

**Experiment title:**

Degradation mechanism of novel carbon and heteropolyacids salts supported fuel cell cathode catalysts: effect of ageing on the microstructure

Experiment**number:**

CH 2879

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BM29

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Report:

In this experiment the structural changes observed in the commercial catalyst $Pt_{3\pm\delta}Co$ supported on Vulcan (E-TEKTM product, 30% of metal and 70% of Vulcan) induced by fuel cell operating conditions was observed. The experiment was focused on two main aspects of the fuel cell: working potential and working time. In both cases, the studied material was in the form of a thin catalytic layer prepared as follows. The structure of the pristine Pt-Co nanomaterial used to prepare the catalytic layers of the studied electrodes was the subject of our previously published work [Greco, G.; Witkowska, A.; Principi, E.; Minicucci, M.; Di Cicco, A. Phys. Rev. B 2011, 83, 134103 [10 pages]].

0.1 Samples preparation

For the measurements at variable potential (XAS *in situ* experiment) membrane electrode assemblies (MEAs), with an active area of 5 cm², were prepared using: Nafion N-117 (DuPontTM) – as a proton conductive membrane, electrode with a Pt-Co/C electrocatalyst (metal loading about 0.1 mg/cm²) – as a cathode, electrode with a Pd nanocatalyst supported on Vulcan (E-TEKTM, metal loading about 1.0 mg/cm²) – as an anode. The Nafion membrane was sandwiched between these two electrodes, hot-pressed and positioned between the graphite collector plates of a commercial single fuel cell specifically optimized for *in situ* XAS measurements. Palladium was used on the anode side, since it is a good catalyst of the hydrogen oxidation reaction and since it does not disturb X-ray absorption measurements of Pt L₃ and Co K edges. For the FC working time-dependent study (XAS *ex situ* experiment), three electrodes

were prepared with a total Pt-Co loading equal to about 1.5 mg/cm². Such electrodes were placed on the cathode side of MEAs (not hot-pressed in this case) composed of Nafion N-112R (DuPontTM) and a Pt standard electrode on the anode side (E-TEKTM, Pt loading 0.5 mg/cm²). Subsequently, MEAs were subjected to the degradation process in a standard single fuel cell. The PEMFC was held for 1 h at 0.6 V and 1 h at open circuit voltage (OCV) for a total time of 0 h, 50 h and 150 h. After the selected working times (0 h, 50 h and 150 h), the electrochemical performance of the cell was checked and then MEA was dismantled and the XAS spectra for the Pt-Co/C cathode catalyst under study were collected *ex situ*.

0.2 XAS measurements

In order to perform *in situ* XAS measurements, an optimized commercial single fuel cell (PEMFC EFC-05-02, Electrochem. Inc.TM) was installed in the X-ray spectrometer BM29 of the ESRF (Grenoble). The optimization consisted in the drilling of a window for the X-ray beam in the shape of a truncated prism. The amount of the tested material in the sample was very small (especially in the case of Co, below 0.01 mg/cm²). For this reason, the measurements were performed in fluorescence mode using a 13-channel Ge X-ray detector, in the energy range of 11.45-12.3 keV for Pt L₃-edge and 7.64-8.30 keV for Co K-edge. Prior to the collection of XAS spectra, the MEA was conditioned at room temperature (RT) at 0.5 V for 17 h. After that, a rapid electrochemical measurement was performed to check the cell performance. The importance of performing a conditioning process, as a part of MEA activation procedure. XAS data were collected for various cell potentials (from the cathode activation region) at RT under room pressure and with a 100/200 ml/min flow of H₂/O₂ on the anode and cathode side, respectively. A 10-minute equilibration was applied to reach a steady state of the catalyst under each of the potential conditions. The acquisition of each spectrum lasted about 60 min.

Ex situ XAFS measurements were carried out in transmission mode under ambient conditions at the Synchrotron Light Laboratory ELETTRA (Trieste, Italy), 11.1 XAFS beam line, in the energy range of 11.45-12.80 keV for Pt L₃-edge and 7.60-8.90 keV for Co K-edge. The acquisition of each spectrum lasted about 30 min.

The sampling procedure in fluorescence and transmission modes was chosen so as to yield high-quality data for both pre- and post-edge background analyses used to normalize the spectra. The noise level and the quality of the XAS data obtained *in situ* using the PEMFC XAS set-up are also shown and discussed in comparison with standard measurements in Refs [Principi, E.; Di Cicco, A.; Witkowska, A.; Marassi, R. J. Synchrotron Radiation 2007, 14, 276281]. The experimental data were analyzed in the near-edge and extended XAFS regions.