

Observing Zn-Fe Galvanic Oxidation at Nanoscale by Aberration-Corrected STEM

Calderon, S.¹, Carvalho, I.^{2,3}, Cavaleiro, A.^{2,3}, Carvalho, S.⁴ and Ferreira, P.^{1,5}

¹ International Iberian Nanotechnology Laboratory (INL), Portugal, ² SEG-CEMMPRE Mechanical Engineering Department, University of Coimbra, 3030-788 Coimbra, Portugal, Portugal, ³ IPN-LED&MAT Instituto Pedro Nunes, Laboratory for Wear, Testing & Materials, Rua Pedro Nunes, 3030-199 Coimbra, Portugal, Portugal, ⁴ CFUM-UP, University of Minho, Department of Physics, Campus of Azurém, 4800-058 Guimarães, Portugal., Portugal, ⁵ Materials Science and Engineering Program, The University of Texas at Austin, Austin, Texas 78712, USA., Portugal

Bimetallic nanoparticles (NPs) have attracted a lot of attention due to their multifunctional characteristics, which can be tuned by modifying their size, distribution and composition. The multifunctional character can be exploited in a wide range of applications, including catalysis, antibacterial, optical and magnetic applications and can be used in a variety of technological fields including textiles, biomedicine, food and agriculture, electronics and renewable energy. The NPs applicability strongly depends on their oxidation and dissolution kinetics, which require a fundamental understanding of the oxidation mechanisms. In this context, a combination of techniques capable of resolving the spatial distribution of structure and chemical composition is of paramount importance.

In this report, we focus on the study of the oxidation evolution of Zn-Fe bimetallic NPs by aberration-corrected STEM/EDS. Three sets of NPs were studied, namely pure Zn, Zn-Fe alloys and agglomerated Zn and Fe NPs. Morphological, structural and chemical characterization of the NPs was performed before and after exposure to an oxidation environment of 95-98% relative humidity (RH). High angular annular dark field (HAADF) STEM images were acquired on an aberration-corrected FEI Titan ChemiSTEM operated at 200 keV, before and after exposure. Energy dispersive X-ray spectroscopy mapping (EDX-mapping) was performed in an aberration-corrected FEI Titan ChemiSTEM equipped with a Super-X EDX detector, before and after exposure to the high RH environment.

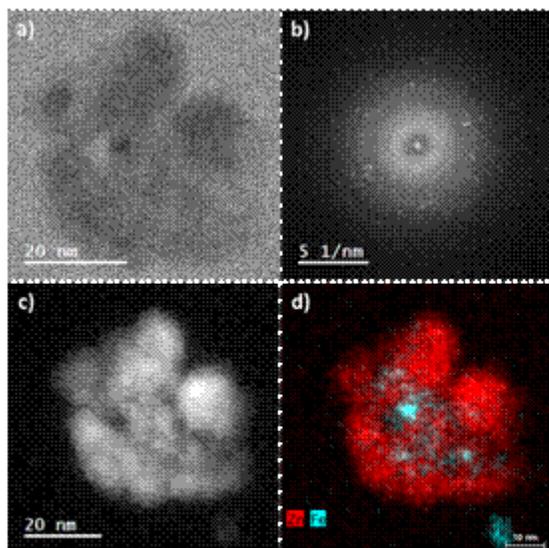


Figure 1. Agglomerated Zn and Fe NPs a) Phase contrast Image, b) FFT of a), c) HAADF STEM image d) EDX spectrum images acquired for Zn and Fe.

For the case of pure Zn NPs, a core-shell-like structure is formed, corresponding to the formation of Zn/ZnO layers, respectively. The zinc oxide is crystallographically aligned with the Zn lattice, as confirmed by electron diffraction. In the case of the Zn-Fe alloy NPs, the core-shell like structure is not observed. Instead, the oxidation is randomly distributed. This behavior may be due to different oxidation mechanisms and rates of oxidation for Zn and Fe, where Zn tends to oxidize by Zn⁺ diffusion through a thin ZnO layer, while in the case of Fe the O²⁻ ions diffuses through Fe_xO_y. On the other hand, when Zn and Fe metals are coupled in an agglomerate-like morphology (Figure 1) a faster oxidation of Zn is observed, attributed to the dissimilar corrosion potential in the NPs, stimulating a galvanic mechanism that can be exploited to accelerate the oxidation of the NPs and use them as oxygen scavenger materials. The results also reveal that the galvanic corrosion occurs spontaneously for bimetallic Zn-Fe NPs composed of Zn and Fe phases, where Zn dissolves faster than for Zn NPs. However, this process is excluded for Zn-Fe NPs

