

Nickel Oxide Reduction Studied by Environmental TEM and *in situ* XRD

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Nickel oxide reduction and subsequent Ni behavior under H₂ is of practical importance in the field of solid oxide fuel cells (SOFC) as it determines the structure of the electronic conductor on the anode side during operation [1]. Despite extensive coverage in literature [2], some discrepancies remain, notably regarding NiO reduction kinetics and its structural evolution.

In situ reduction of an industrial NiO powder from JT Baker™ is performed under 1.3 mbar of H₂ (2 ml_N/min) in a differentially pumped FEI Titan environmental transmission electron microscope (ETEM) [3]. Images, diffraction patterns and electron energy loss spectra are acquired during different temperature ramps (300 to 600°C) to monitor the structural and chemical evolution. Similar experiments are performed in a PANalytical X'Pert PRO X-ray diffractometer equipped with an Anton Paar furnace and a mass spectrometer to complement and extrapolate ETEM data to higher pressure and flow conditions. Peak intensities, crystallite size, H₂ and H₂O signals are monitored.

Reaction kinetics are obtained in the ETEM by electron energy loss spectroscopy using two different techniques based on the change of shape the Ni L_{2,3} white lines (either taking the ratio of Ni L₃ and L₂ integrated intensities or using a multiple linear least squares technique [4, 5]). The results demonstrate that reduction starts below 400°C and proceeds quickly until the rate is slowed down at higher temperature and conversion fraction (Fig. 1). Images and diffraction patterns illustrate that Ni nucleation on NiO is either epitaxial with a small angle misfit in thin areas (Fig. 2) or randomly oriented in thicker regions. Reduction then proceeds through the growth of Ni nuclei and movement of interfaces, the latter inducing particles shrinkage and intragranular pores creation. Significant densification is observed at temperatures higher than 550°C: porosity created at lower temperatures disappears. This reorganization of Ni is detrimental to the connectivity of the Ni catalyst and to the redox stability of the SOFC.

In situ XRD yields comparable results to ETEM for similar pressure and flow conditions. XRD experiments at different flows and pressures underline the effect of H₂O removal on the kinetics. H₂O created upon reaction appears to block H₂ access to the reactive sites when the H₂ flow is low, an effect observed in both XRD and ETEM experiments.

References:

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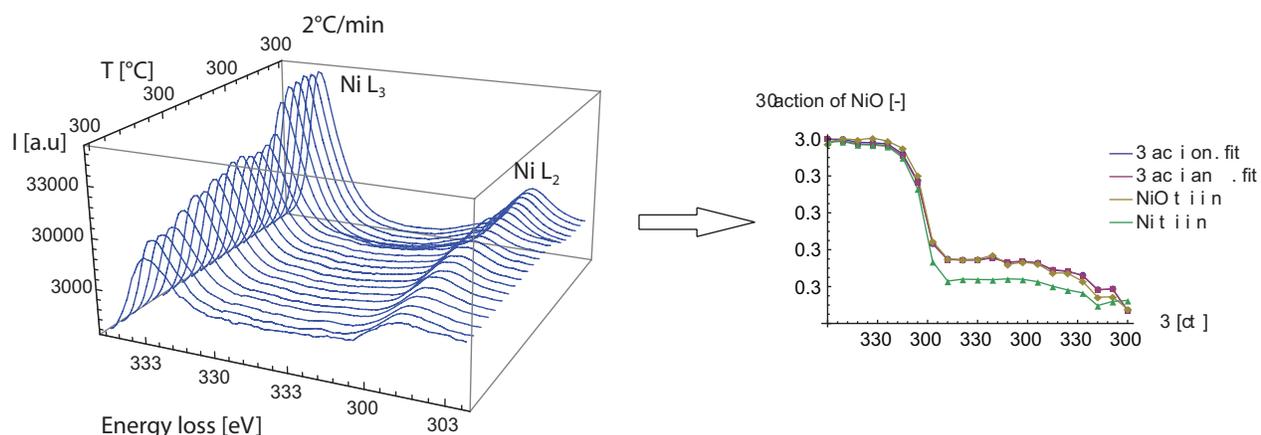


Fig. 1. Electron energy loss spectra evolution as a function of temperature (on the left) are used to extract reduction kinetics (on the right) using the change of shape of the Ni $L_{2,3}$ white lines (either using the ratio of the Ni L_3 and L_2 intensities integrated with a 2 eV window or using a multiple linear least squares (MLLS) technique, which fits a given spectrum with NiO and Ni references).

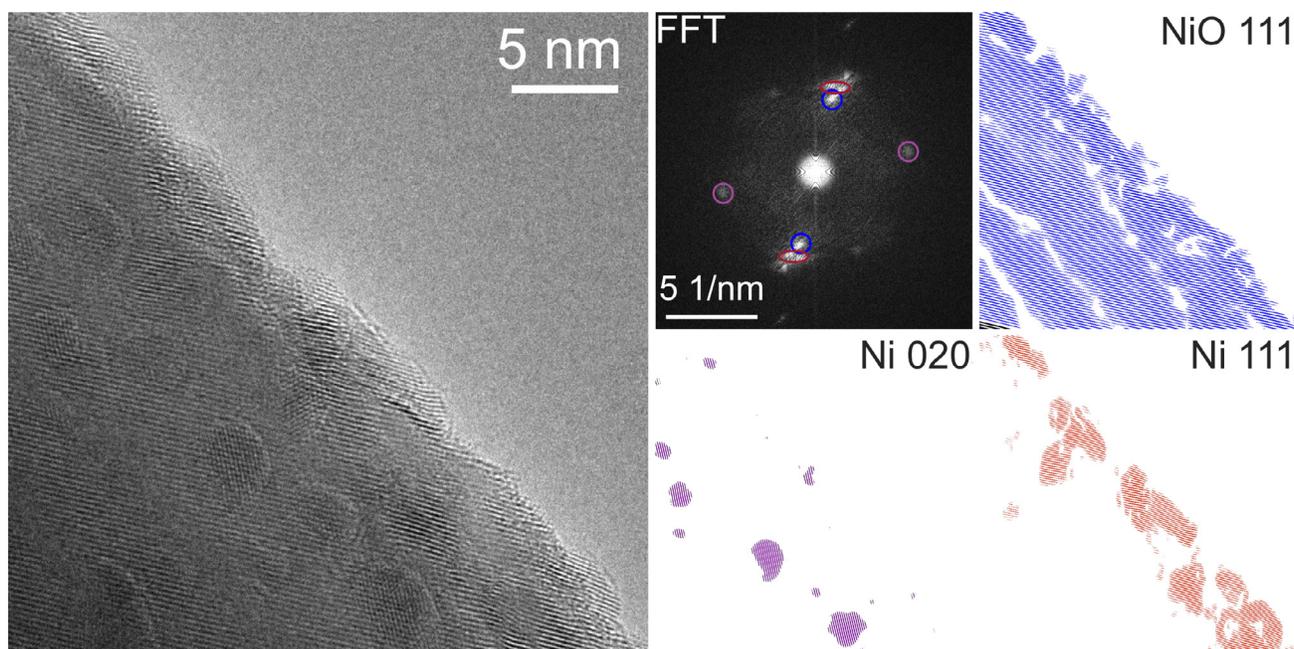


Fig. 2. Ni nucleation on NiO observed by ETEM at 370°C. High resolution images, FFT and inverse FFT images illustrate the epitaxial growth of Ni on NiO in thin areas (with a small angle misfit resulting in a splitting of the Ni 111 reflections).