In situ STXM: Studies of Wet Electrochemical Systems under Potential Control

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Scanning transmission X-ray microscopy (STXM) has great potential for studies of *in situ* modification of samples, since the photon in / photon out character provides the capability to penetrate through complex structures such as electrodes, electrolytic solutions, and support layers. Here we report the first *in situ* measurements with scanning transmission X-ray microscopy (STXM) of an active electrochemical cell. The system used to develop *in situ* electrochemical STXM is an electrochromic layer of polyaniline The electrochemical STXM wet cell (Fig. 1) consists of an electrodeposited polyaniline (PANI) thin film on a thin Au film covered by an overlayer of 1 M HCl solution sitting between two X-ray transparent silicon nitride windows. X-ray absorption images and spectra of the PANI film under potential control were acquired using the beamline 5.3.2 STXM at the Advanced Light Source. The chemical state of the polyaniline film was reversibly converted between reduced (leucoemeraldine) and oxidized (emeraldine chloride) states by changing the applied potential. The electrochemical changes were monitored by spatially resolved C 1s and N 1s X-ray absorption spectroscopy (Fig. 2). Electrochemical state imaging (differences between images at two energies at different potentials) monitors the electrochemical changes of the polyaniline film. Kinematic studies in the sub second regime are demonstrated (Fig. 2). Extension of *in situ* electrochemical STXM to other electrochromic systems, and to situations such as displays where transverse fields are required, will be discussed.

1) D. Guay, J. Stewart-Ornstein, X. Zhang and A.P. Hitchcock, Analytical Chemistry (2005) in press
2) Research supported by NSERC, the Canada Research Chair program. ALS is supported by DoE (DE-AC03-76SF00098).

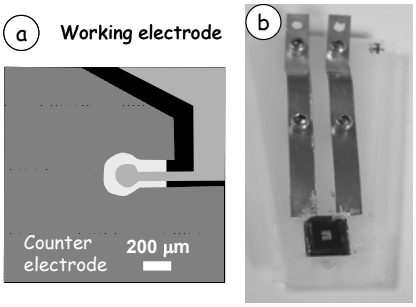

Fig 1 (a) Details of the 2-electrode cell used for STXM with *in situ* potential control. The chemical state of polyaniline electro-deposited on the working electrode is varied by potentials applied via the spring contacts (b)

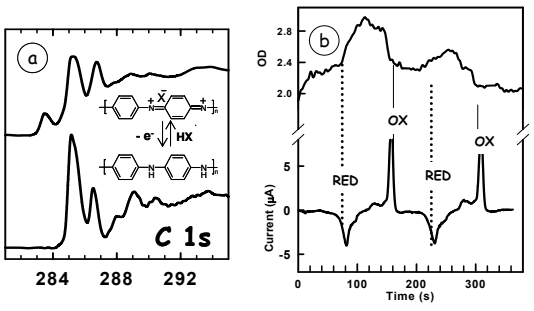

Fig. 2 (a) C 1s spectra of the oxidized (upper) and reduced (lower) states of polyaniline. (b) (upper) Optical density changes at 283.6 eV (quinoid pi*) tracked in concert with cyclic voltammetry (CV). (lower) current flows in CV.