ELECTROCHEMICAL ACTIVITY OF MANGANESE OXIDE/CARBON-BASED ELECTROCATALYSTS

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Introduction

Carbon supported platinum is currently the material of choice to be used to catalyse oxygen reduction reaction (ORR) in an alkaline fuel cell cathode. However, for a simple cost reason, it is preferable to use non-platinized materials in alkaline medium. Manganese oxide (MnO_x) deposited onto carbon powder of great specific surface area was found to be rather active for oxygen reduction [1-5]. MnO_x preparation was described in a previous paper [2]. The present study aims at evaluating the activity of such manganese oxide-based electrocatalysts towards the ORR.

Experimental

A glassy carbon Rotating Disc Electrode (ϕ = 5 mm) was used as a substrate to characterize the active layers of the desired catalyst, as described in previous papers [6-7]. The active layer was deposited from an ink containing 25 mg of MnO_x/C, (MnO_x+Ni)/C or (MnO_x+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. A 10 µL-drop of the ink was deposited on the glassy carbon electrode and the 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. Similar active layers were prepared from 10 wt% Pt/C (E-Tek) for comparison. All solutions were prepared using 18.25 MΩ cm water (Millipore, Elix® + Milli-Q gradient®) and Prolabo (Normapur®) reagents.

Electrochemical measurements were performed in a molar solution of KOH in a four-electrode Pyrex cell [6,7]. Hg-HgO (in 1 M KOH) was used as the reference electrode: all potentials are referred to its potential (+ 0.1 V/NHE). Voltammetry experiments were conducted using a computer-controlled potentiostat (PAR EG&G, model 273). The ORR experiments were carried out under oxygen atmosphere (bubbling for 20 minutes ensured O_2-saturation) at controlled temperature, (25 ± 1) °C. Experiments under argon atmosphere were done to characterize the active layers in term of active area (Pt/C) or stability in the ORR potential range (MnO_x/C-based catalysts).

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Results and discussion

All our electrocatalysts were tested for the ORR in oxygen-saturated molar KOH solution using the RDE. We performed successive voltammetries on the MnO_x-based active layers for various RDE revolution speeds (Fig. 1-a). The ORR current densities corrected from the diffusion in solution, using the classical [8] Koutecky-Levich model (Fig. 1-b), show that Nickel or magnesium doped MnO_x/C exhibit better activity towards ORR than undoped MnO_x/C (Table 1). In comparison, the benchmark catalyst, 10 wt% Pt/C from E-Tek, exhibits ORR activity close to those of the doped MnO_x/C catalysts. We believe that the doping transition metals stabilize an intermediate Mn^{III}/Mn^{IV} phase, which favors oxygen bond splitting, and thus enhances ORR rate (Fig. 2). In consequence these doped MnO_x-based materials exhibit remarkable ORR catalytic activity.

(a) (b)

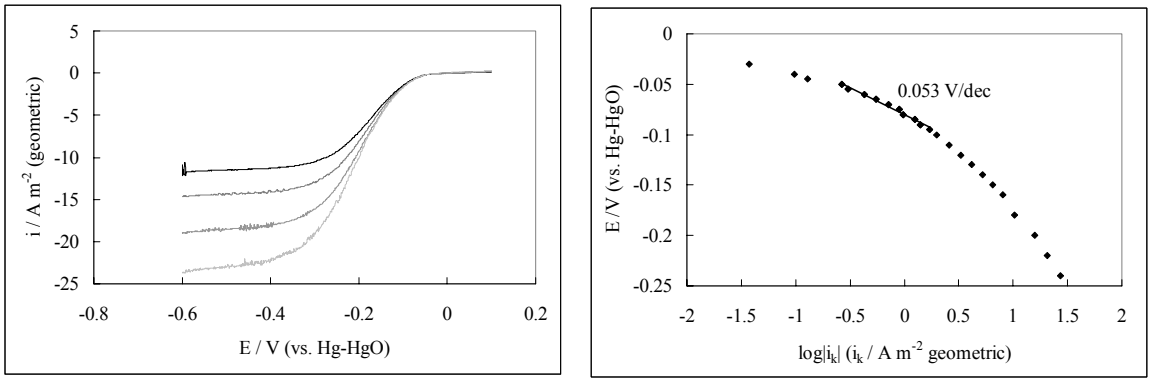
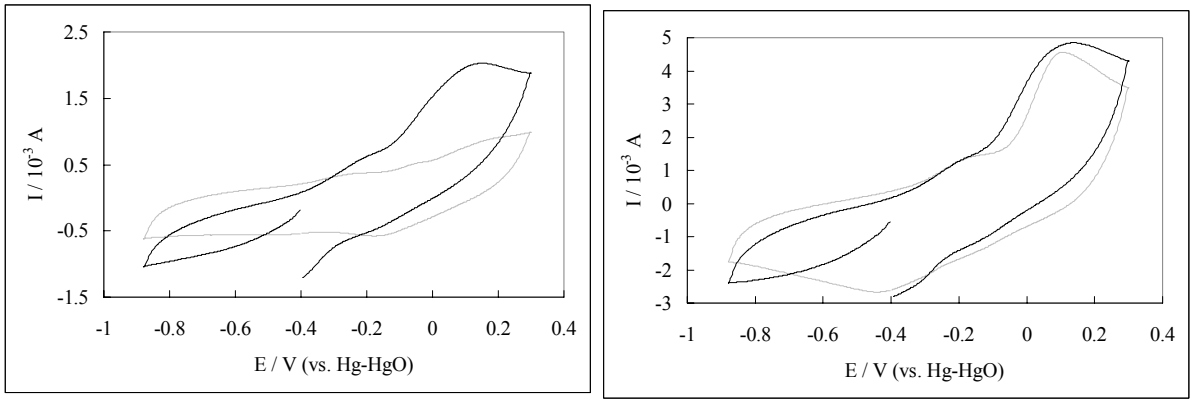


Fig. 1 *quasi-steady state (10^{-3} V s^{-1}) ORR voltammograms for MnO_x/C (geometrical area = 0.196 cm²) in O_2-saturated 1 M KOH at 25 °C – revolution speed 500 (black), 900 (dark grey), 1600 (grey) and 2500 (light grey) rpm (Fig. 1-a - left) and corresponding Tafel plots after correction by the diffusion in solution using Koutecky-Levich model (Fig. 1-b - right).*

Table 1 *Kinetic parameters for the ORR in O_2-saturated 1M KOH at 25 °C - correction from the oxygen diffusion in solution according to the Koutecky-Levich model ; i_{-100}^{s}: values ratioed to the geometric electrode area; i_{-100}^{m}: values ratioed to the mass of platinum (Pt/C) or that of manganese (MnO_x/C, (MnO_x+Ni)/C and (MnO_x+Mg)/C)*

Catalyst	i_{-100}^{s} (A/m²)	i_{-100}^{m} (A/g)	b_1 (V/dec)	b_2 (V/dec)
Pt/C (E-Tek)	32	40	-0.081	-0.40
MnO_x/C	3	1.9	-0.050	-0.11
(MnO_x+Ni)/C	48	30	-0.045	-
(MnO_x+Mg)/C	63	39	-0.038	-0.060



(a) (b)

Fig. 2 *1st (black) and 20th (grey) cyclic voltammogram cycle in argon-saturated 1 M KOH at 25 °C for MnO_x/C (a) and (MnO_x+Mg)/C (b) (geometrical area = 0.196 cm²); sweep rate 0.1 Vs^{-1}.*

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