ESRF	**Experiment title.** Structural modifications in MnO_2 during H+/e- electrochemical insertion in alcaline electrolyte	**Experiment number:** CH137,
Beamline: BM16	**Date of Experiment:** from: 23- to: 28 octobre 1996	**Date of Report:** november 8 1996
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Names and affiliations of applicants (*indicates experimentalists):

C. Poinsignon*, LEPMI-ENSEEG Grenoble (F)
B. Legorrec, "
J.P. Diard, " "
L. MacLean*, Middlesex University London (UK)

Report The structural modifications study occuring during the in situ reduction of a Chemically prepared Manganese Dioxide (CMD) was performed on BM16 with a 20keV incident energy and a 0.62Å associated wavelength over a 7-50° 2 theta angular range. The beam size at the sample was 0.2mm and the detector system was a multi analyser.With this high energy synchrotron radiation after 20 minutes a well resolved pattern is gained (fig lb) and after 10 minutes with a lower statistics but enough precise to detecte a small structural modification induced by the electrochemical reduction under potentiostatic insertion of H+/e- couple with a scan rate of 10mV/2hours. The electrochemical cell was adapted precisely to the shape of the goniometer plate, in order to carry out the pattern in reflection mode. The working electrode: a plastified CMD thin film electrode, lies in the reflection plane, above the electrolyte (KOH 1N) the reference and counter electrodes. The three electrodes are connected to a potentiostat and a transfer function analyser to controll the reduction potentiostatically.

Figure 1 provides a comparaison between XRD pattern of CMD with synchroton radiation and $FeK\alpha$ of a Siemens D500. The corresponding XRD recorded on classical diffractometer using $FeK\alpha$ exhibit broad lines. A well resolved XRD pattern takes 48 hours to be recorded with a good statistic on a restricted angular range.

The good line profil determination given by BM16 allows to check an immediate evolution of the XRD pattern in terms of angular position displacement and broadening of FWHM after the first potential step of reduction. Figures 2 and 3 present the evolution of the angular position 2theta and FWHM of (221/241)lines with time and reduction rate respectively. The MnO_2 and MnOOH XRD are given on Figure 4 confirming the reduction well occurs among the topotactic reaction $MnO_2 + H^+ + e^- \text{----> } MnOOH$ by H+/e- insertion.

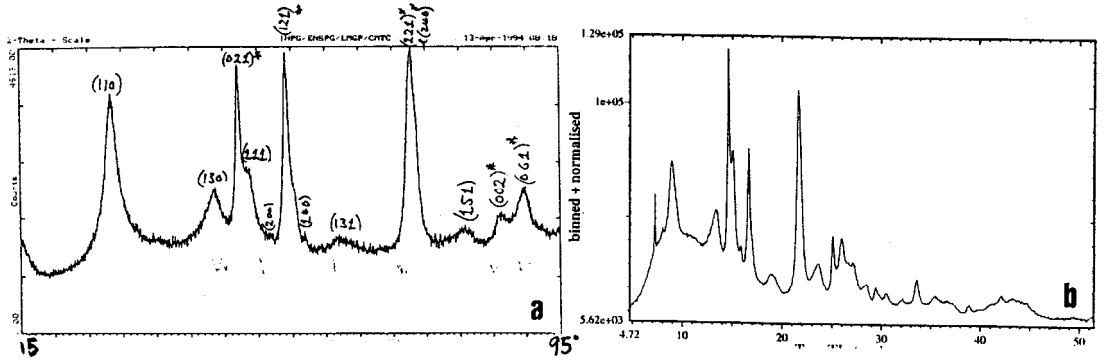

Figure 1: XRD patterns of MnO_2 sample recorded a) on a Siemens D500 with $FeK\alpha$ after 24hours, b) with a 0.62Å (20 keV) synchrotron radiation on D16 after 20 minutes.

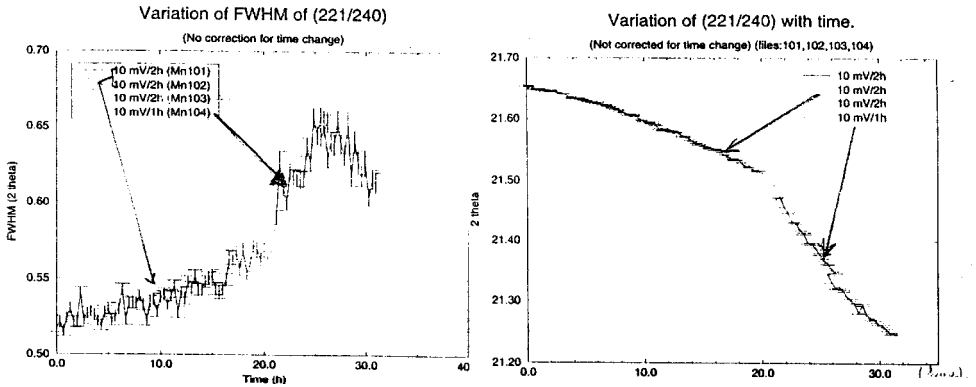

Figure 2: Evolution of the angular position 2theta and FWHM of (221/241) lines versus time: the potential scan rate is l0mV/2h during the first part and l0mV/h during the second part.

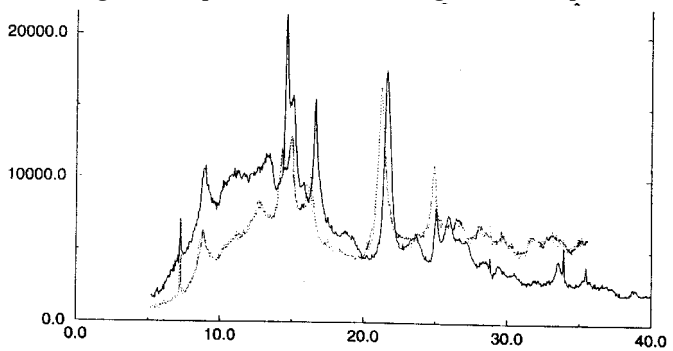

Figure 4: XRD patterns of MnO_2: and MnOOH: the end product of topotactic reduction by H+/e- insertion.

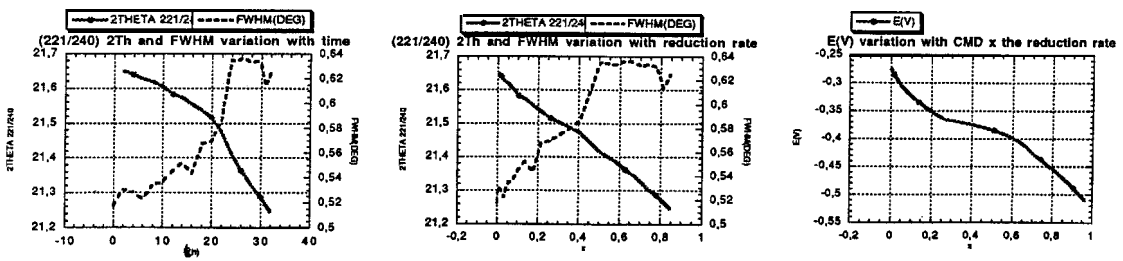

Figure 3: Evolution of the angular position 2theta and FWHM of (221/241) lines versus time and reduction rate.