Electrochromic mechanism in nickel oxide thin films grown by Pulsed Laser Deposition

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Transition metal oxides have been largely studied in regards of their potential application as electrochromic materials in displays, smart windows, variable reflectance mirror [1,2]. In particular, nickel oxide thin films have attracted special interest for suitable use as counter-electrode in electrochromic protonic devices in respect of neutral coloration and moderate cost. However despite of numerous studies, the electrochromic mechanisms involved in the reversible color switch of NiO_x thin films as well as their cycling stability remains largely debated.

Nickel oxide thin films were deposited on SnO_2 : F-coated glass substrate using Pulsed Laser Deposition (PLD). An investigation of the relationship between the electrochromic properties and the deposition parameters shows that good electrochromic properties can be achieved for PLD thin films prepared at room temperature (RT) in a 10^{-1} mbar optimized oxygen pressure [3].

Depending on their thickness, NiO_x thin films present various surface morphologies. Thicker films were constituted by visible cracks whereas thin films (< 30 nm) appear dense with crystallites of no specific shape as determined by microscopy. X-ray diffraction study shows that the films are poorly crystallized in a NiO cubic structure with a (111) preferred orientation. A stoichiometry close to the ideal Ni/O ≈ 1 was deduced from the 4.18 Å cell parameter and confirmed by electronic microprobe analysis.

The electrochemical behavior examined in a Pt/KOH 1M/Hg/HgO/NiO_x cell is quite complex and depends on both the film thickness and potential window. Upon cycling the electrochemical behavior may be divided in three parts : 1) an activation period that may last up to few hundred cycles during which the capacity increases, 2) a cycling range during which the capacity remains constant upon cycling and 3) a decrease in capacity after several hundred cycles. Each step will be discussed in respect of capacity (i.e. number of exchanged electron) and electrochromic response (i.e. contrast and coloration efficiency). Special attention will be focused on the determination of the electrochemical mechanism (i.e. phase nature and kind of ions involved) that governed the faradic process associated to the reversible transparent/brownish color switch.

Finally in this paper, the effect of various substitutions on the film stability and electrochromic performances will be presented. Applications in complete device will be proposed.

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