

## Effect of high-voltage cycling on non-precious metal catalysts for the ORR

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### Introduction

While Proton Exchange Membrane Fuel Cells (PEMFCs) are already entering the portable sector and the market of materials handling vehicles, the long term economic growth of this technology remains subject to further advances in electrocatalysis and to the cost of precious metal catalysts. Today, platinum is used at both the anode and cathode, although in much greater amounts in the latter due to the slower Oxygen Reduction Reaction (ORR). Recent advances in non-precious metal catalysts for the ORR and synthesized from a transition metal (Fe, Co), a nitrogen and a carbon precursor are encouraging [1-2]. However, much remains to be done to convert the try, especially regarding their durability.

The present work will report on the degradation of non-precious metal catalysts caused by high-voltage transients. During the start/stop of large cells, it is known that the cathode potential may for a short time reach values as high as 1.3-1.5 V due to the H<sub>2</sub>-air front passing the anode compartment during air-purging [3]. This effect is deleterious for Pt/carbon catalysts due to carbon electro-oxidation, resulting in loss of porosity and Pt-particles agglomeration. This phenomenon is therefore expected to be destructive for carbon-supported Fe(Co)/N/C-catalysts as well, but the question is how fast and to what extent ?

### Experimental

Fe- and Co/N/C-catalysts were synthesized from the metal salts, phenanthroline and a Zn-based metal organic framework [1]. Wet impregnation, drying and planetary ballmilling were performed, followed by a pyrolysis in Ar at 1050°C and subsequent acid-washing. RDE measurements were performed in aqueous pH 1 H<sub>2</sub>SO<sub>4</sub> electrolyte in a 3-electrode cell with a gold wire as counter and a Pt/H<sub>2</sub> reference. PEMFC measurements were recorded at 80°C, 100% RH and using H<sub>2</sub>/O<sub>2</sub>.

### Results

We first investigated the effect of cycling the potential from 0.6 to 1.5 V vs. RHE in RDE. Figure 1a shows the polarization curves measured for an acid-washed Fe/N/C-catalyst initially, after 300, 600 and 1200 cycles. Each cycle consisted in a potential hold at 0.6 V for 3 s followed by a potential hold at 1.5 V for 3 s. As can be seen from the figure, not only did the activity remain stable but it even increased during the first 300 cycles. This increase was not observed if the electrode had not been cycled at high voltage. Between 300 and 1200 cycles, the activity seems to decrease linearly with cycling number. This degradation was expected since the active sites are located on the carbon surface and non-graphitized carbon is electrochemically oxidized at a significant rate above ca 1.1 V vs. RHE.

We then performed similar experiments in PEMFC. To our surprise, a significant loss of performance was observed after only tens of cycles between 0.9 and 1.4 V for the same catalyst (Fig. 1b). The cycle duration was identical, with a 3 s hold at 0.9 V and 3 s at 1.4 V. Since the catalytic activity was not modified after 300 cycles at 1.5 V in RDE, the catalytic activity

should not have been negatively affected after 300 cycles in PEMFC and even less so after only 50 cycles.

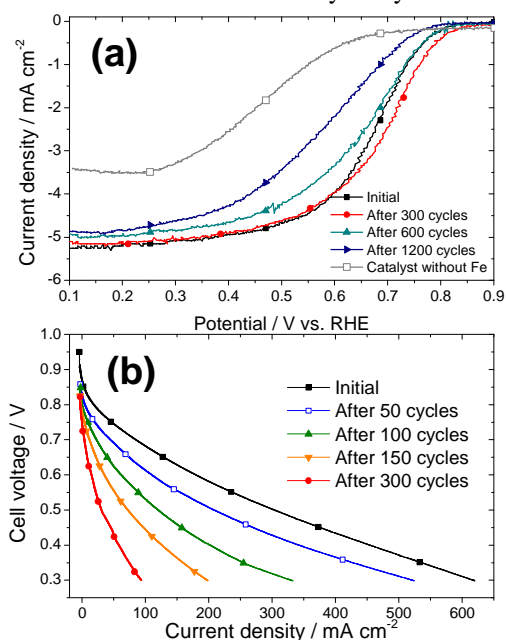


Figure 1. a) RDE polarization curves at 1500 rpm in O<sub>2</sub> saturated pH 1 electrolyte, b) PEMFC polarization curves.

If the activity was not changed, then either the mass-transport or charge transport properties of the cathode layers were. The high-frequency resistance measured by impedance spectroscopy indeed linearly increased with cycle number 1 to 300 (from 0.12 to 0.48 Ω cm<sup>2</sup>). This is a major increase that certainly explains the performance loss. Metal ions (from inactive metallic phases simultaneously present along active metal-based sites) leached during the cycling protocol must be responsible for the decreased ion conductivity. This hypothesis was confirmed by cycling a PEMFC cathode in a liquid pH 1 electrolyte, then assembling it into an MEA. The initial performance was identical to that of a non-cycled electrode. It seems that the large reservoir of protons in the liquid electrolyte did not allow accumulation of metal cations in the cathode ionomer. Additional experiments as well as spectroscopic characterization of electrodes before and after cycling by X-ray absorption and Mössbauer spectroscopy will be discussed.

### Conclusions

This study reveals the negative impact of inactive metal phases present in non precious metal catalysts on their durability in PEMFC, even if these phases are initially protected by a thin carbon layer. Also, a major conclusion is drawn on the difference between RDE and PEMFC durability measurements. Ionomer degradation and cation-exchange effects cannot be observed in RDE due to the presence of the supporting electrolyte. The relative stability of FeN<sub>x</sub> or CoN<sub>x</sub> sites up to 1.5 V is positively surprising, but the presence of inactive metal or metal carbide species is a major concern.

### References

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