# MANGANESE OXIDE/CARBON-BASED ELECTROCATALYSTS FOR ORR IN ALKALINE MEDIUM: ORR MECHANISM

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## Introduction

Platinum is the best known catalyst for the Oxygen Reduction Reaction (ORR) in an alkaline fuel cell cathode. However, for simple cost reasons, non-platinized electrocatalysts have retained the focus of the scientific community since a long time. One promising material is manganese oxide ( $MnO_x$ ) deposited onto carbon powder of great specific surface area, thanks to its rather high activity towards oxygen reduction [1-6]. The preparation of manganese oxide nanoparticles dispersed onto carbon was described in previous papers [3, 7]. The ORR mechanism of  $O_2$  to OH- on  $MnO_x$  was described [8] as an overall 4-electron mechanism in competition with a partial reduction with 2 electrons yielding hydrogen peroxide ions  $HO_2$ - followed by either a 2-electron reduction of HO2- or a disproponation reaction of  $HO_2$ - in solution.  $HO_2$ - ions are corrosive and can generate problems of premature degradation of the electrochemical cells. The aim of the present paper is to elucidate, in complement of the activity evaluation [7], the ORR mechanism on these electrocatalysts in alkaline medium.

### Experimental

A glassy carbon disc / platinum ring RRDE ( $\phi$ disc = 5 mm) was used to evaluate the ORR mechanism on MnO<sub>x</sub>/C-based catalysts. As explained previously [7], each active layer was deposited from an ink containing 25 mg of MnO<sub>x</sub>/C, (MnO<sub>x</sub>+Ni)/C or (MnO<sub>x</sub>+Mg)/C powder, 1 ml of water, 0.6 ml of ethanol and 3 µl of PTFE beads in solution (60 wt%, DuPont). The ink, homogenized by sonication, contained 14 wt% PTFE (on the basis of the dry materials). A 20 µl-drop of the ink was deposited on the glassy carbon disc electrode and solvents were evaporated at room temperature for 30 minutes. The layer, around 4 µm thick, was then heat-treated at 180 °C for 15 minutes to ensure its binding. All solutions were prepared using 18.2 MΩ cm water (Millipore, Elix<sup>®</sup> + Milli-Q gradient<sup>®</sup>) and Prolabo (Normapur<sup>®</sup>) potassium hydroxide.

RRDE measurements were performed in a 0.1 mol I<sup>-1</sup> KOH solution in a four electrodes cell. Hg-HgO (in 1 M KOH) was used as the reference electrode, platinum foil as the counter electrode and the disc and ring electrodes as working electrodes: all potentials are

referred to Hg-HgO (in 1 M KOH). Voltammetry experiments were conducted using a computer-controlled multichannel potentiostat (VMP2, Biologic Science Instruments) in the bistat configuration. ORR voltametries were carried out after oxygen saturation of the electrolyte by bubbling for 20 minutes, the oxygen concentration being kept constant at its saturation value by permanent O<sub>2</sub>-bubbling, the solution temperature being controlled at  $25 \pm 1$  °C. On the glassy carbon disc, successive quasi-steady-state ORR voltammograms were recorded on the MnO<sub>x</sub>/C-based active layers from 0.2 to -0.6 V (Hg-HgO) at quasi-steady state (1 mV s-1) in O<sub>2</sub>-saturated potasium hydroxide solutions. Prior to each voltammetry, the potential was kept two minutes at the starting potential, 0.2 V (Hg-HgO), in order to ensure identical initial surface state in all experiments. The ring potential was maintained at 0.35 V (Hg-HgO) during the whole procedure, so as to in-situ and in-time detect any amount of H<sub>2</sub>O<sub>2</sub> formed on the disc.

### **Results and discussion**

All our electrocatalysts were tested for the ORR in the oxygen-saturated 0.1 M KOH solution using the RRDE. We performed succesive voltammetries on the  $MnO_x/C$ -based active layers for various RRDE revolution speeds (Fig.1). For each of the studied catalysts, starting from the ORR disc currents (ID,k), corrected from the O2 – diffusion in solution by using the classical Koutecky-Levich model, and the ring currents (IR), the number of electrons (nt) exchanged per molecule of oxygen reduced in the RRDE disc was determined in the ORR potential range (Fig.2-a), such as corresponding electronic and molar proportions (Fig.2-b) of peroxide ions formed per reduced molecule of O<sub>2</sub> [9].



**Fig.1** I(ED) curves of the reoxydation of  $HO_2$ - on the ring (a) and of the  $O_2$  reduction on the disc with  $(MnO_x + Ni)/C$  active layer (b),  $O_2$ -saturated 0.1 M KOH solution at 25°C, ER = 0,35 V (Hg-HgO), 500 (black), 900 (dark grey), 1600 (grey) et 2500 (light grey) rpm, vb = 0,001 V s<sup>-1</sup>.

The presence of manganese oxide nanoparticles dispersed onto carbon strongly orientate the oxygen reduction towards the 4-electron mechanism, that do not produce peroxide (Fig.3-a,b). The doping of these catalysts by nickel or magnesium increases this tendency. Doping by insertion metals is beneficial since it contributes



**Fig.2** Number of electrons nt exchanged per O<sub>2</sub> molecules reduced on the RRDE disc (a), in the case of MnOx/C (black), (MnOx + Mg)/C (dark grey) and (MnOx + Ni)/C (grey) active layer, in function of ED, O<sub>2</sub>-saturated 0.1 M KOH solution at 25 °C, ER = 0.35 V (Hg-HgO), 500 rpm. Corresponding molar proportions of HO<sub>2</sub>- ions formed on the disc per reduce O<sub>2</sub> molecule (b).

to direct the oxygen reduction towards the four-electron mechanism and thus to decrease the production of peroxyde ions (Table 1).



**Fig.3** Number of electrons nt exchanged per  $O_2$  molecule reduced on the RRDE disc (a),  $MnO_x/C$  (black) or Chezacarb black carbon (grey) active layer, in function of ED (a),  $O_2$ -saturated 0.1 M KOH solution at 25 °C, ER = 0.35 V (Hg-HgO), 500 rpm. Corresponding molar (b) and electronic (c) proportions of HO<sub>2</sub>- formed on the RRDE disc.

**Table 1** Number of electrons  $n_t$  exchanged per reduce  $O_2$  molecule on disc, corresponding electronic  $x^e$  and molar  $x^m$  proportions of  $HO_2^-$  formed on disc, at  $E_D = -0.04$  V (Hg-HgO),  $O_2^-$  saturated 0.1 M KOH solution at 25 °C,  $E_R = 0.35$  V (Hg-HgO), 500 rpm.

Catalysts	n <sub>t</sub>	x <sup>e</sup> / %	x <sup>m</sup> / %
MnO <sub>x</sub> /C	3.67	9.0	16.5
(MnO <sub>x</sub> + Mg)/C	3.80	5.2	9.9
(MnO <sub>x</sub> + Ni)/C	3.86	3.5	6.8
Chezacarb black carbon	2.7	48.7	65.5

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