HAADF and STEM EELS studies of a new generation of materials for Ni-MH batteries

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Keywords: Batteries, HAADF, STEM-EELS,

Applications for Ni-MH batteries are driven by increased energy density. Hydride forming compounds such as La–Mg–Ni ternary compounds show improved performance demand, in particular new crystallographic phases of $A_2B_7$ and $A_5B_{19}$ types [1, 2, 3, 4]. Such compounds can be described as the growth along the c axis of two different sub-units $[AB_5]$ (C layer) and $[A_2B_4]$ (L layer), where A is a rare earth or an alkali earth and B is a transition metal, forming either a rhombohedral $[3R]$ ($R-3m$) or hexagonal $[2H]$ ($P63/mmc$) crystallographic structure. A series of compounds in this family of materials has been prepared by spark plasma sintering (SPS) and characterized by X-ray, microprobe and TEM analysis [5].

Here we present analyses of those compounds by spatially resolved Transmission Electron Microscopy in order to identify the local structure and defects.

Observations were performed on an image-corrected FEI Tecnai (SACTEM-Toulouse) operating at 200 kV and HAADF imaging and STEM EELS on a probe-corrected FEI Titan 60-300 microscope operating at 300 kV (Zaragoza).

For the studied samples, the atomic resolved HAADF images allow us, for the first time, to clearly identify the majority structure as rhombohedral $[3R]$ in agreement with the majority phase determined from Rietveld analysis of the X-ray diffraction patterns. This is illustrated on figure 1a in the case of the sample La$_{0.8}$Mg$_{0.2}$Ni$_{3.67}$.

Dislocations and stacking faults have been also observed, as illustrated for example in the figure 1b for the sample La$_{0.8}$Mg$_{0.2}$Ni$_{3.67}$. Figure 1b locally shows the stacking corresponding to the hexagonal structure.

Figure 1c displays the La and Ni edges extracted from two different areas of a spectrum image recorded using a 0.13 nm probe size for the sample La$_{0.8}$Mg$_{0.2}$Ni$_{3.67}$. The La-M5 and Ni-L3 are clearly visible. Images and STEM-EELS analyses of defects showing in particular the La/Ni elemental chemical maps will also be presented. This will be very useful to relate the crystal structure and bonding to the hydrogenation properties and to correlate structural and thermodynamic properties. [6]

References

[6] This work was supported by the ANR program MAHYA (n° ANR-07-STOCK-E-MAHYA-07-01).
Figure 1. HAADF images of the sample La$_{0.8}$Mg$_{0.2}$Ni$_{3.67}$ along the 110 direction showing the rhombohedral structure (a), and locally the hexagonal structure (b). The rhombohedral and hexagonal structures are also represented. c) EELS spectrum showing the superimposed La M4.5 and Ni L2.3 edges, in Ni rich (red) and Ni poor (blue) areas (probe size 0.13 nm, monochromator on).