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Performance of a fuel cell optimized for *in situ* X-ray absorption experiments

Emiliano Principi,[a]* Andrea Di Cicco,[a,b] Agnieszka Witkowska[a,c]‡ and Roberto Marassi[d]

[a]CNISM, CNR-INFM CRS SOFT, Dipartimento di Fisica, Università di Camerino, I-62032 Camerino (MC), Italy, [b]IMPMC-CNRS UMR 7590, Université Pierre et Marie Curie, 140 rue de Lourmel, 75015 Paris, France, [c]Department of Solid State Physics, Gdansk University of Technology, 80-952 Gdansk, Poland, and [d]Dipartimento di Chimica, Università di Camerino, I-62032 Camerino (MC), Italy. E-mail: emiliano.principi@unicam.it

A commercial fuel cell has been successfully modified to carry out X-ray absorption spectroscopy (XAS) measurements under optimized *in operando* conditions. The design is conceived for the performance of XAS experiments in transmission mode over a wide range of X-ray energies above 6 keV, owing to the reduced absorption of the cell. The wide angular aperture allows the collection of XAS in fluorescence mode and of X-ray diffraction patterns when needed. Details of the design of the cell and its performances are given. The quality of the extended X-ray absorption fine-structure spectra under working conditions has been verified at the ESRF and ELETTRA synchrotron radiation facilities, showing that relatively fast and low-noise transmission measurements on electrodes over a wide range of catalyst concentrations and energies are feasible.

Keywords: *in situ* XAS; fuel cell.

1. Introduction

Fuel cells are promising sustainable energy systems which may replace most current combustion systems in various energy end-use sectors in the long term. There are several types of fuel cell which have been developed and undergone commercial development (Larminie & Dicks, 2003; Markovic & Ross, 2000; Steele & Heinzel, 2001). One of the most important and universal is the proton exchange membrane (PEM) fuel cell (Scott & Shukla, 2004; Ralph & Hogarth, 2002*a*,*b*). Owing to its numerous advantages, the PEM fuel cell is a viable choice for portable power, automobile and residential applications.

Many efforts are currently devoted to the study of metallic electrocatalysts in order to improve the performances of PEM fuel cells and to reduce their cost, mainly by reducing the amount of noble metals in nanocatalysts.

Characterization and understanding of the catalyst structure and properties is recognized as a forefront research activity for improving performances and reliability of the fuel cells. In this context, X-ray absorption spectroscopy (XAS) (Koningsberger & Prins, 1988; Filipponi *et al.*, 1995) is a powerful tool providing unique information on the local atomic arrangement around selected catalytic metal sites and their average oxidation state (Russell & Rose, 2004). Moreover, XAS measurements can be realised at synchrotron radiation facilities under actual fuel cell working conditions. Nevertheless, owing to the background absorption of the cell components and to the low mass content of metal catalysts, reliable and high-quality data can only be obtained using specially designed fuel cells and an optimized experimental set-up.

In the literature, electrochemical cells specially designed for XAS (McBreen *et al.*, 1987; Herron *et al.*, 1992 Maniquet *et al.*, 2000) and modified for transmission and fluorescence XAS (Viswanathan *et al.*, 2002; Roth *et al.*, 2002; Wiltshire *et al.*, 2005) have been described. In all cases, cell elements were conceived to reduce the background absorption owing to the various components of the cell.

For example, in a particular cell design for XAS (Viswanathan *et al.*, 2002) in transmission mode, the graphite plates were thinned to about 4 mm in a small rectangular X-ray window, a solution also used by other authors (Roth *et al.*, 2002, 2005). This solution was found to give good results for collecting near-edge absorption data (Pt L_3-edge) but the absorption background is still very high for collecting low-noise EXAFS spectra, especially for catalysts with low atomic number and for metal loading below 1 mg cm^{-2}. However, a typical noble metal loading for a promising electrocatalyst is below 0.3 mg cm^{-2} and under these conditions *in situ* XAS measurements can be carried out in fluorescence mode. We are aware of only one *in situ* fluorescence study of a PEM fuel

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‡ Present address: CNR-ISM, Via del Fosso del Cavaliere 100, 00133 Roma, Italy.

cell (Wiltshire *et al.*, 2005), using a 1.5 mm thin graphite X-ray window in a miniature fuel cell.

In this work we present a modified fuel cell for XAS measurements under *in situ* conditions, with the specific aim of realising a more efficient device for this purpose. The original design of the cell is conceived for the performance of low-noise XAS experiments in transmission mode, as well as for the collection of XAS in fluorescence mode and of X-ray diffraction patterns, over a wide range of X-ray energies and metal loading. The paper is organized as follows: in §2 we report on the design and expected performances of the cell; in §3 we discuss important details of the XAS set-up, and some examples of typical *in situ* XAS measurements collected using this set-up at the ESRF and ELETTRA facilities are presented; §4 is devoted to the conclusions and perspectives of the present work.

2. Design and performances of the XAS PEM fuel cells

The basic need for *in situ* X-ray investigations of active materials in fuel cells is to reduce the background absorption owing to the various components of the cells. If we focus our attention on investigations of the valence and structure of metals participating in the catalytic process, severe restrictions are imposed on the thickness of the electrodes and membranes used in the construction of the cell. Most of the commercially available PEM fuel cells must be modified for this purpose, by designing suitable windows for X-ray investigations in the body of the cell. In fact, metal shields and thick graphite plates (at least of the order of 10 mm) usually do not allow photon transmission at energies below 20 keV, while the amount of catalyst is usually too low for obtaining low-noise XAS measurements in transmission mode. In order to perform low-noise XAS measurements in transmission mode, we have modified an EFC-05-02 (Electrochem) fuel cell with the specific aim of achieving high transmission rates for photon energies in the 5–15 keV energy range, where most of the core levels of the metals used in the catalytic process are located.

The basic characteristics of the commercial fuel cell are the presence of two isotropic graphite separator plates, a 5 cm^2 active area (serpentine flow pattern) and two gold-plated current collectors. The graphite plates are held together by eight screws, inducing a high enough compression on the membrane electrode assembly (MEA) and providing a good electrical contact.

The EFC-05-02 cell has been modified to have thin graphite windows for maximum X-ray transmittance, still being light- and gas-tight. The overall thickness of the graphite was carefully thinned by drilling truncated prism-shaped holes, up to 0.25 mm in thickness, over a flat 1 mm × 7 mm area, providing a double window for XAS in transmission mode and possible X-ray fluorescence and X-ray diffraction measurements owing to the wide angular acceptance ($\sim$100° on the beam plane, $\sim$5% covered solid angle), as shown in Fig. 1. The X-ray window is positioned to be parallel (y) and in correspondence (z) with the serpentine channels (width 0.8 mm) in order to minimize absorption. This allows XAS measurements under standard conditions at EXAFS beamlines, using a typical beam size of $\sim$0.4 mm × 5 mm (see §3). The position of the cell with respect to the beam can be easily changed, thus obtaining the best geometry requested by the experimental technique used.

As shown in Fig. 2, the calculated transmittance of the graphite windows and of the Nafion membrane strongly limits the energy window available for X-ray absorption studies. In particular, two 4 mm graphite windows (see Viswanathan *et al.*, 2002; Roth *et al.*, 2002, 2005) limit the available X-ray range above 10 keV (transmittance is below 10% at the Pt L_3-edge). Therefore, using a proper drilling geometry, graphite can be safely machined up to the hundreds of µm thickness range. The 250 µm thin graphite windows used in this work have been found to match the requirements of tightness and mechanical stability necessary for a smooth operation of the fuel cell and to increase transmittance significantly (*e.g.* for 10 keV up to 80%, see Fig. 2). At the same time the absorption of typical PEMs is comparable with that of the graphite windows, so, for experiments at low energies, both absorption components must be accounted for. The calculated transmittance for typical membranes (Nafion N-117 and Nafion N-115 by DuPont; see also Oberbroeckling *et al.*, 2002) is also shown in Fig. 2. Absorption of Nafion was tested at fixed energy in our in-house X-ray laboratories (Di Cicco *et al.*, 2006). Other

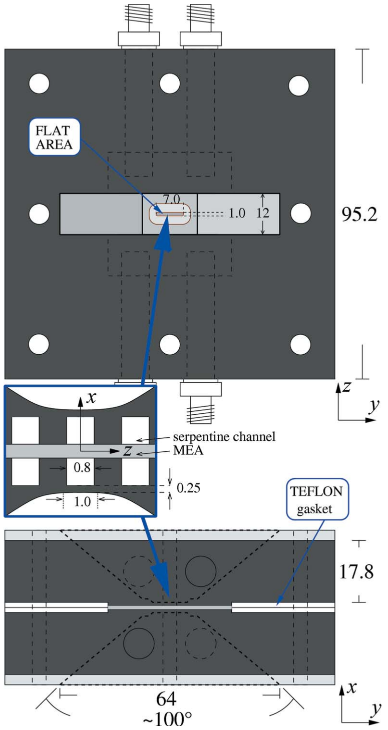

Figure 1
Design for a fuel cell optimized for *in situ* X-ray absorption measurements (front and side views, dimensions given in mm). The front view shows the perforation of the graphite electrode for reducing the X-ray absorption while saving space for the inlets and paths of the fuel (hydrogen and oxygen). The minimal thickness of each graphite plate is reduced to about 0.25 mm, thus minimizing the absorption along the X-ray path (x, see inset). The side view shows the wide angular aperture allowing for possible X-ray diffraction and X-ray fluorescence measurements, as well as the positioning of the MEA inside the cell.

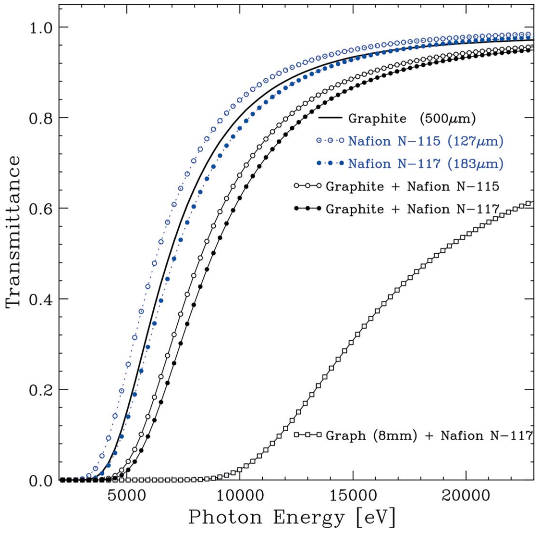

Figure 2
Transmittance of the fuel cell as a function of the photon energy, considering the major sources of background absorption: graphite, Nafion membrane. The reduced thickness of graphite allows us to perform *in situ* XAS measurements of metal catalysts at energies well below 10 keV.

possible sources of absorption under working conditions, namely gases and water flowing into the gas channels and impregnating the membranes, and the background absorption owing to the gas diffusion layers and catalysts layers, have been found to be practically negligible in the energy region of interest.

Fig. 2 shows that the present fuel cell gives more than 50% transmission at 9 keV. The use of thinner Nafion membranes (Nafion N-115, 127 μm) improves transmission at low energies and we can easily arrive at transmissions of around 10% at 6 keV. Using this fuel cell prototype, XAS measurements can be performed in transmission and fluorescence mode for a wide selection of catalyst materials (atomic numbers above $Z = 23$).

3. *In situ* XAS measurements

3.1. Fuel cell set-up for XAS experiments

The XAS fuel cell described in §2 has been tested during dedicated beam time at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and ELETTRA Synchrotron Light Laboratory (Trieste, Italy). In Fig. 3 we show a typical set-up used for *in situ* XAS experiments in transmission mode both at the BM29 (Filipponi *et al.*, 2000) (ESRF) and XAFS 11.1 (ELETTRA) beamlines. The fuel cell has been positioned and aligned along the beam with motorized translation stages, in a standard transmission configuration including a reference sample for precise monitoring of the energy calibration. The cell was operated by connecting its inlets to oxygen and hydrogen gas lines working at 1.2 bar and using specially designed heating and gas humidification systems (the gas flow was set to ~100 ml min^{-1}). The voltage output was remotely controlled by a computer-driven potentiostat/galvanostat and measured and stored continuously during XAS data acquisition. The cell worked in the temperature range 293–353 K, heated by a power supply as shown in Fig. 3. The designed heating system allowed us to control the cell temperature and fuel gases temperature separately (to optimize better the relevant working conditions of the fuel cell).

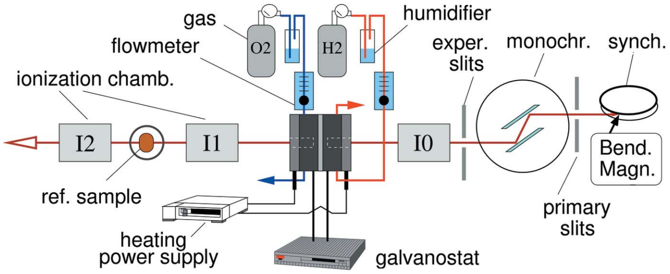

Figure 3
Typical set-up for XAS experiments on fuel cells under operating conditions.

MEAs were prepared for XAS measurements using various types of materials as a cathode catalyst (with typical loading of about 1.0 mg cm^{-2}), Nafion N-117 as a proton-conductive membrane and Pd (30% Pd/Vulcan XC-72 powder, Pd loading 1.0 mg cm^{-2}) as an anode catalyst. Use of a Pd counter electrode (like in Viswanathan *et al.*, 2002; Wiltshire *et al.*, 2005) was preferred to the removal of the counter electrode in the X-ray beam window region (Roth *et al.*, 2002, 2005) in order to avoid perturbations of the electrical field and current distribution on the catalyst under consideration. MEAs were stored in distilled water prior to insertion in the fuel cell. Each fresh MEA, before XAS measurements, was conditioned at working temperature and at a voltage of ~0.5 V for 15 min, and then rapid electrochemical cycles were performed to check cell performances. Finally, for each potential condition, a 10 min equilibration time was applied to reach a steady-state of the catalyst.

The prototype of the cell installed on a motorized stage at BM29 (ESRF) is shown in Fig. 4. The cell is shown without heating unit for better visualization of the details, and is fully connected to the gas supply and potentiostat systems. The wide angular acceptance of the X-ray windows, useful for possible X-ray fluorescence and X-ray diffraction measurements, can be appreciated in the figure. Alignment of the X-ray window of the cell along the beam (x axis) has been performed using yz precise motorization and fluorescent screens.

3.2. Details of XAS experiments

As mentioned above, XAS experiments on working MEAs and on some reference samples have been performed at ELETTRA (XAFS 11.1 station) and at the ESRF (BM29) using a double-crystal monochromator equipped with Si(111) and Si(311) crystals, respectively. Successful measurements have been performed at the Pt L_3- and L_2-edges (11564 eV and 13273 eV, respectively) and at the Co K-edge (7709 eV) with metal loading even below 1 mg cm^{-2} (see following

Figure 4
Photograph of the prototype of the fuel cell during dedicated synchrotron radiation beam time at ESRF (BM29). The fuel cell has been tested under operating conditions for various working temperatures ($293 < T < 353$ K), and used in different experiments at synchrotron radiation facilities (ESRF, ELETTRA).

section) under ambient conditions and at higher temperatures, up to optimal PEM fuel cell working temperature (cell temperature 353 K; gas temperature 346 K). Potential-dependent XAS measurements have been focused mainly on the cathode activation region, $E \in (0.8; 1.0)$ V. XAS measurements at ESRF and ELETTRA were typically conducted using an integration time of 1 or 2 s per point (average ring current 75 mA and 200 mA, respectively). Each XAS measurement, lasting about 1000–2000 s, was repeated twice and averaged (giving a final integration time per point of 2 or 4 s) for successive elaboration.

Current beamlines in advanced synchrotron radiation facilities can easily provide intense and stable X-ray beams on samples of limited size. Considering the dimensions of the internal serpentine channels and of the X-ray window, we see that the present fuel cell offers an area of about 0.8 mm × 7 mm where the background absorption is minimized and spatially homogeneous, both very crucial aspects for performing reliable low-noise XAS measurements in transmission mode.

The position of minimum background absorption can be found using a simple alignment procedure, requiring precise yz motorization. The optimal beam dimensions for XAS experiments with a homogenous sample are limited by the size of the channels in our cell. Typically we used a 0.4 mm (vertical) × 5 mm (horizontal) aperture, fitting the size of the X-ray window of the fuel cell. Particular care has been taken for checking homogeneity and positioning of the beam in the channel with thinner windows (see Fig. 1). We emphasize that proper alignment of the cell is crucial for obtaining high-quality XAS data.

3.3. XAS results

In this work we shall focus our attention on the quality of XAS spectra obtained on a standard Pt cathode catalyst (20% Pt/Vulcan XC-72 powder, Pt loading 1.0 mg cm^{-2}) working at different temperatures. Moreover, preliminary measurements carried out *in situ* on a low metal loading PtCo cathode catalyst at room temperature are also presented. These spectra can be taken as an example of the performances of the fuel cell prototype.

In Fig. 5 we show a typical L_3-edge X-ray absorption spectrum collected at the XAFS 11.1 beamline (ELETTRA) on a standard Pt-based cathode working at 293 K, inside the fuel cell prototype (Pd-based counter electrode) under open-circuit voltage conditions (OCV; $U \simeq 1$ V). The absorption discontinuity is of the order of 0.1, as expected for this metal loading. The noise level, for a typical integration time of 2 s per point, is in the 10^{-4} region in the whole energy range under investigation, approaching that of standard samples measured without any sample absorbing environment. The noise level was evaluated using standard routines within the *GNXAS* suite of programs (Filipponi & Di Cicco, 1995, 2000). The noise level associated with other sample conditions, like different temperature, cell potential or different catalysts in the same loading range, has been found to be very similar to those presented here. We point out also that during operation, especially at high temperatures, we occasionally observed the presence of step-like features in the absorption spectra, which we identified tentatively as due to the presence of water bubbles trapped in the serpentine paths for a limited period of time. This effect can be avoided by positioning the beam

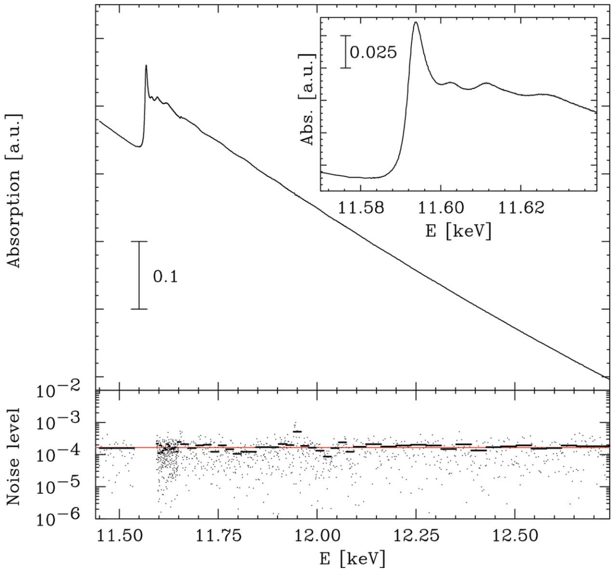

Figure 5
Upper panel: typical quality of the *in situ* XAFS measurement on a Pt cathode catalyst (20% Pt/Vulcan XC-72 powder, Pt loading 1.0 mg cm^{-2}) working at 293 K and under open-circuit voltage conditions. Beam size: 0.4 mm × 5 mm; integration time per point: 2 s. Lower panel: estimated noise level as a function of the energy of the raw XAS spectrum shown in the upper panel.

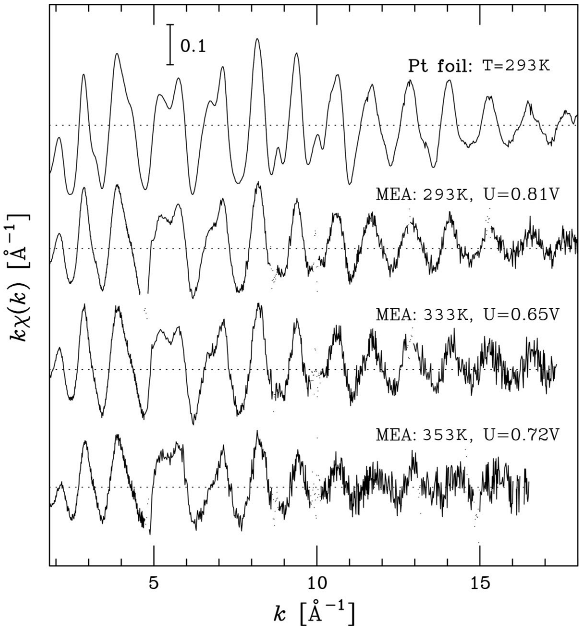

Figure 6
Comparison between EXAFS signals obtained from a Pt foil and *in situ* MEA (cathode: 20% Pt/Vulcan XC-72 powder, Pt loading 1.0 mg cm^{-2}; anode: 30% Pd/Vulcan XC-72 powder, Pd loading 1.0 mg cm^{-2}) at different temperatures and cell potentials. *In situ* measurements have been obtained with a beam size of 0.4 mm × 5 mm and an integration time per point of 4 s. The dotted lines serve as a guide to the eye.

outside the serpentine paths when much higher absorption from graphite can be tolerated.

Three EXAFS spectra of the MEA described above at three different temperatures are reported in Fig. 6. They are compared with the raw data collected for a 5 µm Pt foil (upper curve) at ESRF (BM29). While the noise level is obviously higher owing to the reduced absorption discontinuity, well defined EXAFS oscillations associated with the catalysts powders are measured *in situ* within reasonable collection times also at the optimal cell operating temperature (T = 353 K). The EXAFS amplitude reduction, noticeable in the MEA signal, is mainly related to the nanometric size of the catalysts.

In order to test the X-ray transmittance of the cell at energies below 10 keV, a 20% PtCo (1:1)/Vulcan XC-72 (Pt loading 0.6 mg cm^{-2}, Co loading 0.2 mg cm^{-2}) nanopowder has been used as the cathode electrocatalyst. Preliminary XAS measurements carried out at both the Co K-edge and Pt L_3-edge under working conditions (OCV) at room temperature are shown in Fig. 7 (2 s per point acquisition time). The noise level of the data is in the same range as shown in Fig. 5 but, owing to the low catalysts loading corresponding to a small Co K-edge discontinuity (jump 0.03), the corresponding EXAFS signal is obviously more noisy. The quality, however, is very good and data can be safely analysed under those conditions. These findings are very promising for future more accurate investigations on recent non-noble low-Z metal-based catalysts.

Of course, a detailed structural analysis of the EXAFS spectra of the distribution of nanocrystalline catalyst powders needs application of quite sophisticated data-analysis methods beyond the scope of the present work and discussed elsewhere (Witkowska *et al.*, 2007). As an example, see a review of previous applications of EXAFS to fuel cells (Russell & Rose, 2004). As the final aim of this research is the collection and understanding of reliable and low-noise XAS spectra of metal catalysts in a fuel cell, we only stress here that another crucial aspect to be considered, besides the realisation of an efficient fuel cell, is a proper knowledge of the distribution of nanocrystalline particles. In fact, homogeneity and particle size distribution on the electrodes are known to affect collected data, and their knowledge through scanning electron microscopy, transmission electron microscopy and X-ray diffraction is essential for reliable investigations of the local structure (Witkowska *et al.*, 2006).

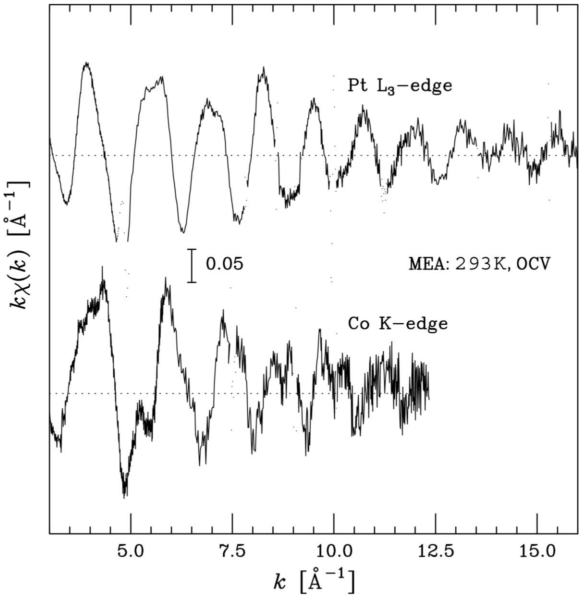

Figure 7
Preliminary *in situ* measurements on 20% PtCo (1:1)/Vulcan XC-72 cathode electrocatalyst at room temperature. EXAFS signals after Pt L_3-edge (11564 eV) and Co K-edge (7709 eV). Pt loading: 0.6 mg cm^{-2}; Co loading 0.2 mg cm^{-2}. Integration time: 2 s per point. The dotted lines serve as a guide to the eye.

4. Conclusions

In this work we have presented an original PEM fuel cell optimized for *in situ* X-ray experiments, designed to achieve unprecedented X-ray transmission capabilities. The design allows XAS experiments in transmission mode over a wide range of X-ray energies above 6 keV, owing to the reduced absorption of the cell. Moreover, the X-ray window has a wide angular acceptance, which allows the performance of *in situ* X-ray fluorescence and X-ray diffraction experiments. Details of the technical solutions and expected performances have been given, showing several improvements with respect to previous works. The cell has been realised in our laboratories and tested at synchrotron radiation facilities (ESRF, ELETTRA), showing that its performances are particularly suitable for detailed *in situ* structural analysis of metal catalysts. In particular, a noise level in the 10^{-4} range has been obtained for XAS measurements in transmission mode on a Pt-based electrode inside a working fuel cell. Successful measurements have been obtained *in situ* also at the Co *K*-edge, confirming the high transmittance of the cell at low X-ray energies. To the best of our knowledge, the performance of this cell allows collection, in a reasonable length of time, of XAS spectra of unprecedented quality for relatively low metal concentrations. We believe that, by taking advantage of the cell and of the improvements in the experimental conditions, it will be possible to obtain key structural information about possible structural and chemical modifications occurring at catalytic sites as a function of the operating conditions.

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