Université de Liège

GREEnMat

‘’DIP-COATED AND ELECTRODEPOSITED MESOPOROUS WO_3 THIN FILMS FOR ELECTROCHROMIC APPLICATIONS’’

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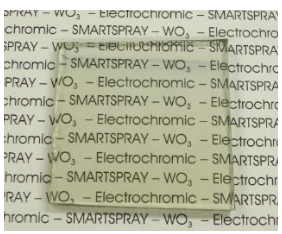
16th International Conference on Thin Films

13-16 October, Dubrovnik, Croatia

WO_3 (PROPERTIES/APPLICATIONS)

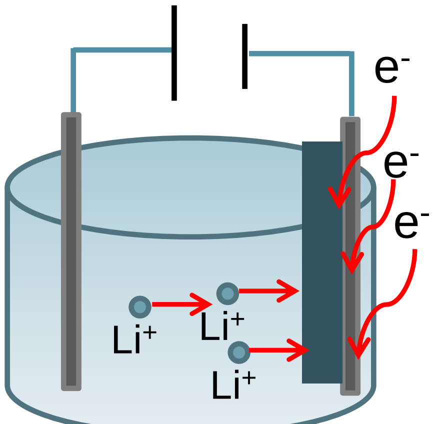
- **n-type semiconductor (2.6-3.25eV)**
  - Photocatalyst
  - Gas sensing applications
  - Dye-Sensitized Solar Cells (DSSC)

- **Optical properties/Chromism**



W(VI) (transparent) → ***W(V)*** **(blue)**

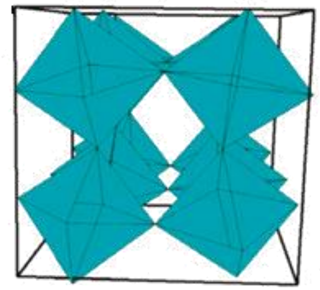
  - Gasochromism
  - Electrochromism
  - Thermochromism
  - Photochromism



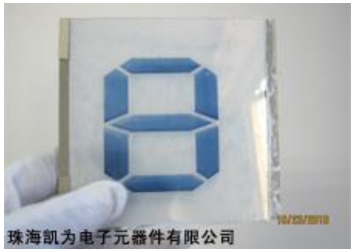
WO_3(ELECTROCHROMISM/APPLICATIONS)

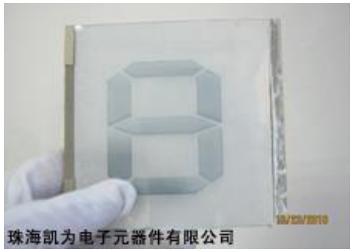
$$WO_3 + xLi^+ + xe^- \leftrightarrows Li_xWO_3$$

Bleached state Coloured state



- Electrochromic displays

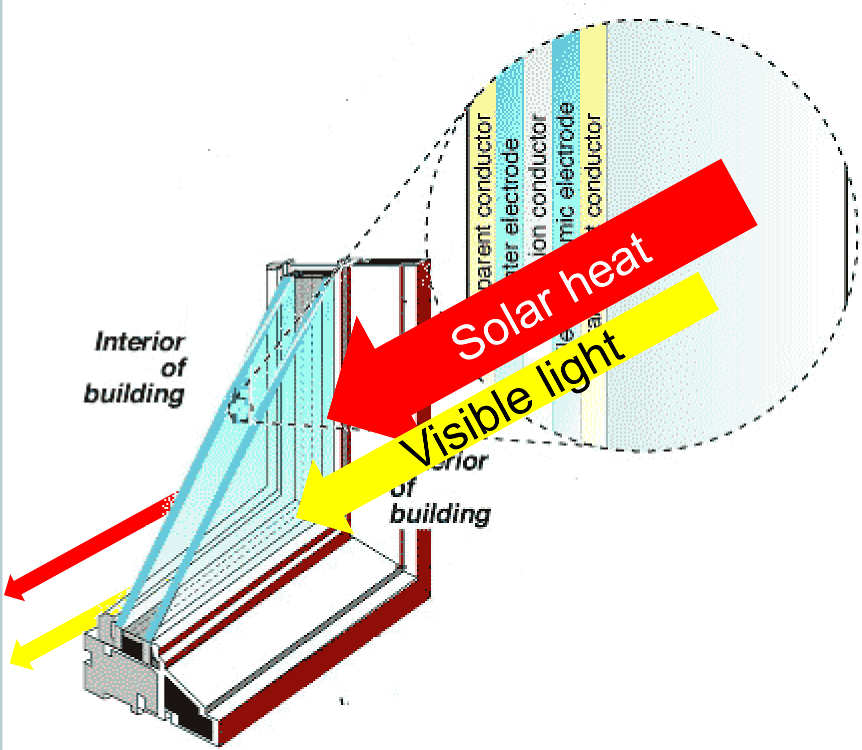




- Auto-dimming car mirrors

- Smart windows

SMART WINDOWS



- Control heat, glare, fading
- Reduce the need for air-conditioning
- Better management of natural light
- Require less than 5V (DC)

↓

Reduce energy demands

PROBLEM!!! HIGH COST (3x) ➔ SMALL MARKET

NEED FOR A MORE COST-EFFECTIVE BUT EFFICIENT PRODUCTION ROUTE

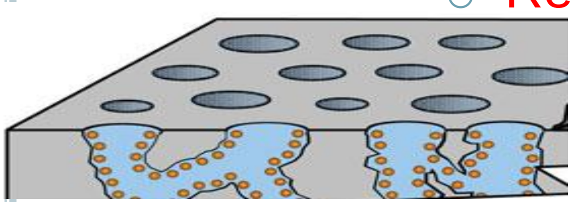
GOAL OF THIS WORK

↓ COST

- No vacuum techniques
- Cheap materials

↑ EFFICIENCY

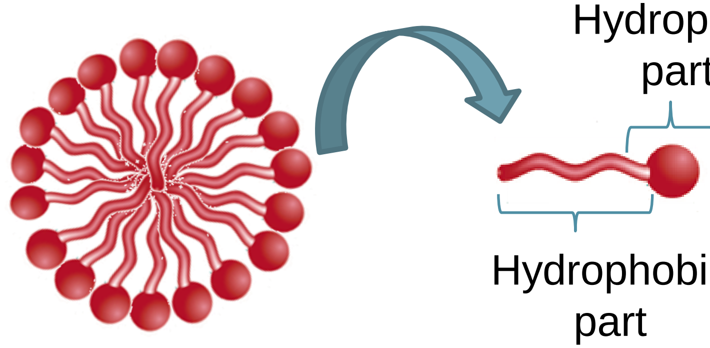
- Cyclic stability
- Reversibility
- Optical modulation
- Color/Bleach time
- Charge density
- Coloration efficiency



- Increased surface area ➔ increase of ‘’active’’ material
- Reduces the diffusion length of cations

POROUS FILMS THROUGH **TEMPLATING**

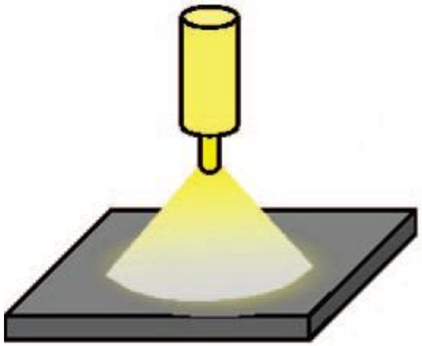
metal precursor



template

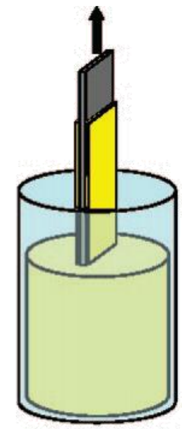
Acc. Chem. Res. 2007, 40, 784-792
Chem. Soc. Rev., 2013, 42, 4198-4216

TECHNIQUES

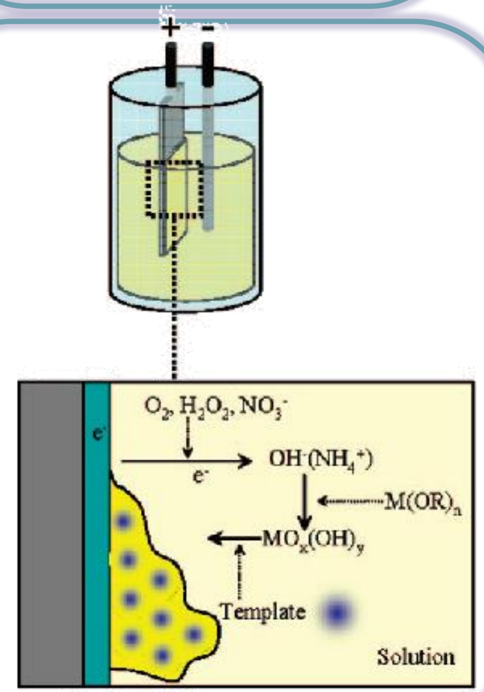


Spray-coating

Spin-coating



Dip-coating



Electro- assisted deposition

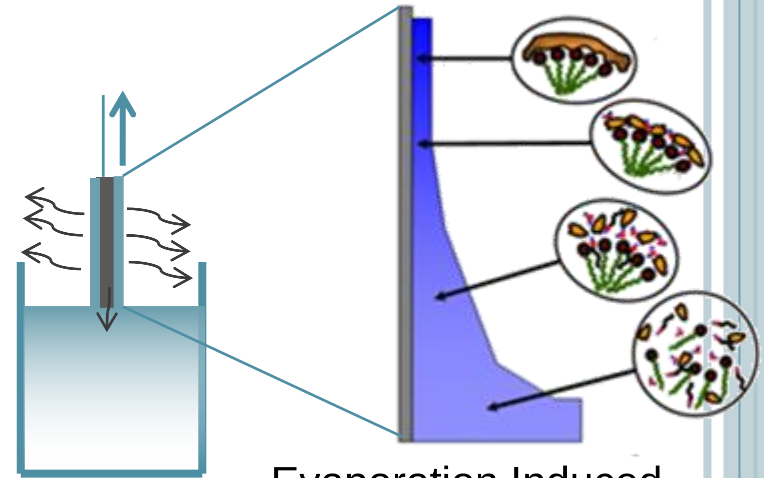
Chem. Mater. 2008, 20, 682-737

EXPERIMENTAL PROCEDURE OF THE **DIP-COATING** TECHNIQUE

$C_{16}H_{33}$-[O-CH₂-CH₂]$_n$-OH

Brij-56 in $EtOH/H_2O$

$W_x(H_2O_2)_y$(acetic acid)$_z$ in $EtOH/H_2O$



Evaporation Induced Self-Assembly (EISA)

Calcination at elevated temperatures

Porous *amorphous* films

Superior electrochromic properties

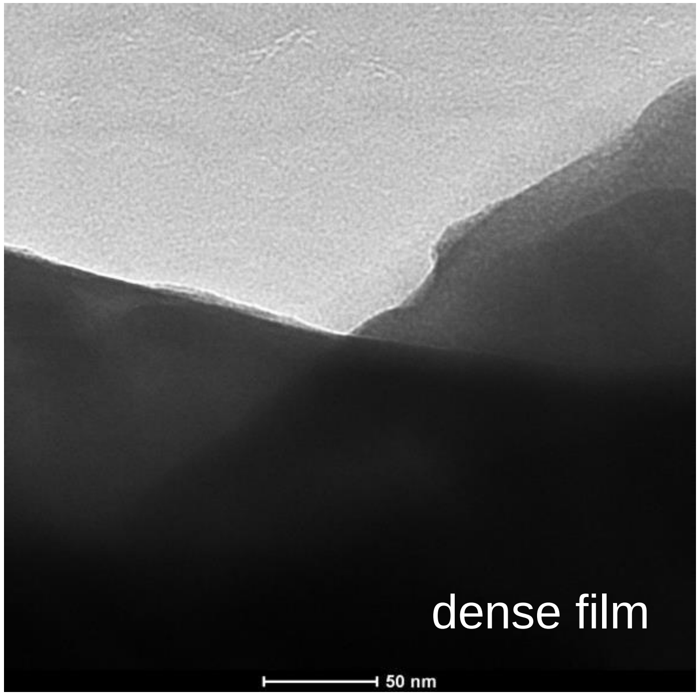
Crystalline films

- Robust and rigid materials
- Less absorption of visible light

D. Chatzikyriakou et al., Electrochimica Acta 137 (2014), 75-82

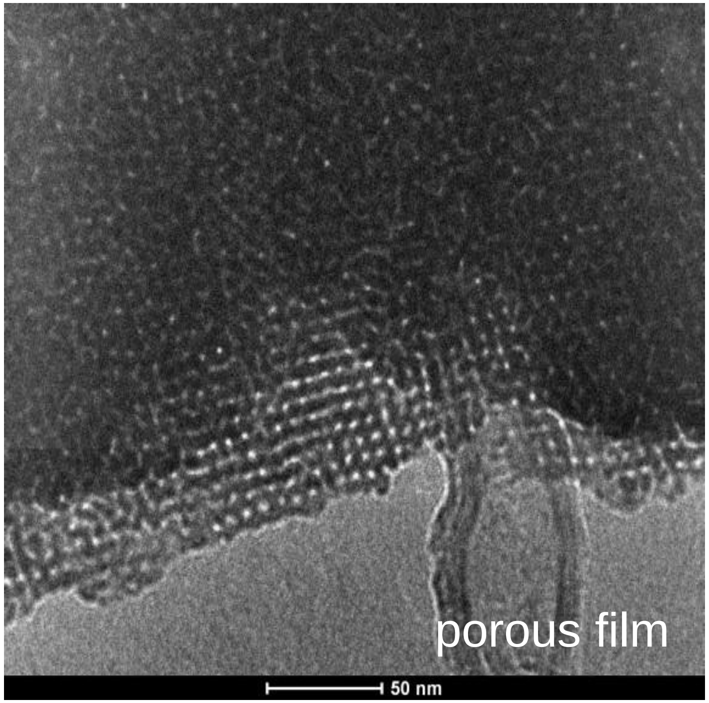
STRUCTURAL CHARACTERIZATION OF THE **DIP-COATED** FILMS

Without template



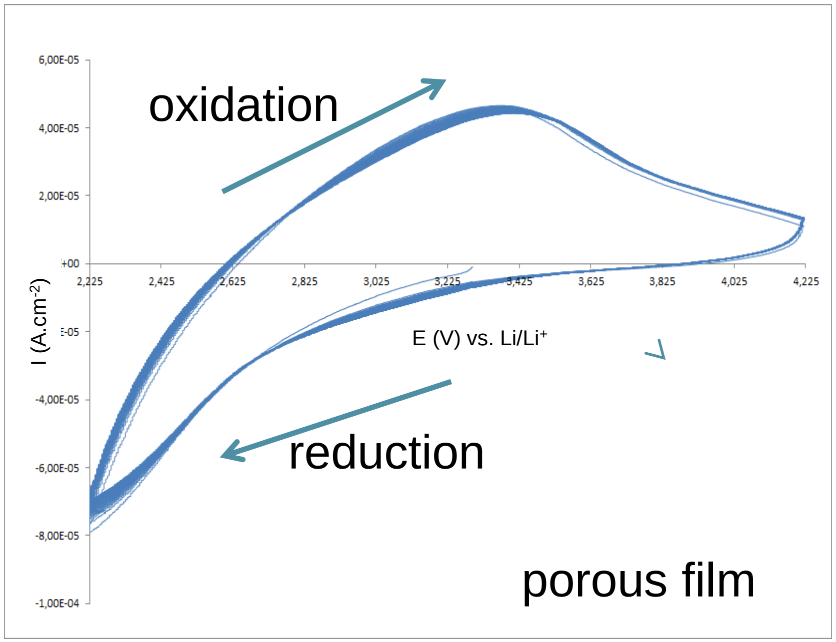
Compact and smooth surface

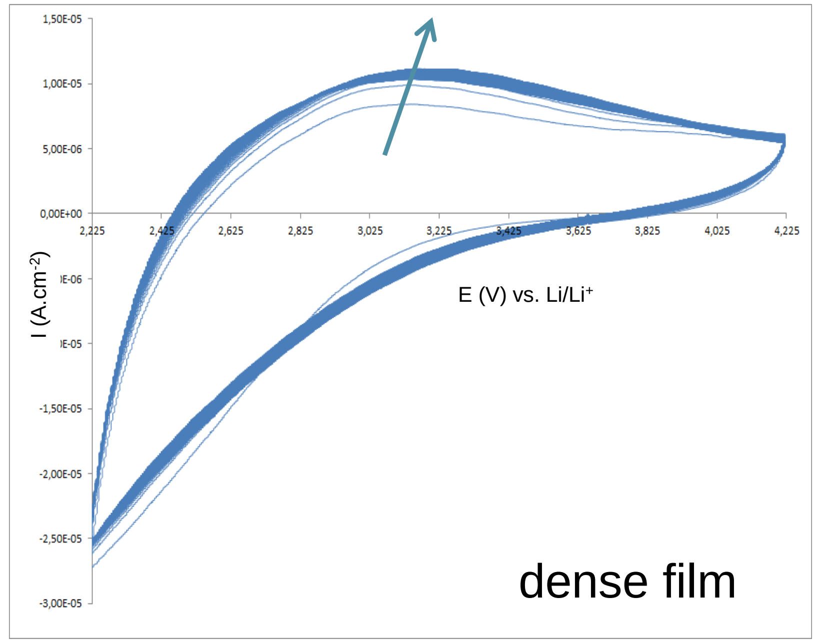
With template



- Regular porosity
- Pores diameter: 2-3nm
- Pore-pore distance: 6nm
- Wall thickness: 3-4nm

ELECTROCHROMIC CHARACTERIZATION OF THE **DIP-COATED** FILMS: CYCLIC VOLTAMMETRY

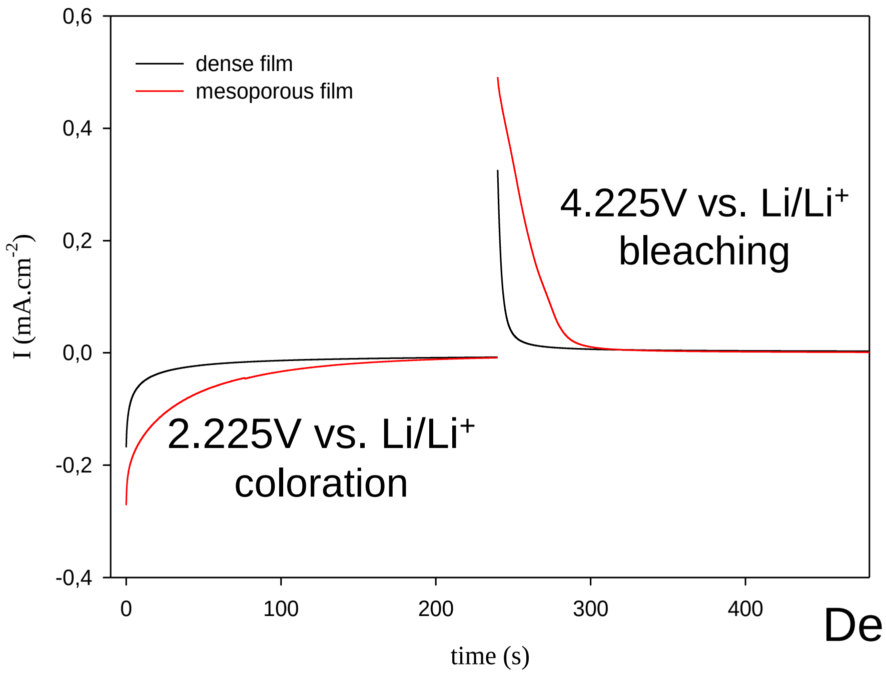




	Reversibility %	
	1stcycle	20th cycle
Dense film	**54%**	94%
Porous film	**93%**	98%

→ Permanent coloration

ELECTROCHROMIC CHARACTERIZATION FOR THE **DIP-COATED** FILMS: CHRONOAMPEROMETRIC MEASUREMENTS



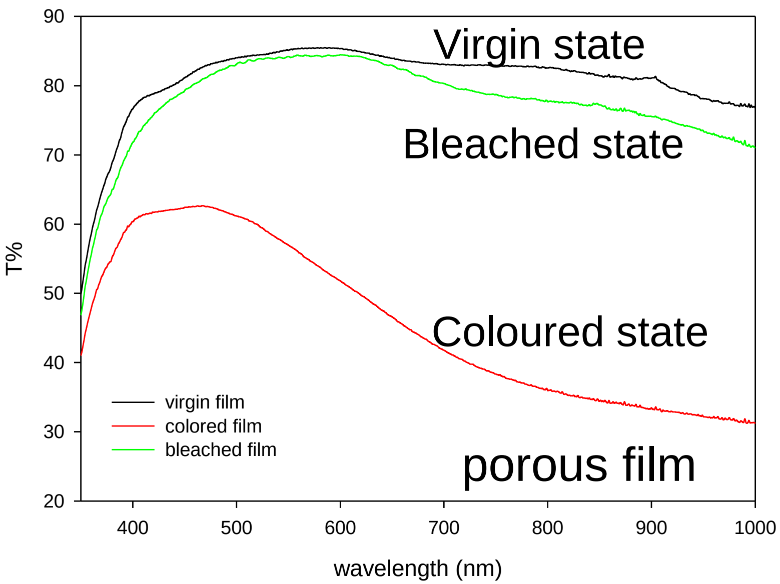
Sample	Time for attaining the 10% of total current capacity (20th cycle)	
	Coloration time (s)	Bleaching time (s)
Dense film	**48**	**11**
Porous film	100	32

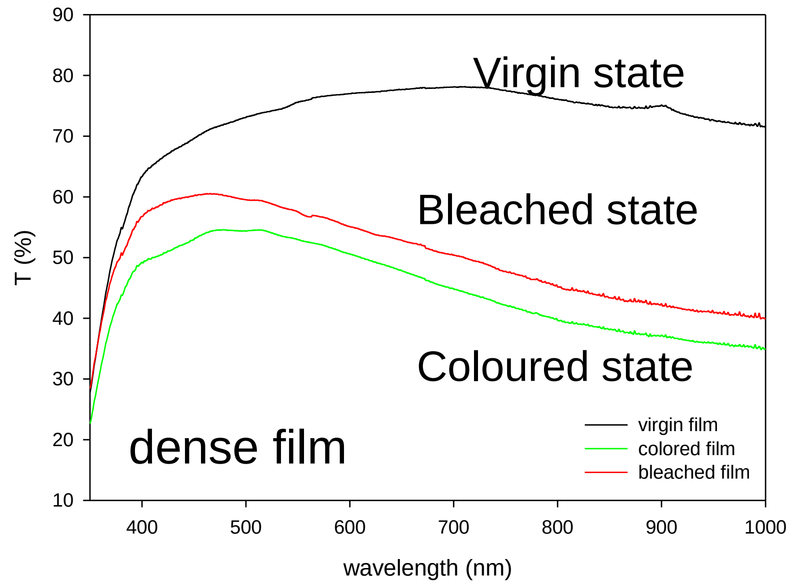
Dense film ➔ faster inter-/de-intercalation

Charge capacity ($mC.cm^{-2}$)	
Intercalation (20th cycle)	De-intercalation (20th cycle)
3.3	3.1
18.0	**17.4**

	Charge capacity ($mC.cm^{-2}$)	
Sample	Intercalation (20th cycle)	De-intercalation (20th cycle)
Dense film	3.3	3.1
Porous film	**8.0**	**7.8**

ELECTROCHROMIC CHARACTERIZATION OF THE **DIP-COATED** FILMS





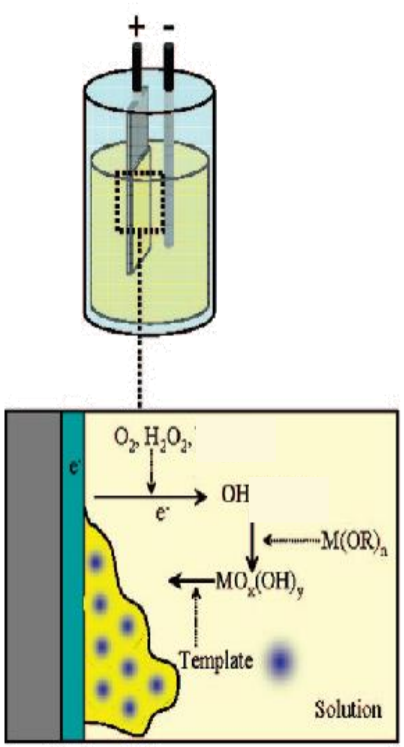
Sample	ΔT% (550/750nm)	Optical Efficiency (cm^{-2}/C)
		20^{th} cycle (550/750nm) $\eta = \frac{\log (Tb/Tc)}{C}$
Dense film	4.6/5.6	12/17
Porous film	**27.2/40.4**	**33/60**

Summarizing for the dip-coated films

	Mesoporous film	Dense film
Switching kinetics	*Worse*	Better
Charge capacity ($mC.cm^{-2}$)	Better	Worse
Reversibility	Better	Worse
ΔT%	Better	Worse
Coloration efficiency	Better	Worse

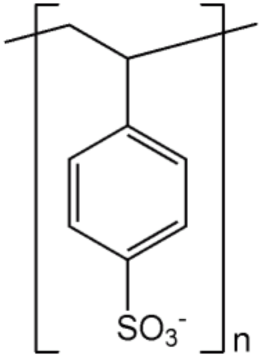
Porous film has better properties than the dense film

EXPERIMENTAL PROCEDURE FOR THE ELECTRODEPOSITION

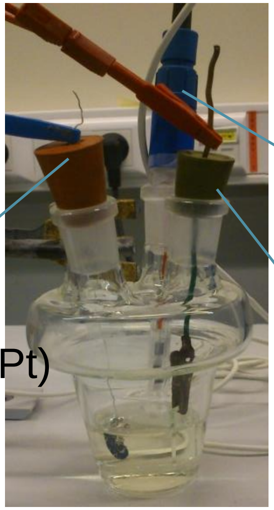


Electro- assisted deposition

- Reduction of H_2O_2 ($W(H_2O_2)_x(CH_3COO)_y$) to OH^-
- Precipitation of $MO_x(OH)_y$ on the surface of the electrode
- Framework's built-up around the template
- Calcination (350°C/2h or 400°C/1h)

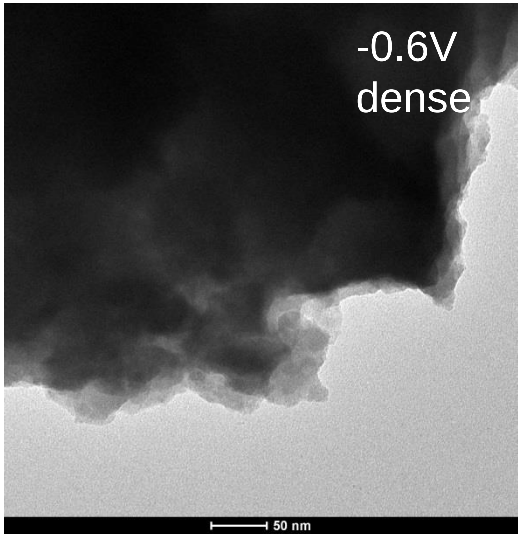


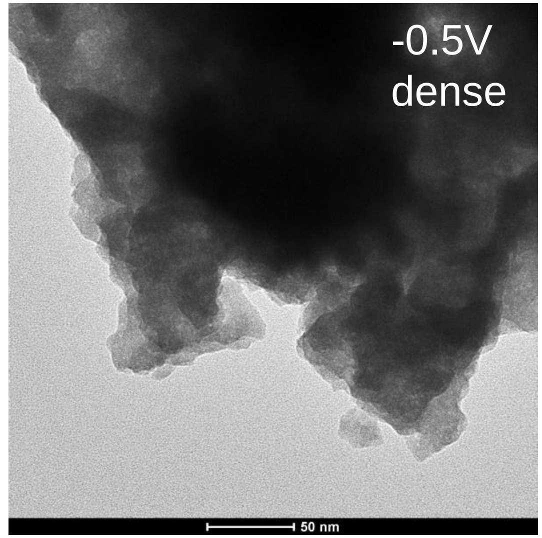
PSS-Na

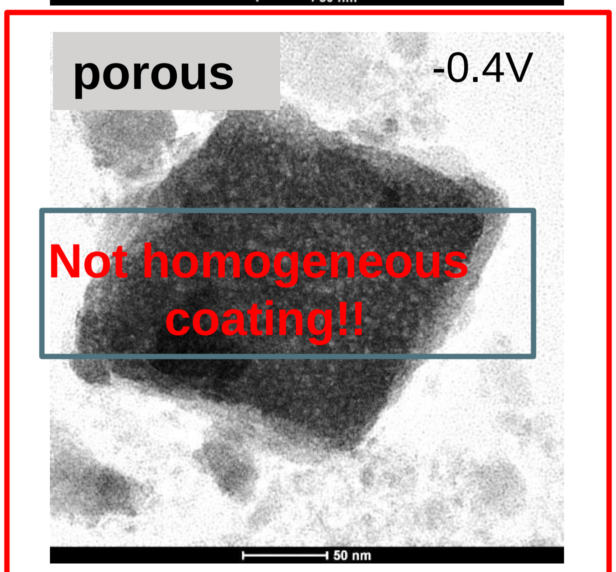


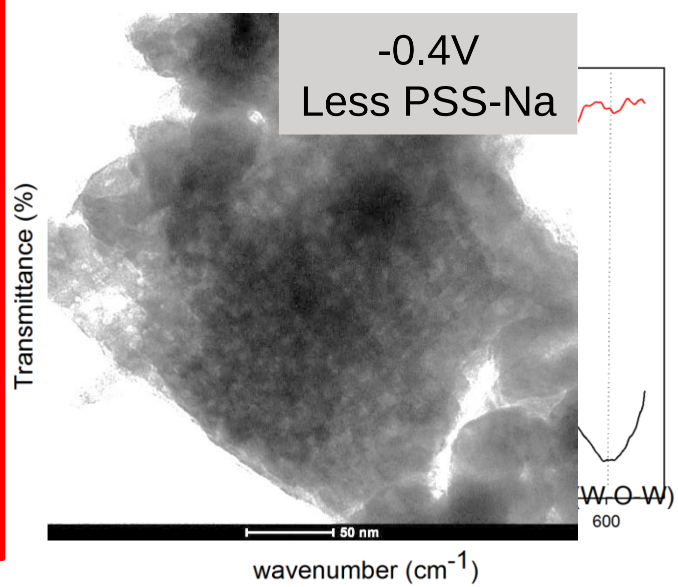
$350 mC.cm^{-2}$

STRUCTURAL CHARACTERIZATION OF THE ELECTRODEPOSITED FILMS CALCINED AT 350^{O}C



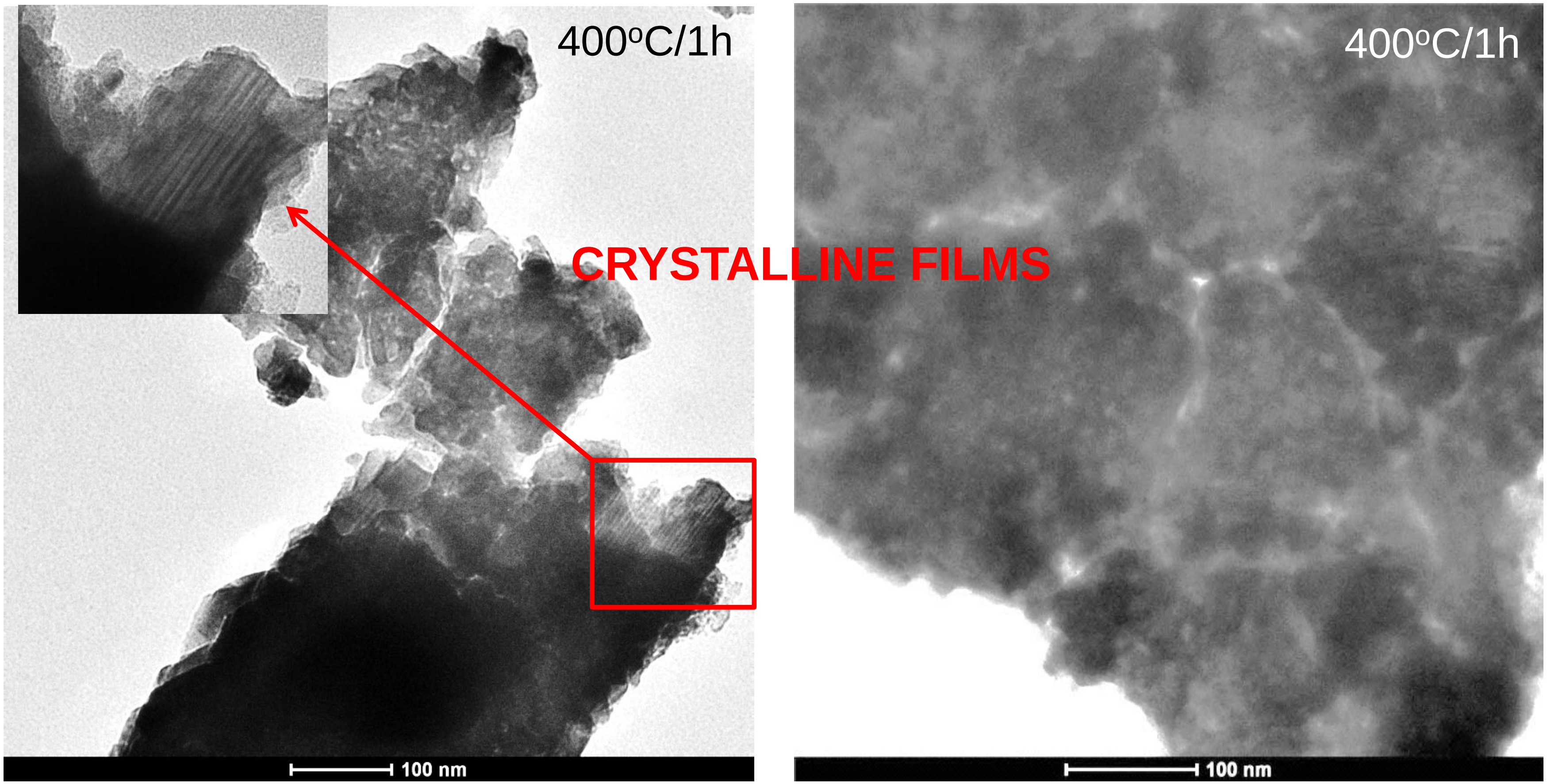




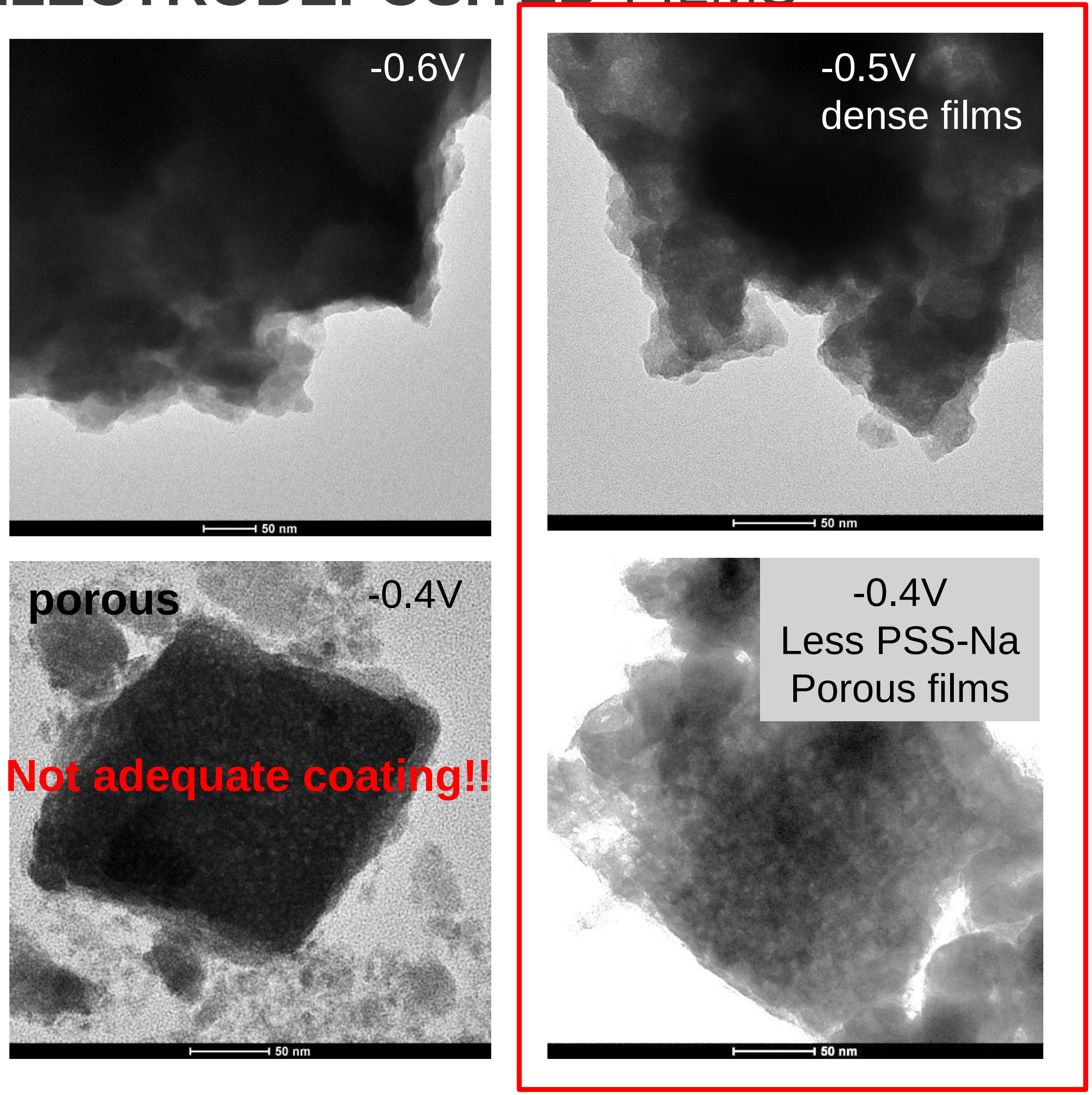


Balance between condensation and co-assembly formation

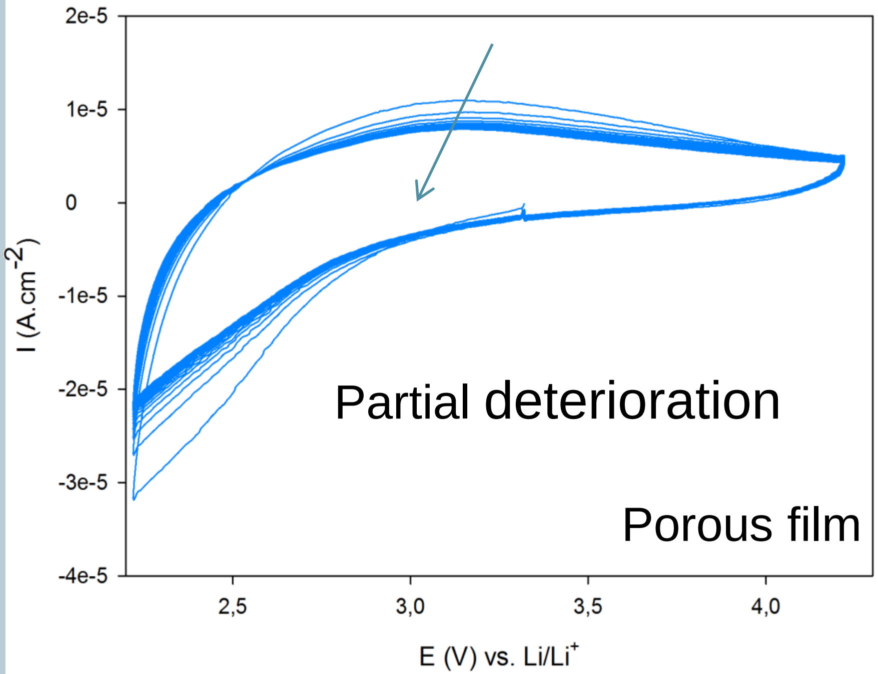
STRUCTURAL CHARACTERIZATION OF THE ELECTRODEPOSITED FILMS

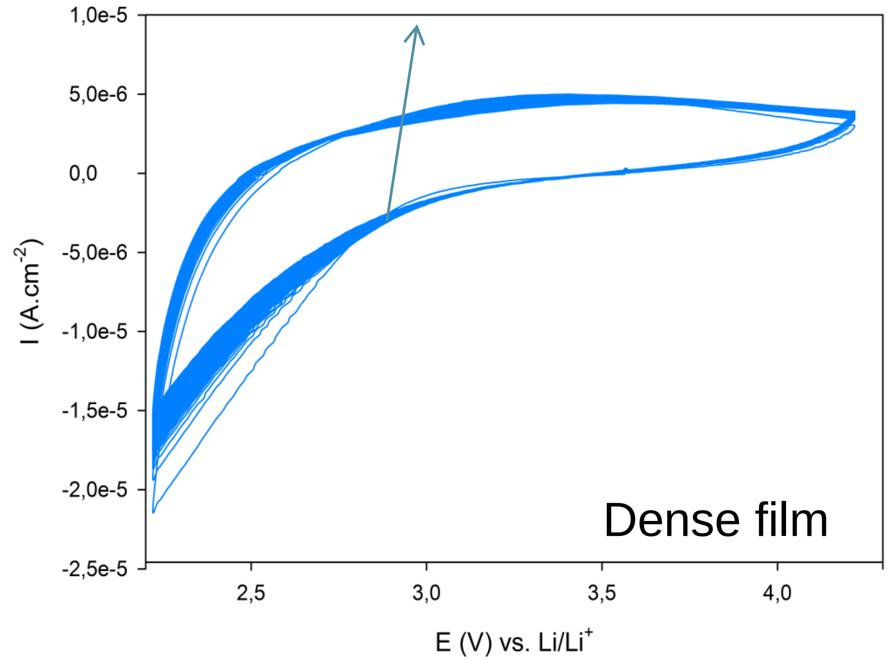


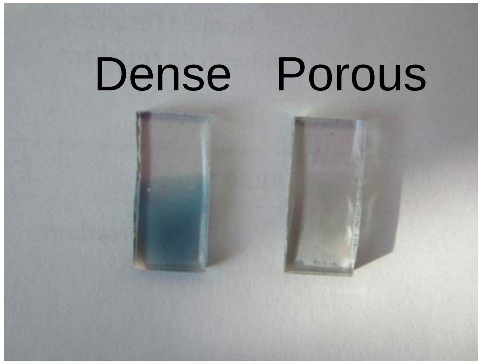
STRUCTURAL CHARACTERIZATION OF THE **ELECTRODEPOSITED** FILMS



ELECTROCHROMIC CHARACTERIZATION OF THE **ELECTRODEPOSITED** FILMS: CYCLIC VOLTAMMETRY

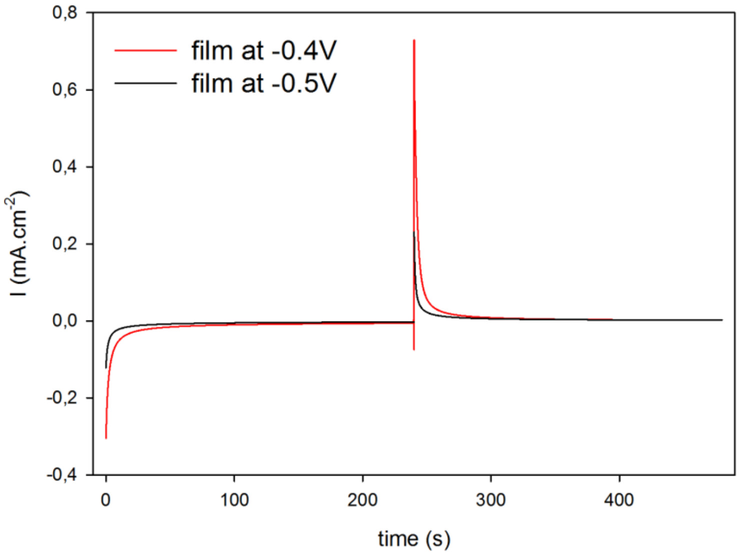






	Reversibility %	
	1st cycle	20th cycle
Dense film	83%	**(54%)**
Porous film	91%	**(77%)**

ELECTROCHROMIC CHARACTERIZATION FOR THE **ELECTRODEPOSITED** FILMS: CHRONOAMPEROMETRIC MEASUREMENTS



Sample	Time for attaining the 10% of total current capacity (20th cycle)	
	Coloration time (s)	Bleaching time (s)
Dense film	26	10
Porous film	20	9

	Charge capacity ($mC.cm^{-2}$)	
Sample	Intercalation (20th cycle)	De-intercalation (20th cycle)
Dense film	1.8	1.5
Porous film	3.8	3.5

Thickness and relative amount of W have not been adjusted yet

SUMMARIZING FOR THE ELECTRODEPOSITED FILMS

- Porous films at -0.4V but not at -0.5V/-0.6V
- Calcination at 400^{o}C gives porous but crystalline films
- Deterioration of the porous film upon cycling (porous are still filled with polymer)
- Film at -0.5V (dense film) similar behavior with the dense film of the dip-coating technique
- Higher charge capacity for the films at -0.4V (porous films)

Thank you for your attention!