Ethanol tolerant manganese oxide electrocatalysts for the oxygen reduction reaction in alkaline medium

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Manganese oxides (MnOx) are widely studied catalysts for use at the cathode of alkaline fuel cells, owing to their low cost, high activity of oxygen reduction reaction (ORR) [1, 2], electrochemical stability [3] and tolerance to reducind species, such as $NaBH_4$ [4, 5]. This paper investigates the ethanol tolerance of nickel-doped carbon-supported nanostructured MnOx materials for the ORR in alkaline media; our goal is to use these electrocatalysts as cathode material in Direct Ethanol Alkaline Fuel Cell (DEAFC).

The carbon-supported nickel-doped nanometric MnOx were prepared by a mild hydrothermal treatment first described by Bezdicka et al. [6]. After thorough physico-chemical characterizations, they were evaluated with regards to the alkaline ORR, in the rotating disk electrode setup. The experiments were conducted in 1.0 M NaOH solutions at 25, 40 and 60°C, in the absence/presence of 0.1 M of ethanol.

In absence of ethanol, the quasi-stationary ORR voltammograms for all the NiMnOx/C electrocatalysts show diffusion-convection plateaus typically observed on RDE experiments [2]. In the present experimental conditions, the onset of the oxygen reduction wave is similar for all NiMnOx/C, independently of the Ni load and the nature of the carbon substrate. The increase in temperature caused negligible changes in the onset potential. All electrocatalysts present reasonable tolerance to the presence of 0.1 M ethanol, as shown for example for NiMnOx/E350G (Figure 1). At high overpotential, a small decrease of the limiting currents is observed, indicating a small decrease of the apparent number of electrons exchanged per O_2 species. At low overpotential, the presence of ethanol modifies the total current produced by the ORR for all electrocatalysts, but this effect is less pronounced at high rotation rates, particularly for the materials dispersed onto the MM225 and E350 carbons. Since the decrease of the ORR currents is rather similar in the activation region, it is likely that this effect is caused by changes of the ORR kinetics/pathways (as for example an inhibition of the catalytic decomposition/reduction of HO_2^- anions).

Fuel cell tests conducted using these NiMnOx/C materials at the cathode of DEAFC demonstrate that these materials compete favorably with state-of-the-art Pt/C cathode electrocatalysts (Figure 2), thereby confirming the good tolerance monitored in the RDE characterizations.

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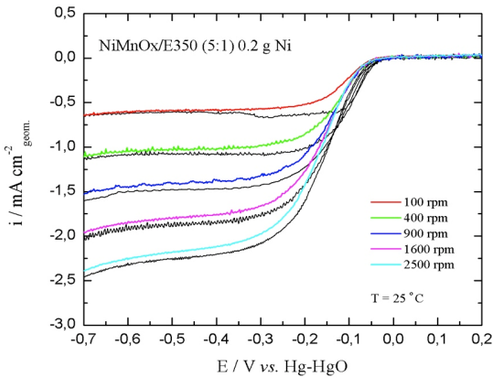

Figure 1: ORR voltammograms (v = 5 mV s^{-1}) plotted on NiMnOx/E350G in 1 M NaOH (black lines) and 1 M NaOH + 0.1 M EtOH (colour) at 25, 40 and 60°C.

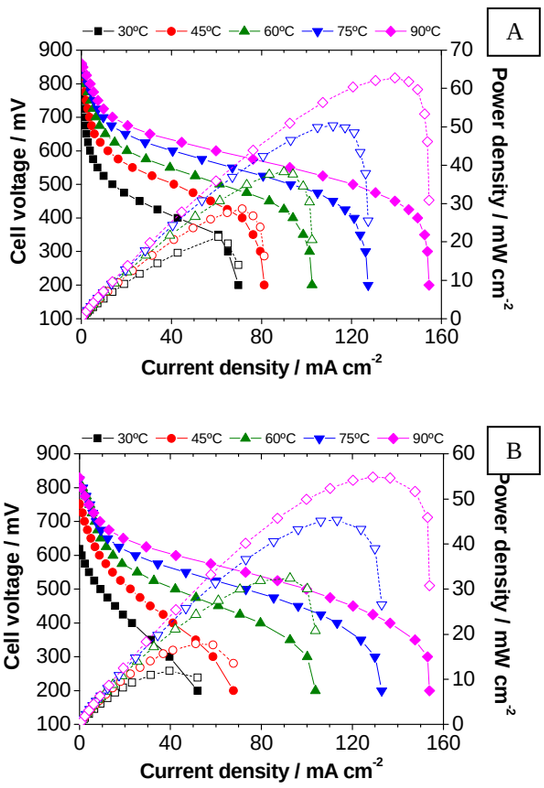

Figure 2: Cell potential and Power density *vs.* Current densities for alkaline single cells. Pt/C anodes (0.4 mg Pt cm^{-2}) fed with 1.0 M KOH and 1.0 M EtOH. (A) Pt/C (0.4 mg Pt cm^{-2}) or (B) NiMnOx/C 0.2 g Ni (0.4 mg NiMnOx/C cm^{-2}) cathodes fed with water-saturated O_2 at several temperatures. (PBI + 5 M KOH) membranes were used as electrolyte.