Experiment Report Form

	Experiment title: Kinetics of the electrocatalytic mechanisms of water spitting by IrO2: an in-situ dispersive XAS investigation	**Experiment number:** CH-4090
Beamline: ID24	**Date of experiment:** from: 03/03/2014 to: 11/03/2014	**Date of report:** 10/09/2014
Shifts: 18	**Local contact(s): Giovanni Agostini**	*Received at ESRF:*

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Report:

This experiment goal was to perform time-dependent and in-situ XAS measurements on iridium oxide (IrO_x) layers for electrochemical processes of importance in the field of energy conversion.In this experiment, aming at studyng the kinetiks and mechanisms of the different reactions taking place at the elecrode, dispersive-XAS data were collected at ID24 beamline (European Synchrotron Radiation Facility, ESRF, Grenoble). The energy calibration was made by measuring the absorption spectrum of a Pt foil (Pt-L_{III}: 11564 eV; Ir-L_{III}: 11215 eV). To avoid distortions of the spectra, the count rate of each element of the detector is kept well below the saturation limit. Series of 10000 and 20000 spectra were acquired in 116 and 232 seconds respectively (each single spectrum is registered every 0.0116 s), after havinge appied a potential jump as detailed below. Averages were calculated every 10 spectra in order to obtain a better signal to nois ratio: this gives a final time resolution equal to 0.116 s. The experiment was repeated with two different kinds of electrolyte (0.5 M aqueous H_2SO_4 and 0.5 M aqueous NaOH) with the application of different potential jumps (both in oxidation and in reduction). All measurements were carried out at room temperature. The experiments were conducted controlling the electrochemical instrumentation similar to that used in exp. CH3511 from the control room. In all experiments, EXAFS spectra have been recorded after the sample is kept at E1 for about 12 0s and the acquisition and the potential jump were synchronized by means of a TTL signal.Data processing consists of a preliminary stage, in which spectra are normalized, and a subsequent analysis aimed studying the kinetics of the processes involved. The analysis is based on three major steps: (i) fitting of the sequences of normalized

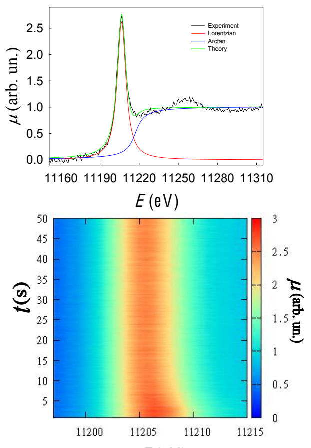
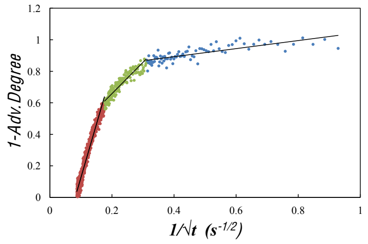


Figure 1: Ir L_{III} spectrum of the raw material (above) and its varition vith time after a



spectra, (ii) calculation of the advancement degree and (iii) estimation of a kinetic law and of the diffusion coefficient associated. In the preliminary stage, each XAS spectrum of every series was normalized by (i) calculating a pre edge and a post edge functions with a straight line or a cubic function and (ii) normalizing to unit jump in the absorption coefficient at the edge, via the PRESTOPRONTO code. The calculated pre and post edge functions were the same for all spectra of a single sequence. The fitting step of the data analysis was carried out by means of MINUIT program. Fig. 1 shows the Ir-L_{III} XANES spectrum of the IrO_x electrode at an applied potentiential of 1 eV. The spectrum is mainly constituted (apart from EXAFS oscillations that are clearly apparent above the noise level) by a White Line (WL) that is due to transition from 2*p* to empty 5*d* states, and an artangent step that accounts for transitions from the 2*p* to continuum states. Both these features directly reflect the local electronic structure around the photoabsorber. The main spectral features are fully caught in Fig. 1 and the spectra collected in different conditions display sensible variations thereof. Indeed, in Fig. 1 the variations in the XANES structure are plotted vs. time after the application of a step in the applied potential from 1 to 0.3 eV. It is apparent that the spectra move towards low energy, indicating an overall reduction of Ir from Ir(IV) to Ir(III) and the WL FWHM decreases, in agreement with previous findings. The process appears to be concluded after 10 s. The data presented in figure 1 allow extracting the pertinent kinetics parameters. First, the advancement degree was then calculated both on the basis of the Lorentzian position and on the basis of the Lorentzian width. When plotted vs. time, the advancement degree, shows an immediately detectable parabolic behaviour: this is typical of diffusion driven processes. On the other hand, the common understanding for the redox processes involving the IrO_x material is that the rate determining step of the reaction is the diffusion of H^+ ions in the electrodic moiety. According to the Fick's laws, a plot of the concetration $N(l,t)$ *vs.* $(1/\sqrt{t})$ should then give a straight line and, assuming $n_0 = 0$, the diffusion coefficient can be obtained by the slope as: $D = \frac{l^4}{4\pi(slope)^2}$. This plot is shown in Fig. 2, evidencing the presence of three different processes, all of them being diffusion limited. In particular: i) at the beginning the reaction is quite fast, with a diffusion coefficient of ca. 10^{-6} cm^2s^{-1}. This figure is of the same order of magnitude of the H^+ diffusion coefficient in acqueous solutions at RT. Thus, we can safely attribute this first and fast process to the diffusion of H^+ inside the pores and channels of the highly hydrated IrO_x material; ii) this fast diffusion driven process rapidly sets stationary conditions between the solution that is trapped in the pores of the electrodic material and the rest of the solution. After these stationary conditions are established, diffusion in the pores and channels of IrO_x cannot take place any more and other diffusive processes control the reaction kinetics. These processes can be attributed to the diffusion of H^+ in and outside IrO_x. In more details, for intermediate advancement degrees, the reaction follows a diffusive mechanism with *D* of *ca.* 10^{-7} cm^2s^{-1}, while at the end of the reaction the kinetics is limited by *D ca.* 10^{-9} cm^2s^{-1}. Both these values are compatible with what reported in the literature for the diffusion of H^+ in the IrO_x moiety, but these different figures show that this diffusion can follow "easy" and "difficult" paths during the course of the reaction as different Ir sites can be available at different advancement degrees. For each potential jump considered, the experiment has been repeated more than once on the same sample or on samples of the same kind in order to check for the reproducibility of the results. The diffusion coefficients for the three processes are very similar for all the measures and average values are reported in the table below.

0.2 → 1.05 V		**1.05 → 0.2 V**	
1° process	**3.7(4) 10^{-7}**	**1° process**	**3(1) 10^{-6}**
2° process	**5.23(9) 10^{-8}**	**2° process**	**1.0(1) 10^{-7}**
3° process	**6.816(9) 10^{-9}**	**3° process**	**1.89(2) 10^{-8}**
1.05 → 1.3 V		**1.3 → 1.05 V**	
1° process	**1.1 (7) 10^{-5}**	**1° process**	**1(2) 10^{-2}**
2° process	**5.6(3) 10^{-8}**	**2° process**	**9.6 (1)10^{-8}**
3° process	**1.44(2) 10^{-8}**	**3° process**	**1.079(7) 10^{-9}**