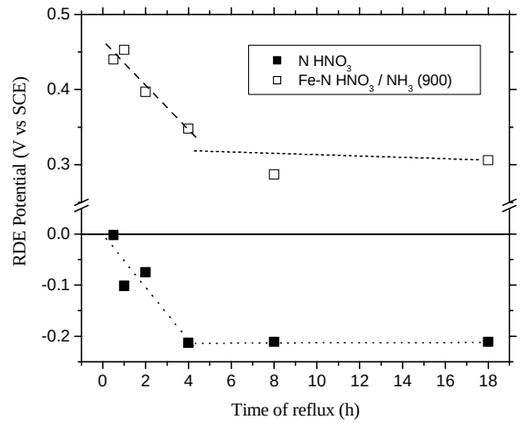

Figure 1: Evolution of the catalytic activity for O_2 reduction of : (i) Norit carbon support refluxed for several time durations in concentrated HNO_3 and (ii) catalysts prepared with these carbon supports by adsorbing 0.2 wt% Fe, as iron acetate, followed by a heat-treatment at 900°C in NH_3 : H_2 : Ar (2:1:1) atmosphere.

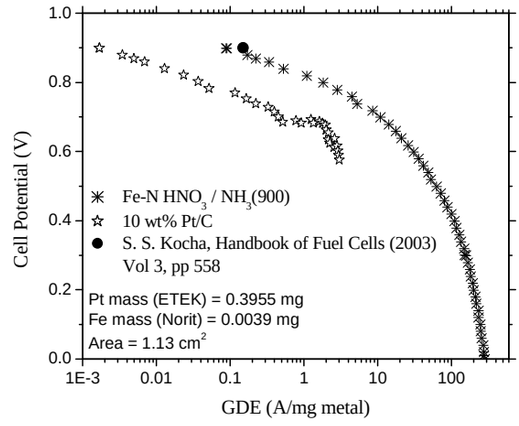

Figure 2: Tafel plots of the polarization curve for the best catalyst obtained on Norit and with 10 wt% Pt (with 0.35 mg Pt/cm^2) from ELAT, expressed in GDE current in A/mg metal. The black circle is the mass activity of a state-of-the-art Pt electrocatalyst.

[1]: F. Jaouen, S. Marcotte, J.-P. Dodelet, G. Lindbergh, *J. Phys. Chem. B*, **2003**, *107*, 1376-1386.