Synchrotron-based in situ soft X-ray microscopy of Ag corrosion in aqueous chloride solution

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Abstract. In this paper we report an in situ X-ray microscopy study of a model metal electrochemistry system, incorporating faradaic reactivity: the anodic corrosion and cathodic electrodeposition of Ag in aqueous systems. The information at sub-µm scale about morpho-chemical evolution of the electrified interface, provided by this novel electroanalytical approach fosters fundamental understanding of important issues concerning material fabrication and stability, which are crucial in developing the next generation electrochemical technologies, such as fuel cells and biosensors. The key methodology challenge faced in this pilot electrochemical experiments is combining a three-electrode configuration and wet environment, which required metal electrodes suitable for transmitting soft X-rays and a sealed cell allowing working in high vacuum. This has been solved via lithographic fabrication route fabricating 75 nm thick Ag electrodes and using Si₃N₄ membranes as X-ray windows and electrode support. Imaging in the STXM mode with phase contrast allowed us to monitor the corrosion morphologies and metal outgrowth features. Localised thickness variation and the build-up of reaction products of electron density different from that of the starting material have been detected with high sensitivity.

1. Introduction

In situ electrochemical synchrotron-based soft X-ray transmission spectromicroscopy has been recently considered as an advanced electroanalytical tool combining nanoscopic capability with chemical and structural sensitivity, typical of X-ray spectroscopies. In addition, working with beam energies in the range encompassing the water window, opens up the investigation of dynamic processes in aqueous solution (see [1] and references therein contained). To the best of our knowledge - before our approach developed at the TwinMic beamline - the only electrochemical STXM work reported in the literature is [2], where the redox behaviour of polyaniline is studied in a two-electrode cell. This paper reports the first achievements of a long-term collaboration project between the X-ray Microscopy Section of ELETTRA and the Electrochemistry Group of Salento University, aimed at developing a unique in situ spectromicroscopy tool for the fundamental investigation of material degradation processes, that are critical for advanced electrochemical technologies: chiefly fuel cells. In order to prove the feasibility of the target electrochemical experiments, we focused on a widely-investigated - though still warranting research efforts - electrochemical system: the Ag/Ag⁺ couple in aqueous Cl⁻ [1].

2. Experimental

The electrochemical cell was fabricated in collaboration between the TwinMic beamline at Elettra and TASC/INFM lithography group. The construction consists of two main parts, depicted in Figure 1.
Figure 1.1 - Electrode assembly, containing: four square Ag electrodes (5 nm Cr adhesion layer and 75 nm Ag top layer) A; cross-shaped electrolyte compartment B; X-ray transparent Si$_3$N$_4$ C1 membrane onto which the electrodes A are deposited and confining the electrolyte present in the compartment B; Si frame D1, providing mechanical resistance of the cell body and support to the Si$_3$N$_4$ membrane. Figure 1.2 - Cell cover, consisting of the second optical window C2, supported by the Si frame D2. A cross-sectional view of the way the electrode-membrane (Figure 1.1) and the cover-membrane (Figure 1.2) are assembled is shown in Figures 1.3A and 1.3B. The process-flow for the fabrication of the electrodes comprised the following steps: (i) chemical vapor deposition of a 100 nm thick Si$_3$N$_4$ layer on both sides of a bare Si(100) wafer; (ii) opening of the optical window on the back side of the wafer by selective dry etching of the Si$_3$N$_4$ layer through a photoresist mask, removal of the mask by hot acetone, followed by wet etching in hot KOH of the Si down to the nitride layer on the opposite side, and thorough rinsing in deionised water; (iii) integration of four metal electrodes by properly masking the nitride side of the wafer and consecutive deposition of Cr and Ag. The X-ray beam crosses the electrode/electrolyte assembly normally to the optical windows C1 and C2 and the transmitted X-rays are monitored by the detector placed behind the cell. The electrolyte employed in this study was 0.02 M NaCl aqueous solutions in ultra-pure water (resistivity of 18.5 MΩ cm). Potentiostatic and galvanostatic experiments were performed in a conventional three-electrode configuration (see [1] for details).

The experiment was performed using the European twin X-ray microscopy station operating TwinMic at ELETTRA [3-4]. The performance of TwinMic matches well the requirements for this experiment, offering a broad-energy range from 0.25-2 keV with scanning and full-field imaging modes in a single instrument, and versatile contrast techniques, such as bright-field, differential phase [5] and differential interference contrast [6-7]. The lateral resolution better than 100 nm can be achieved over the entire photon energy range, by means of diffractive zone plate optics. In this experiment, TwinMic was operated in the scanning mode and the specimen was raster-scanned across the X-ray probe of 200 nm, provided by a Au zone plate of 250 μm in diameter. The STXM images were recorded by an Andor Ixon fast read-out camera, collecting absorption and phase information simultaneously. Dwell time per pixel of the raster scan have been adapted to follow dynamically the evolution of the corrosion processes of the electrodes. A photon energy of 477.5 eV was used.

Results

The electrochemical experiments were performed by applying galvanostatic sequences across couples of electrodes. In this paper we report two typical examples of morphologies developing at the anodically and cathodically polarised electrodes. Complementary information regarding Ag behaviour in the chloride system - under different electrochemical conditions - as well as more detailed information about processes taking place in an ammonium electrolyte, can be found in [1].

Cathodic (Figures 2.1 and 2.2) and anodic and morphological changes were observed, brought about by the circulation of 0.2 mA cm$^{-2}$. The reduction process gives rise to the growth of Ag dendrites.
(location $\gamma$ in Figure 2.1) in correspondence of high current density areas of the cathode: dynamic shape changes (overgrowth of peninsula $\delta$ in Figure 2.2) were found, typified by Figures 2.1 (after 20 min) and 2.2 (after 25 min).

**Conclusions**

For expanding the research fields of the TwinMic beamline towards in-situ electrochemical studies an approach for the fabrication and utilization of sealed wet cells with electrochemical control has been developed and implemented. Its potential for electrochemical experiments has been demonstrated using a model system, highlighting non-trivial dynamic morphological aspects of corrosion and electrodeposition processes in a confined electrolyte. The unique feature of this approach is the possibility of observing subtle details of corrosion products and small electrodeposit features that are exclusively stabilised by the aqueous environment and would be either altogether destroyed or at least profoundly distorted by ex situ observations. In conclusion, very recently we have proved feasibility of applying the XAS spectroscopic facility to work with electrochemical wet cells, thus building the full capability of the TwinMic beamline into this class of experiments.

**References**

[1] Bozzini B, D’Urzo L, Gianoncelli A, Kaulich B, Kiskinova M, Prasciolu M and Tadjeddine A 2008 *Electr Comm*, 10(11) 1680.

[2] Guay D, Stewert-Ornstein J, Zhang X, Hitchcock A P 2005 *Anal. Chem.* 77 3479.

[3] Bianco A, Sostero G, Nelles B, Heidemann K F, Cocco D 2005 *SPIE* 5918 591810.

[4] Kaulich B et al. 2006 *Proc. 8th Int. Conf. X-ray Microscopy* IPAP Conf. Series 7 22.

[5] Gianoncelli A, Morrison G R, Kaulich B, Bacescu D, Kovac J 2006 *Appl. Phys. Lett.* 89 251117.

[6] Wilhein T, Kaulich B, Fabrizio E, Romanato F, Cabrini S, and Susini J. 2001 *Appl. Phys. Lett.* 78(14) 2082.

[7] Kaulich B, Wilhein T, Di Fabrizio E, Romanato F, Altissimo M, Cabrini S, Fayard B and Susini J 2002 *Journal of the Optical Society of America A* 19(4) 797.

**Figure 2.** STXM Brightfield images (30$\mu$m by 30$\mu$m scan size, 100 by 100 pixels, 100ms CCD dwell time). (2.1) cathodic growth of Ag dendrite $\gamma$, (2.2) cathodic overgrowth of Ag peninsula $\delta$ on dendrite $\gamma$. 

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