Thin Film Route for Optimization of Electrode Materials

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Since few years, the thin film route has been demonstrated to be of high interest for the search of new materials exhibiting promising properties as electrode materials. Among potential candidates, insertion compounds have been largely studied for their use as storage materials for applications such as battery or electrochromism. For the last application, the amount of inserted species (i.e. capacity) is not the main parameter. Indeed, it is linked to the resulting optical contrast yielding a figure of merit featured by the coloration efficiency. The requirements being different for each application, one should optimize the materials synthesis. Nowadays a large number of thin film techniques such as evaporation, sputtering, chemical vapor deposition, pulsed laser deposition and sol-gel are available. Among them, pulsed laser deposition, which allows combinatory chemistry, is a unique tool for material optimization.

As well known, the properties of the films are strongly dependent on the conditions of deposition and are often quite different from compositionally similar bulk material. Herein, through several examples mainly taken in the field of electrochromism, we will illustrate how one can monitor the property of electrode materials by playing with the conditions of deposition.

Thins films of transition metal oxides were deposited using Pulsed Laser Deposition (PLD). This technique widely used for the preparation of complex metal oxides is well adapted to the search of new materials in relation with the small amount of required material, the rapid growth and the advantage of maintaining the target to film composition. In addition, comparison with other technique such as sol-gel will be established.

The most studied electrochromic material remains by far WO_3 that switches reversibly from white/yellow to blue upon electrochemical oxidation and reduction. A careful investigation of the relationship between the electrochromic properties and the deposition parameters shows that good electrochromic properties were achieved for pulsed laser deposited films prepared at room temperature in a 10^{-1} mbar optimized oxygen pressure. In these conditions films are homogeneous and porous.

The light blue coloration of the tungsten oxide in the reduced state is undesirable for building applications for which a more neutral color is commercially required. In search of color neutrality, two different routes were investigated : the first one consisted in preparation of binary mixed tungsten oxides exhibiting a neutral color in the reduced state whereas considering the neutral colour of a complete device, the cathodic electrochromic tungsten oxide WO_3 can be combined to anodic electrochromic material such as NiO_x.

Based on a survey of various elements (Ni, Ti, Cr, Mo, Nb, V..), the W-V-O system was determined as being the most promising. In this work, the influence of the vanadium content and its role on the film performance will be examined in details.

A broad study of the conditions of deposition (in-situ atmosphere, duration, substrate temperature, substrate nature, substrate target distance) of NiO_x films suggests an optimum value of 10^{-1} mbar oxygen pressure for the films deposited at room temperature and 100 °C. Applying these conditions, the films switch reversibly from brownish to transparent in association with a reversible faradic process. For higher substrate temperature, their electrochemical behavior examined in a Pt/KOH 0.1M/Hg/HgO/NiO_x cell is quite complex and not fully understood. It involves capacitive and faradic type behavior of which ratio will be discussed. The relationship between these various behaviors and the film nature will be presented.

Finally the characterization of a third system namely the tin-antimony system will be reported. We will show that depending on the oxygen pressure and substrate temperature, the Sn-Sb-O films could be either colored in relation with a faradic behavior and a porous morphology, or presenting a capacitive-like behavior associated to a neutral switching over a wide range of potentials for denser films. Thus, by tuning the conditions of deposition, one can make device having the same material on both electrodes but that differ only by their morphology.

In summary, in this work we will show through the examples of various mixed oxide systems how one can control and optimize the desired property by playing with the composition, the structure, and the morphology of the films (i.e. the conditions of deposition).