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DELIVERABLE REPORT

WP11 JA1 - Real-time observation and control in microscopy and spectroscopy of nano-objects

D11.7

Implementation of STM microscopy for investigation of solid/liquid interfaces under well-defined gas atmospheres and with electrochemical control (EC-STM)

Due date
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This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

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Prof. Giovanni De Ninno (UNG)

DELIVERABLE DETAILS

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D11.7	Implementation of STM microscopy for investigation of solid/liquid interfaces under well-defined gas atmospheres and with electrochemical control (EC-STM).

DELIVERABLE DESCRIPTION

Set-up of electrochemical STM (EC-STM) systems reaching high resolution imaging and a great flexibility concerning various electro-chemical environments and exploration of the possible implementation of fast measurement techniques therein

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AUTHORS

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NATURE

☐ R - Report

☒ P – Prototype - Demonstrator

☐ DEC - Websites, Patent filing, Press & media actions, Videos, etc.

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INTRODUCTION

Investigating materials and processes in realistic environments is crucial for understanding and designing materials for applications in energy storage, catalysis, corrosion resistance, and nanotechnology. In this context, one of the key objectives of JA1 is to integrate operando capabilities into scanning tunneling microscopy (STM) experiments in multiphase environments. Specifically, sub-task 11.1.2 focuses on setting up versatile electrochemical STM (EC-STM) systems and developing user-friendly protocols for in-situ electrochemical STM, enabling operation at solid/liquid interfaces under well-defined gas atmospheres and with electrochemical control. To this end, two custom-built EC-STM systems have been set up that are based on the same platform developed by the Wandelt research group (Uni Bonn) that is characterized by a rugged design, great flexibility concerning various electro-chemical environments, and excellent performance regarding lateral spatial resolution [1]. While the system at ICN2 has been developed to offer optimized, user-friendly protocols for external users and will complement the advanced characterization tools available at ICN2 through the NFFA, the reference system at TUM has been optimized to host high-speed capabilities, enabling operando experiments on electrochemically relevant systems with sub-s time resolution. Given TUM's extensive technical and research experience in electrochemical STM, and the fact that both systems share the same design, the transfer of knowledge in nearly all technical aspects has been crucial for the successful implementation of the ICN2 system.

EC-STM at ICN2

The electrochemical STM at ICN2 (Figure 1) is situated in a lab that had to be prepared to install the vibrational damping stage, fixed to the ceiling. Once the stage was mounted, the setup of the microscope could start. During the initial stages of installation, it became clear that the wiring of the STM stage needed to be replaced, as many of the very thin Kapton-insulated wires were not properly secured or stable. This delicate task took longer than anticipated due to technical challenges and incomplete documentation of the wiring schema. Additionally, setting up the control electronics, control computer, and control software required extra time due to the lack of precise information and a software operation manual, making it necessary to spend additional time familiarizing with the connection layout and software operation.

After the installation was completed, the first electrochemical cell with an integrated sample holder was constructed (Figure 1e). Additionally, a basic setup for coating the STM tips to ensure their compatibility with the electrolyte environment was assembled.

The first preliminary images of an Au/Mica sample in air were obtained (Figure 2). However, there are still some issues with electronic noise and mechanical vibrations that impact image quality. Additionally, the success rate for producing high-quality tips needs further optimization. Achieving atomic resolution will depend on resolving these challenges.

The next steps will focus on implementing electrochemical measurements at liquid/solid interfaces under well-defined gas atmospheres (e.g., inert gases or controlled humidity). To ensure optimal service for external users, special attention will be required to optimize user-friendly standard operating procedures.

The EC-STM is expected to be added to the NFFA-Europe Pilot offer to users starting from call 16.

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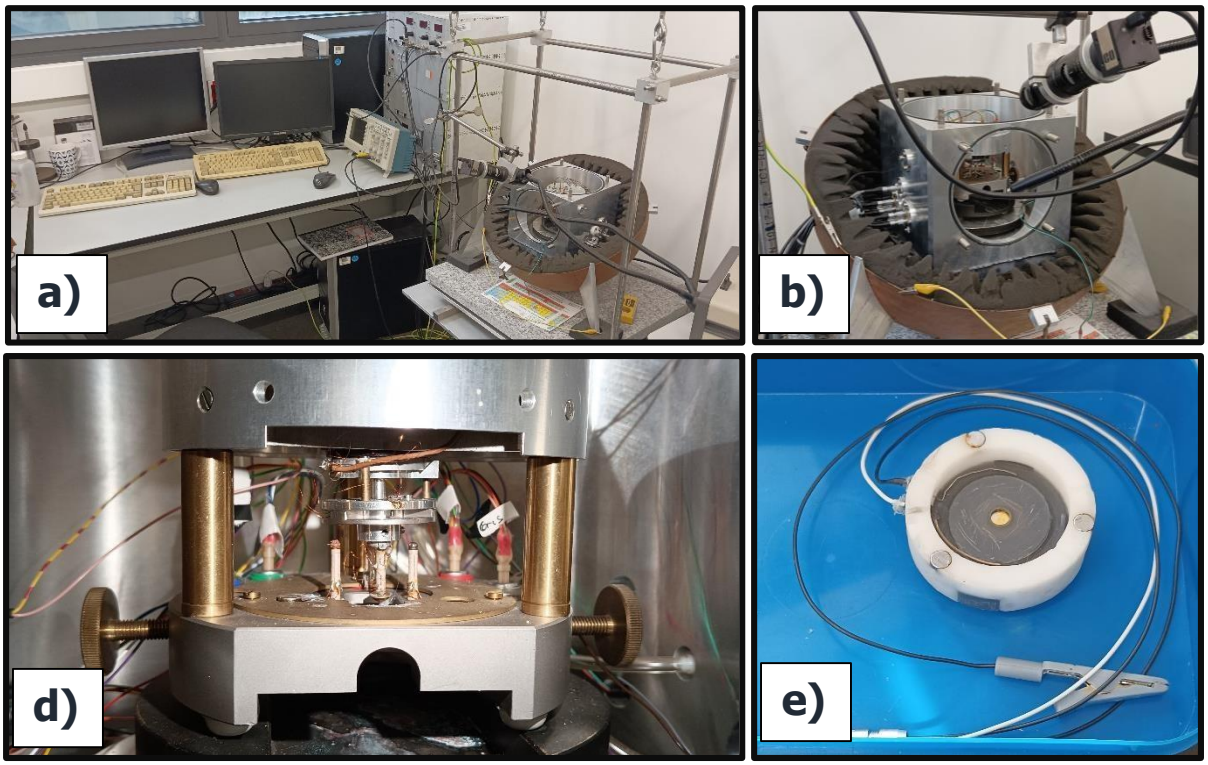

Figure 1 a) Picture of the electrochemical STM (EC-STM) set up implemented at ICN2 with control electronic, control computer, and the STM on the vibrational damping stage; b) controlled atmosphere gas chamber with the microscope inside; d) STM stage; e) electrochemical cell.

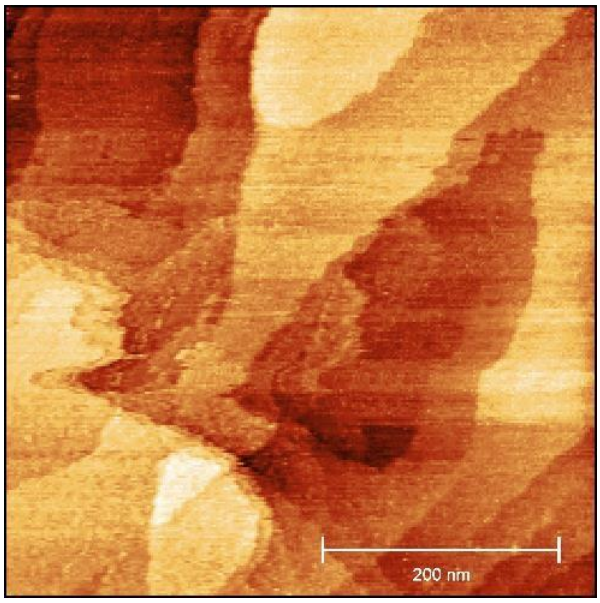

Figure 2 STM image of a Au/Mica sample recorded in air with the ICN2 EC-STM.

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EC-STM at TUM

The Wandelt EC-STM at TUM, while identical in its mechanical properties to the one at ICN2, differs in its wiring since the tip is kept at the ground potential while the potentiostat with all the other (working, counter, and reference) electrodes is floating on the tip bias (see Fig. 3). This particular scheme, controlled by an RHK SPM100 controller, allows the implementation of a fast FEMTO DLPCA-100 preamplifier capable of reaching 200 kHz bandwidth at an amplification of 10^8. Its output is converted by a logarithmic amplifier that converts the current signal to a pseudo-topographic height signal that serves as input to the FAST add-on module. This module was developed within the first NFFA funding period and has proven to work effectively within UHV experiments under constant current conditions [2].

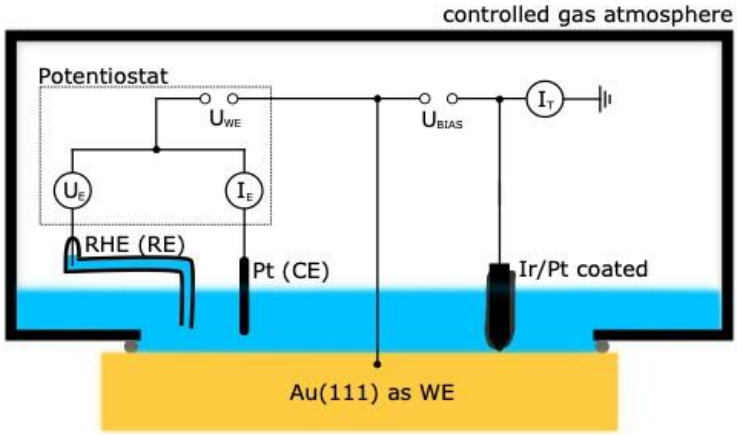

Figure 3 Electrochemical setup for FAST measurements in the EC-STM at TUM.

The transition from solid-gas interfaces into solid-liquid ones came, however, with a lot of challenges that needed to be overcome:

1. Reliable tip etching and tip coating within automatized protocols to obtain resistant, sharp PtIr and W tips with stable spatial resolution
2. Suppression of electronic noise signals up to frequencies of 200 kHz required thick flat band grounding cables with low-resistance connections, sophisticated screening of the current signal, insertion of decoupling capacitors, dedicated power supplies with active noise control, repositioning and screening of monitors, etc.
3. Suppression of mechanical noise signals by a sand-supported suspension system acting with damping bungee ropes
4. Implementation of an electrochemical control system that allows for programmed electrochemical potential sequences (cyclic voltammetry, chronoamperometry, etc.) that are synchronized with the FAST measurements to capture local dynamics in a controlled way.
5. Generating adequate samples to explore the local redox chemistry on an array of identical active sites. We decided to use as flat, ordered adsorbate systems iron octaethylporphyrins supported on Au(111) that are Fe^{3+}-Fe^{2+}-redox-active and catalyze the oxygen reduction reaction (ORR) in a potential range, where the ordered adsorbate structures considerably resist to desorption [3].

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Thanks to the Elettra Instrumentation and Detectors Laboratory, the FAST system had in the meantime been redesigned based on a new, proprietary FPGA architecture that allows the seamless transition between three different measurement modes on different time scales – movies (100 ms), particle tracking (1 ms) and high-speed time traces (5 µs) [4]. This new system was tested in the setup at TUM and adapted to the experimental requirements. In the background, a continuous drift correction permits to cope with the intrinsic drift observed when measuring in electrolyte. The automatic drift correction can fully compensate for these thermal drifts and maintain atomic precision over the time scale of a minute. We could show that the Wandelt setup has the potential to reveal atom scale dynamics in a FAST setup with stable spatial resolution over periods of hours. Frequency windows, in which such high-speed scanning can be performed without exciting the microscope's eigenfrequencies, can now easily be characterized by the measurement program itself. And, most importantly, thanks to the new possibility to rotate the scan angle, intricate z-scale corrections for the sample inclination can be avoided when scanning along the contour lines.

The combined improvement of the mechanical, electronic, and software performance gives the Wandelt EC-STM the required reliability to pave the way for new dynamic investigations of local electrocatalytic processes (reactions, particle redox and dissolution, etc.) with a time resolution down to hundreds of ms and below. As an example, we show in Fig. 4 the reduction and oxidation of Fe octaethylporphyrin molecules in a neutral phosphate buffer imaged with 10 fps.

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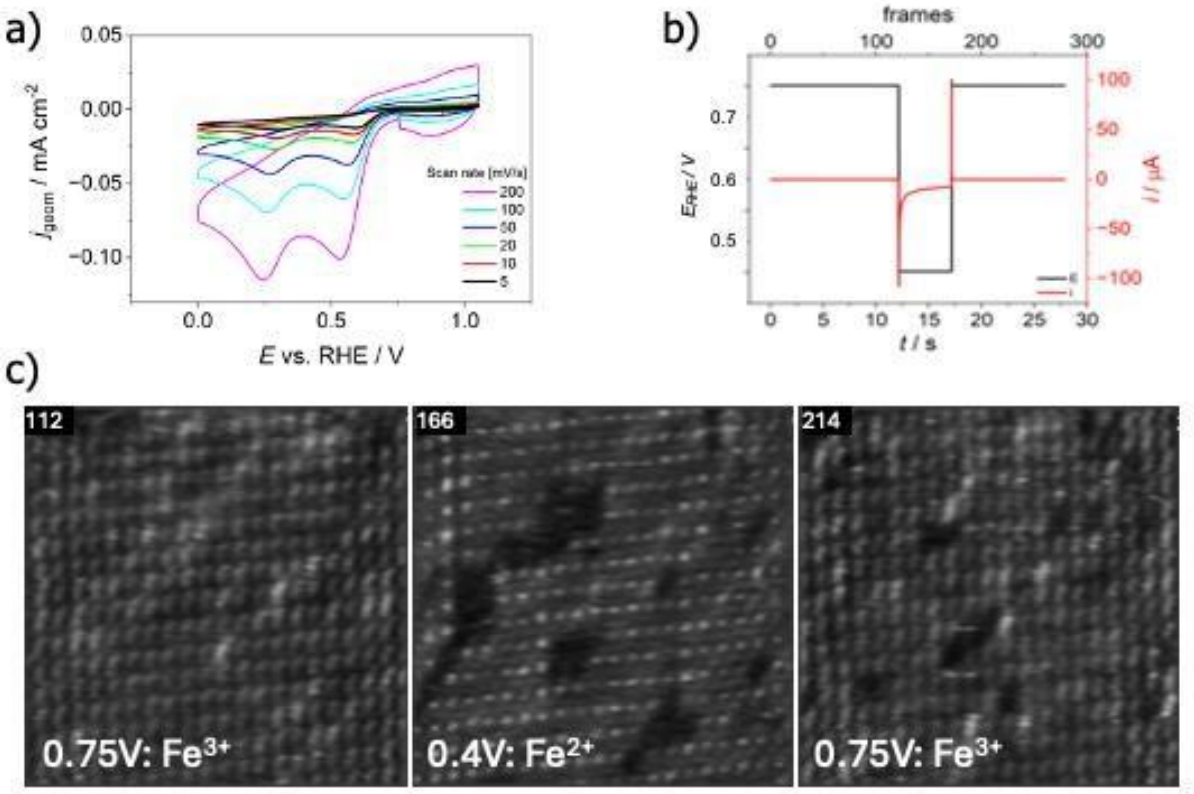

Figure 4 Fast EC-STM investigation of an Fe octaethylporphyrin monolayer supported on Au(111) as obtained by drop-casting, under a 0.2M phosphate buffer, pH=7 electrolyte. a) Cyclic voltammogram obtained at different scan rates that documents the Fe^{3+} to Fe^{2+} reduction upon potential changes between 0.75 and 0.4 V vs RHE. b) Cycloamperometry recorded during fast imaging that documents the reduction/oxidation current upon stepwise change of the electrochemical potential. c) Single frames taken taken from the corresponding 10 fps movie over a 30x30 nm^2 area; each dot represents one porphyrin-bound Fe center. Fe^{2+} appears brighter due to its higher density of states. The contrast at more oxidizing potential is recovered. Dark spots indicate sites were porphyrin molecules desorbed upon switching to the lower potential.

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