A mechanism study of $M_3B_2O_6$ (with M = Co, Ni and Cu) towards lithium

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Since the publication of Idota et al.,[1] the borates have been studied to be used as negative electrode materials in lithium-ion batteries. This interest is nested first in the low atomic weight of boron (specific capacity gain). Then, its high electronegativity as well as its ability to be either three- or four- oxygen coordinated offer a great variety of redox potentials for the adjunct cation. From environmental (no toxicity) and economic (material cost) factors, only iron borates and inductive effect were widely studied up to now.[2,3] However, these authors have to deal with two major problems: purity of initial materials and difficulties to characterize the amorphous phases obtained during cycling. To our knowledge, only Mössbauer spectroscopy studies were undertaken on the amorphous phases resulting from the reduction of iron borates; no other spectroscopic study was reported.

Based on published borates electrochemical curves, a parallel could be drawn between these curves and 3d-metal oxides ones: low potential, extra capacity, important polarization, and amorphization of the initial material.

With the wealth of experience acquired in the field of oxides reactivity (CoO, NiO and CuO) towards lithium,[4] we decided to study the borates using a combination of various techniques. In order to identify the implied electrochemical mechanism, the cycled materials were characterized by Transmission Electron Microscopy (TEM), infrared spectroscopy (IR), and ^{11}B Nuclear Magnetic Resonance (NMR)

The electrochemical properties of $M_3B_2O_6$ (with M = Co, Ni and Cu) powders with respect to Li were found to be similar to those of 3d-metal oxides. In fact, the reduction process of 3d-metal borates involves their decomposition into metal nanograins dispersed into a lithia matrix surrounded by an organic layer which is responsible for the observed extra capacity. The lithia matrix consists of a mixture of crystallized lithium oxide (Li_2O) and amorphous orthoborate (Li_3BO_3). During the subsequent charge, the organic layer vanishes and the metal grains are partially or fully oxidized with a concomitant decomposition of Li_2O. The formation of Li_2O and metal nanograins during the discharge as well as the one of oxides nanograins during the following charge were identified by HRTEM studies (fig.1) while Li_3BO_3 was detected by IR spectroscopy, and ^{11}B NMR techniques.

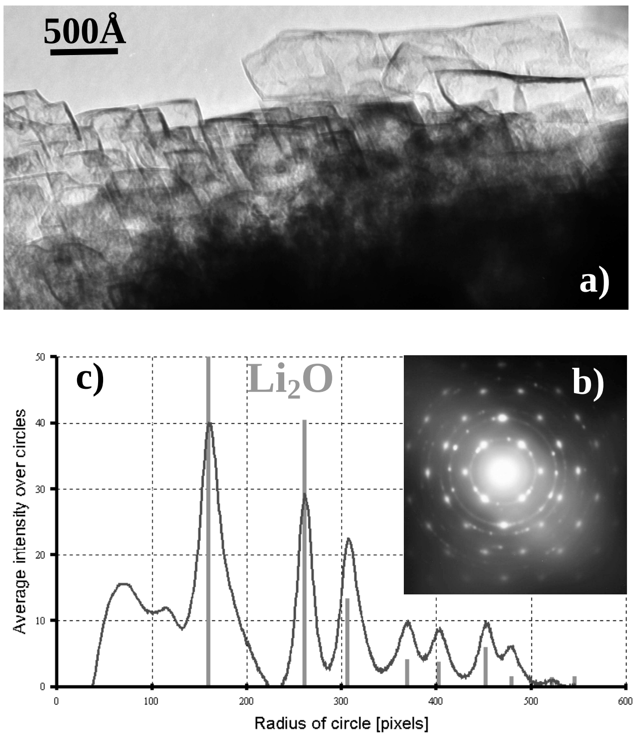

Figure 1: a) Bright Field TEM image of the reduced $Ni_3B_2O_6$ powder. b) Corresponding SAED pattern. c) Corresponding XRD-like diagram obtained with Process Diffraction 2.1.7.[5]

References

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