Proceeding Accepted at 10th International Conference on Materials for Advanced Technologies (ICMAT), Marina Bay Sands, Singapore, 23-28 June 2019

Structural evolution of OER catalysts via ex-situ and in-situ (S)TEM cycling

E. Tyukalova[1], Y. Duan[1], Z. J. Xu[1], A. Demortiere[2], A. Grimaud[3], M. Duchamp[1].

[1] School of Materials Science and Engineering, Nanyang Technological University, Singapore.
[2] Laboratoire de Reactivite et de Chimie des Solides, CNRS, Amiens, France.
[3] Chimie du Solide et de l'Energie, UMR 8260, Collège de France, Paris, France

Catalysts for oxygen evolution reaction (OER) are important components for the efficiency increases of the overall water-splitting reaction for the generation of hydrogen, an efficient energy carrier. During operation, electrochemical reactions introduce structural and chemical changes to the active materials that are not necessary reversible. These alterations cause the degradation of the performance and limit their lifetime. Thus, detailed understanding of correlation between electrochemical processes and atomic-scale transformations are essential to improve efficiency of catalysts.

In this work two promising catalysts for OER $ZnCo_{1.2}Ni_{0.8}O_4$ (ZCNO) and La_2LiIrO_6 (LLIO) have been studied using high-resolution scanning transmission electron microscopy (HRSTEM) and spectroscopy methods after different state of OER activation.

Initial characterization of ZCNO material revealed a high sensitivity of the nanoparticles and phase transformations under electron beam exposure. In order to eliminate the degradation of the structure, cryo-temperature experiments were implemented. Under cryo-TEM conditions, the degradation of the structure during HRSTEM imaging was not observed for a total electron dose ten times higher in comparison to the room temperature imaging. Further, ZCNO nanoparticles were studied after 1000 ex-situ OER cycles in 1M KOH solution at cryo-T. OER cycling cause formation of the shell around the particles, which were mainly not present on the pristine material. Future experiments will be focused on the understanding of correlation between the presence of shell after cycling and the structural properties at the specific surface via *in-situ* STEM.

LLIO particles were observed after different OER cycles. A previous study has shown the evolution of the structure versus the number of OER cycles [Ref. Nature Energy paper]. Electrochemical activation of LLIO material causes the formation of IrO_2 nanoparticles on the surface after 50 OER cycles. Further cycling up to 100 cycles revealed transformation into polycrystalline structure with nonhomogeneous distribution of La_2O_3 and IrO_2 phases. From the knowledge gained from ex-situ TEM cycling experiments, we are setting up their cycling inside a liquid cell were the phase separation and the change of the crystal structure will be observed on an individual particle in real and diffraction TEM modes.