Development of mesoporous tungsten oxide WO_3 thin films for electrochromic applications

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WHAT IS AN ELECTROCHROMIC FILM?

Electrochromism is the ability of some materials to change their optical properties in a reversible and persistent way under the action of a voltage pulse. This phenomenon finds applications in the area of smart windows and subsequently it contributes to building energy savings. The reaction that takes place between the colored (right part) and bleached state (left part) is :

$$WO_3 + xLi^+ + xe^- \rightleftharpoons Li_xWO_3$$

In this work, we prepared amorphous thin films of WO_3 via the sol-gel technique and studied their electrochemical behaviour in the presence and absence of mesopores, induced by the micelles of a non-ionic surfactant. The existence of mesopores in a film results in the increase of the framework's surface area and consequently it reduces the diffusion length of cations. These advantages could potentially lead to electrochromic materials with better reversibility, coloration efficiency, charge capacity and switching kinetics.

EXPERIMENTAL PROCEDURE

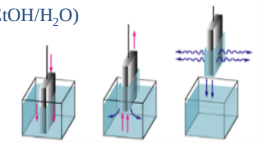
Four steps

1) Preparation of the solution

$([W_{12}O_{42}H_2]^{10-}/EtOH/H_2O)$ + (Brij-56/EtOH/H_2O)

2) *Dip-coating*

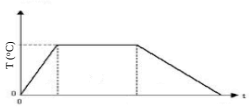
- Controlled RH%
- Controlled deposition speed



3) Stabilization at 170°C

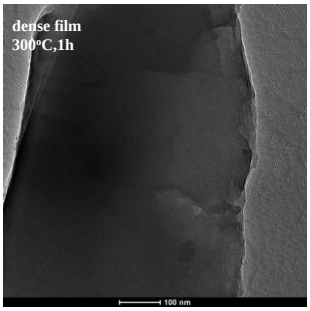
4) Calcination at high temperatures

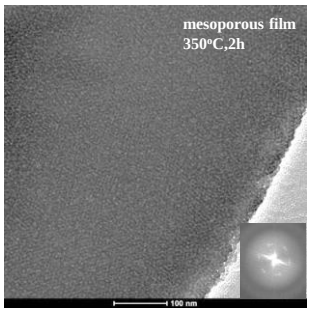
- *Elimination of the surfactant*
- *Preservation of mesoporosity*
- *Solidification of the material*



Observation: The presence of surfactant delays crystallization

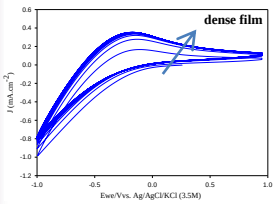
STRUCTURAL CHARACTERIZATION

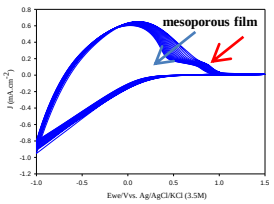


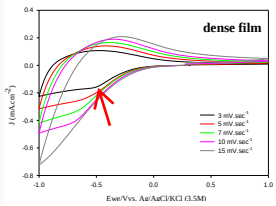


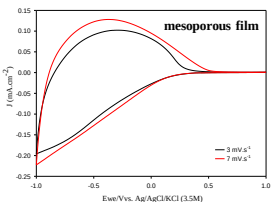
Dense film is composed by a compact and smooth surface
Mesoporous film consists of regular pores with diameters less than 4nm

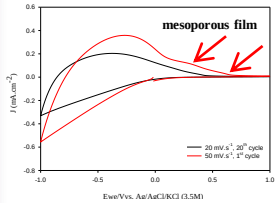
CYCLIC VOLTAMMOGRAMS











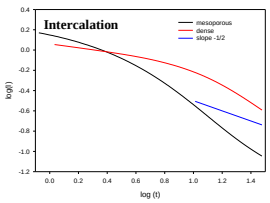
Sample	Diffusion coefficient ($cm^2.s^{-1}$)	
	10^{th} cycle	20^{th} cycle
Dense film	2.15×10^{-10}	2.29×10^{-10}
Mesoporous film	7.31×10^{-10}	7.30×10^{-10}

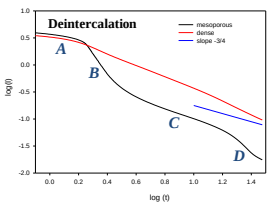
Dense film: *Irreversible traps cause substantial modifications in the first few cycles. At low voltage scan rates, traps are designated by a small cathodic peak.*
Mesoporous film*: Gradual degradation with cycling. Multiple anodic peaks during cyclic voltammetry due to multiple sites for lithium intercalation.*
Enhanced diffusion coefficient implying that mesopores facilitate deinsertion of lithium cations.

KINETIC MEASUREMENTS

Sample	Time for 90% of total charge capacity (10^{th}/20^{th} cycle)		Reversibility (%)	
	Coloration time (s)	Bleaching time (s)	1st cycle	20^{th} cycle
Dense film	24/24	18/18	54%	99%
Porous film	21/21	9/10	73%	96%

Dense film: *Low reversibility in the first cycle. Slower kinetics in regard to mesoporous film*
Mesoporous film: *Improved reversibility in the first cycle. Fast deintercalation.*





During intercalation both films decline in a non-linear way.
Mesoporous film possesses fast (B, D) and slow (A, C) regions of current's decline due to the presence of multiple Li+ sites

CONCLUSIONS

The electrochemical behaviour of WO_3 films depend on the surface chemistry of the material. Mesoporous films possess an open structure with multiple sites for Li+ intercalation/deintercalation improving the electrochemical properties of the film. This is evident by the enhanced diffusion coefficient, the decrease of irreversible traps in the first cycles and the faster deintercalation process. Moreover due to the existence of multiple sites in mesoporous film, current's decline with time follows a multistep progression during deintercalation with fast and slow regions.

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