Direct insight on the dynamical behaviour of cobalt oxide electrocatalysts under operation conditions by electrochemical in situ STEM

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The direct monitoring of physical and chemical transformations in real time and by real space imaging is mandatory for understanding reversible processes in systems like catalysts. The rudimentary comparison of their analyses in the initial state and post-mortem is not enough to explain the mechanisms occurring in the reaction. Thus, the development of *in situ* characterization techniques is unavoidable to move forward in the comprehension of reaction mechanisms, phase transitions and morphological changes, among other processes that take place during the catalysis in real operation conditions, such as reactive gas atmosphere or liquid media. Moreover, in the last case, considering the enormous relevance of electrocatalysts in the promotion of more efficient, clean and affordable energy production methods[1], it is fundamental to understand their behavior in real conditions in order to be able to improve their performances in terms of activity and stability. In this regard, the development of Liquid Phase Transmission Electron Microscope in Scanning mode (LP-STEM) and notably the electrochemical set-up provides a unique opportunity for exploring the dynamical behaviour of electrocatalysts under operation.

In the present study, we followed the behavior in *operando* conditions of Co_3O_4, a well-known material typically use to catalyze the Oxygen Evolution Reaction (OER). Thanks to the LP-STEM set up it was possible to observe the surface amorphization of the catalyst crystals at the oxidation potential during a cyclic voltammetry experiment. By depositing the catalyst over an electron transparent electrode, it was possible to monitor the changes in the morphology of the nanostructured material parallel to the electrochemical detection of the catalysis. In contrast with the studies reported by other *in situ* techniques like GIXRD[2] and XPS[3], our results show that after several cycles this amorphization tends to become irreversible. Furthermore, this structural modification seems to improve the catalytic activity. The combined analysis of the *in situ* results, in agreement with the general ex-situ behaviour of the same electrocatalysts, with other data obtained by post mortem High-Resolution STEM and elemental analysis by Energy Dispersive Spectroscopy (EDS) allowed us to conclude that the crystalline part remains encapsulated within an amorphous matrix of cobalt. Although there have been several reports of the used of LP-STEM in the study of Li-ion batteries materials[4], this study is the first one on this type of system of high interest in electrocatalysis and more generally in the field of renewable energies. These results are very encouraging and stimulate the practical implementations of such *in situ* experiments since they clarify long-standing questions related to the behaviour of the materials under operation.

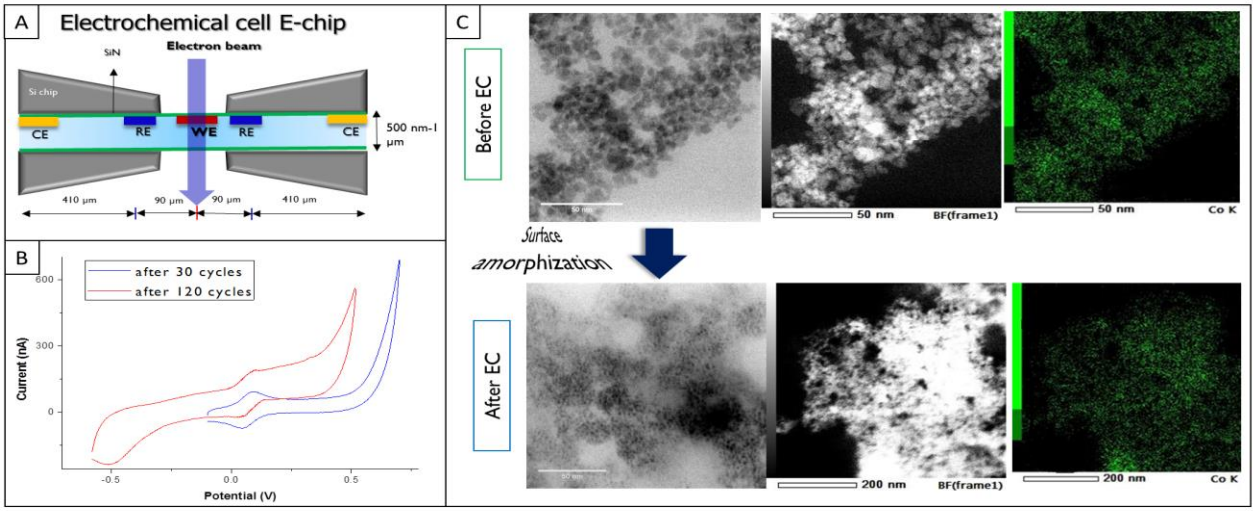

Figure 1. (A) Electrochemical E-chip use in the in situ LP-STEM set-up. (B)Cyclic voltammograms of Co_3O_4 in OER conditions in situ after 30 cycles and after 120 cycles. (C) Pre and post-mortem STEM images and EDX mapping of the catalysts nanoparticles.

References

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