

Dynamic observation of electro-assisted Fe oxidation by Operando Atom Probe

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Heterogeneous catalysis is of the pillar of chemical industry, playing a key role in the optimization of chemical processes and their conversion towards “*green chemistry*”. Physics governing the surface chemical reactions involved in heterogeneous catalysis depends on the synergistic interactions existing between reactants and specific surface structures composing the catalyst. The design of high-performance catalysts requires a deep understanding of those mechanisms at the nanoscale; and surface science techniques are continuously pushing their technical limitations to bridge gaps between fundamental research and real-world applications. In the past decade, an increasing number of analytical techniques successfully achieved their evolution towards an in situ and operando version of themselves, and recently such approaches are being developed for atom probe microscopy (APM) techniques^{1,2}. In this work, we will present the recent advances in the conversion of Atom Probe Tomography (APT) to study surface dynamics of O₂/Fe using two different APM techniques and modifications: Field Ion Microscopy (FIM), and Operando Atom Probe (OAP).

APM are capable to image the apex of sharp needles with nanometric lateral resolution. Those apices of few tens of nanometers diameter can be seen as model of single nanoparticles by their size and shape³. FIM images such needles with atomic resolution and enables to identify the crystal orientation along with the local surface reaction dynamics during oxygen interaction with Fe. Resulting FIM image (Fig.1.a) corresponds to a stereographic projection of the apex allowing crystal orientations identification with atomic resolution (0.2 nm lateral). APT, from which the OAP derives, relies on the thermally assisted phenomenon known as “field evaporation”. Individual surface atoms of the apex are extracted, positively ionized, before being projected towards a position sensitive detector. Atoms are removed one by one, layer per layer, thus making the APT a destructive technique. Field evaporation is controllably initiated by applying short voltage pulses in the presence of a steady electric field. In regular use, the APT is performed in an Ultra High Vacuum (<10⁻¹¹ mbar) while the sample is cooled at cryogenic temperatures (<50 K)³. OAP modification consists of performing the atom probe analysis in the presence of reactive gas (~1.1×10⁻⁷ mbar of pure O₂ (99.993%)) at 300 K. Fe samples are prepared via an electrochemical etching technique from high purity Fe wire (99.8% dia~0.127 mm)⁴.

Before O₂ exposure, Fe surface is cleaned by field evaporation in the Atom Probe system (LEAP 4000XHR CAMECA) and the surface structure is characterized and identified by FIM. We can observe a (011) oriented sample with a central Fe(011) pole surrounded by two pairs of Fe{222} and Fe{024}, and a set of four Fe{112} facets. Once the characterization is complete, the system is warmed up to room temperature and the sample is maintained at 300K before starting APT analysis and introducing

$\sim 1.1 \times 10^{-7}$ mbar of pure O_2 . As soon as the oxygen is introduced to the chamber, we can observe the surface formation of Fe oxides by monitoring the local concentration of Fe_2O^{n+} and FeO^{n+} ion species extracted from the surface over time. We can track the local concentration over the different surface regions in real time. Over one hour of exposure in the presence of a strong electric field (~ 25 V/nm) we observe the progressive surface oxidation starting from open facets structures, such as Fe{222} and Fe{112}, towards the central Fe(011) and the Fe{024} which show significantly higher resistance toward oxidation (Fig.1.b and c). Whereas APT reconstructs a 3D atomic map of the apex, OAP allows us to reconstruct the full movie of the surface composition, and its oxidation. Additionally, OAP measurements are performed in the presence of very strong electric fields (>10 V/nm) which makes OAP a promising technique to study the potential influences of it on the system.

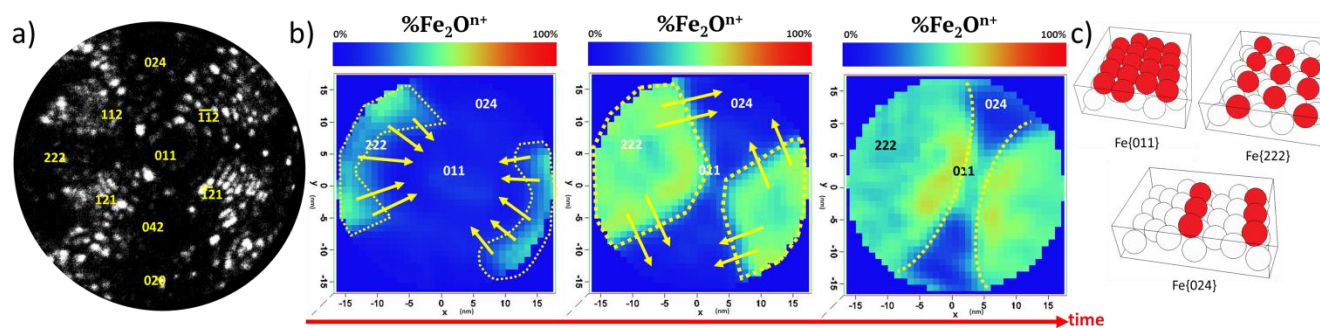


Figure 1. **a.** Fe sample FIM image “011 oriented”. (10^{-8} mbar Ne, 60K). **b.** 2D projections of the $Fe_2O\%$ concentration of the same Fe sample exposed to 1.1×10^{-7} mbar O_2 at 300K in the presence of ~ 25 V/nm over time (total time ~ 67 min). Yellow arrows indicate the progression of the surface oxidation fronts drawn with yellow dashed lines. **c.** Ball models of the main crystallographic structures composing the surface: (011), {222} and {024}. Red balls represent the first layer of the surface.

OAP shows a promising development for studying surface chemistry at the nanoscale and in real time over complex surfaces. Additionally, the application of strong electric fields opens the unique opportunity to experimentally measure the influence of those on surface chemistry and thus gas phase electrocatalysis. The mastering of this new technology and the confrontation of the experimental results with theoretical models will lead to the development of instruments capable of experimentally measuring the different energies of activation over the different crystallographic facets simultaneously.

References:

- [1] SV Lambeets et al., *J. Phys. Chem. Lett.* **11** (2020), p. 3144.
- [2] SV Lambeets et al., *Top Catal* **63** (2020), p. 1606.
- [3] B Gault et al. in “Atom Probe Microscopy”, ed. Springer (New York Heidelberg Dordrecht London)
- [4] EW Müller in “Field ion microscopy principles and applications, 1st Edition”, (Elsevier Publishing Company Inc., New York, USA).