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CO Methanation Reaction for Improving the CO Tolerance in PEMFC Anodes

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The CO reduction reaction has been frequently discussed in the literature [1], but not often considered as a real alternative for improving the CO tolerance of PEMFC anodes fed with H_2/CO mixtures. In fact, much more attention has been devoted to find more efficient ways to oxidize CO, as it is also of practical interest in the oxidation of other small organic molecules such as methanol, formic acid, and ethanol [2]. However, converting CO into CH_4 instead of CO_2 avoid the back-contamination effects of the Reverse Water-Gas Shift reaction that may take place when, for example, PtMo/C catalysts are considered for converting CO into CO_2 [3].

Recently we have demonstrated that a Ru/C catalyst reduces CO to CH_4 (namely, CO Methanation) in a transient fashion when it is placed in a PEMFC anode [4]. In this work, we demonstrate how the Ru/C catalyst can be used in two distinct configurations to promote the CO methanation at steady-state conditions, and thus greatly reducing the CO poisoning effect of Pt/C anodes.

Ru/C nanoparticles were synthesized by wet chemical reduction with formic acid to give 40 wt.% metal on carbon (confirmed by EDS measurements) with particle size ranging from 2-4 nm, as determined by TEM images. We employed two distinct alternatives to promote de CO methanation reaction over the Ru nanoparticles. The first method involved the use an external filter unit, where the Ru/C powder was inserted into a porous stainless steel cup, housed at a pre-engineered unit that allows inlet and outlet gas flows. This setup was kept at 200 °C, which is a standard temperature used in heterogeneous catalysis to promote the methanation reaction. The other method consisted of preparing the gas-diffusion layer (GDL) of the electrodes with the gas side containing Ru/C instead of pure carbon. For both configurations the single cell (5 cm^2 geometric active area) used pure Pt/C (0.4 mg cm^{-2}, E-Tek) as the electrocatalyst either at the cathode and the anode. In both cases we used the equivalent of 23 mg of Ru. On line mass spectrometry (OLMS) measurements were employed to quantify the amount of CH_4 produced in each approach.

Figure 1 shows that the external filtering unit improves the cell performance when H_2/CO 100 ppm is used as the anode fed. Typical S-shaped polarization profiles are observed for the cell with and without the filter unit; however, this profiles is dislocated to higher current densities when the Ru/C unit is in place, indicating a lower CO partial pressure at the anode stream.

When the Ru/C catalyst is placed in the GDL of the anode it is seen that, at a standard temperature (85ºC), the cell performance is little enhanced when compared to that of a GDL consisting of only carbon (Fig. 2). However, if the cell temperature is increased to 105 ºC, the response in the presence of CO and without Ru GDL in the anode improves significantly, while that with Ru/C is barely altered when compared to that pure H_2.

OLMS results in Fig. 3 clearly show that the Ru/C catalyst is able to convert CO into methane, and that the increase of temperature leads to an increase of the amount of methane produced, which is consistent with the tolerance effects observed by the cell polarization data.

In summary, here we show that Ru/C nanoparticles can be satisfactorily employed to reduce the CO poisoning of standard Pt/C anodes.

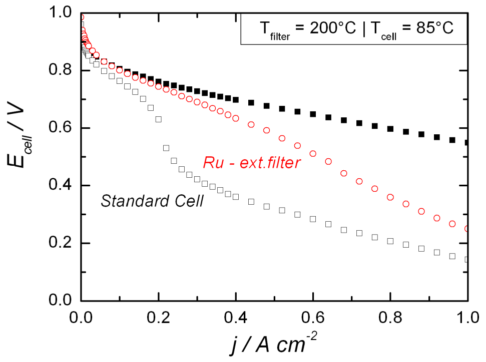

Fig. 1 – Cell polarization data showing the increase in performance when a Ru external filter is present in the anode fuel fed. T_{cell} = 85 ºC; T_{filter} = 200 ºC. Closed symbols: pure H_2; open symbols: H_2/100 ppm CO. Nafion® 115.

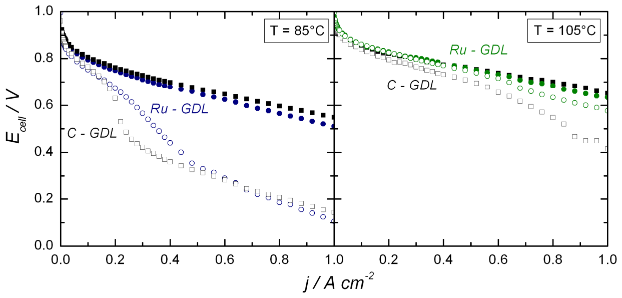

Fig. 2 – Cell polarization data showing the increase in performance when Ru is present in the Gas-Diffusion Layer of the anode electrode. Closed symbols: pure H_2; open symbols: H_2/100 ppm CO. Nafion® 115.

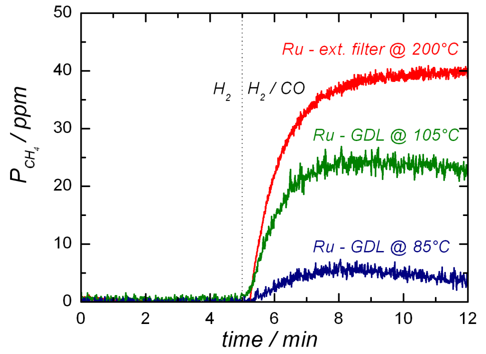

Fig. 3 – OLMS results showing CH_4 production when CO is present in the H_2 stream (100 ppm) for Ru/C employed on both configurations. Detections were made in the outlet of the filter or of the single cell anode.

Acknowledgments

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