

Electrochromic ink based on a cellulosic matrix for fully printed multilayer electrochromic devices

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Short abstract

Printed electronics is a growing market, requiring high-performance inks with tailored functionalities, particularly for flexible devices. Electrochromic devices are especially promising, as they can be integrated into flexible displays, solar cells and smart building for sunlight regulation. The application potential of these multilayer devices is therefore considerable.

Printed electrochromic devices consist of multiple functional layers that must interact efficiently with each other to enable redox reactions responsible for color switching. Ensuring stable and homogeneous ink formulations is essential to warrant the functionality of electrochromic particles. In this context, the objective of our research is to develop innovative bio-based ink formulations, with a specific focus on the design of sustainable binders suitable for screen-printing.

The electrochromic ink developed in this work combines tungsten oxide (WO₃) particles as the functional material with a cellulose nanofibril-based matrix. Previous works have showed the interest of using cellulose nanofibrils for ink formulation. Besides its natural abundance and non-toxicity, cellulose nanofibrils owns an excellent dispersing capability, and a favorable rheological behavior for screen-printing applications.

The developed inks were coated onto polymer films PET coated with indium tin oxide (ITO). To assess electrochromic performance under the behavior, a specific methodology was developed to monitor color changes of the printed layer as a function of the applied electrical potential.

Stable and homogeneous electrochromic inks integrating a biobased binder were successfully formulated. Preliminary results show that a weak electrochemical response can be achieved with as little as 5 wt% electrochromic particle loading. These results are very promising, and further investigations are currently underway to optimize device performance.

Keywords: printed electronics, electrochromism, tungsten oxide ink, nanocellulose

1. Introduction and background

In the 1950s, the foundation of *The Journal of The Electrochemical Society* lays the foundations for research on electrochromism, even though the term was only created in 1961 by J. Platt. First, related to the color change by light named *photochromism* and by temperature variation named *thermochromism*. Electrochromic devices (ECD) have been developing for several years, the first research about the devices can be linked to the discovery of Prussian blue in 1704, leading to its use in electrochromic field in the 1980s, by V. Neff (Neff, 1978) and also K. Itaya (Itaya et al., 1982). Another material discovered in 1815 by J. Berzelius (Futsch, 2022) led to important progress in electrochromic field: works on tungsten oxide (WO₃).

Since, electrochromism contributes to operating several technologies in visibility spectrum such as logistic monitoring, medical devices, smart labels, buildings smart windows (Danine et al., 2014; Leite et al., 2025). The most well-known applications of electrochromic devices are those that switch from a transparent (bleached) state to a dark blue state depending on light intensity such as car rearview mirrors and airplane windows, thereby enhancing visual comfort. Electrochromic devices are also considered as promising solutions for building climate regulation. In particular, they can modulate the amount of sunlight entering indoor spaced according to outdoor light intensity, contributing to improved thermal comfort and reduced energy consumption.

An electrochromic device (ECD) is defined as a device which has the capacity to change its optical properties (typically color or transmittance) when an electrical voltage is applied. Basically, an ECD is composed of several functional layers, each having a specific role in the operation of the device. Regardless the number of layers, the working principle is based on redox reactions occurring between the two electrochromic layers (Khan, 2025). Upon application of an external electrical voltage, electrons are injected or extracted through the conductive electrodes, while an electrolyte layer ensures ionic transport within the device to maintain charge neutrality. The electrochromic effect results from this coupled electron and ion transfer process. Because the redox reactions are reversible, the device can switch back and forth between its bleached and colored states.

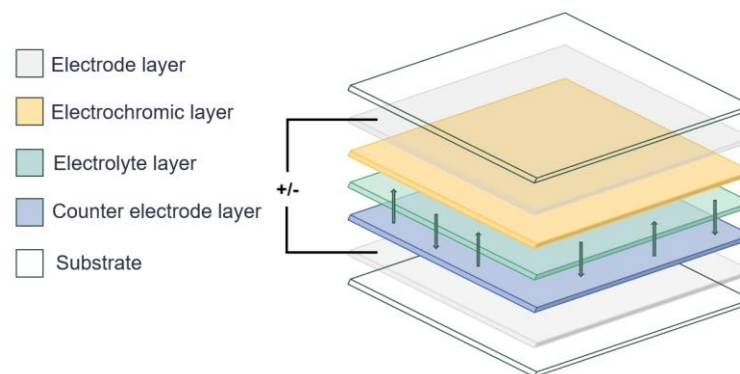


Figure 1: Multilayer electrochromic device

Recently, flexible electrochromic devices have emerged to answer new needs, in particular to address increasing demands for mechanically deformable systems. Achieving such flexibility requires adapted fabrication strategies and compatible materials. In this context, printed electronics represents a particularly relevant approach, as it encompasses a set of manufacturing technologies that enable the deposition of functional materials onto flexible substrates through scalable printing processes. Compared to conventional electronic manufacturing methods, printing processes allow to produce large-area devices on various substrates, with simplified processing steps and lower production costs (Danine, 2016). Therefore, the fabrication of ECDs using printing techniques a highly promising strategy to further enhance their scalability and commercial viability.

Each printing process has specific requirements and is compatible with particular classes of materials. Keys parameters such as rheological behavior, viscosity, particle sizes and colloidal stability are critical in selecting the appropriate printing process, depending on the targeted resolution and application constraints.

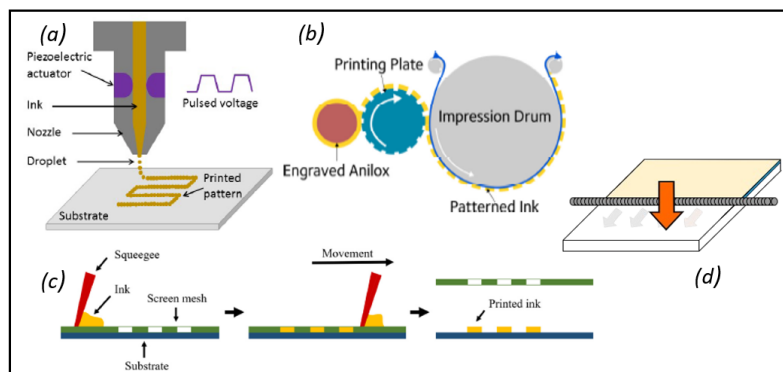


Figure 2: Printing process operating scheme (a) inkjet, (b) flexography, (c) screen-printing, (d) coating

Among the different deposition techniques, coating enables the formation of thin, homogeneous layers with controlled thickness on a substrate. Although not strictly a printing process, it is commonly used to evaluate the printability and film-forming behavior of ink formulations (Burton et al., 2022). Screen printing is one of the most widely used techniques for depositing functional inks. It involves an aluminum frame supporting a patterned mesh screen through which ink is transferred by the movement of a squeegee, enabling the fabrication of well-defined and reproducible patterns. Flexography is a rotary relief printing process in which a flexible photopolymer plate engraved with the motif to print is mounted on a cylinder. The ink, typically low-viscosity and fast-drying, is transferred from an anilox roller (a metered micro-engraved roller) onto the raised areas of the plate, which then deposits it directly onto the substrate. Inkjet printing, in contrast, is a non-contact digital technique in which controlled droplets are ejected from a nozzle, via piezoelectric actuation (Zhang et al., 2024), allowing pattern design to be modified at every printing.

The formulation of electrochromic inks requires the combination of an electrochromic material and a mechanically deformable matrix. Among the large variety of available electrochromic materials, metal oxides, particularly tungsten oxide, are most commonly used due to their high cycling stability and coloration efficiency (Buch et al., 2016). However, alternative materials can be used such as PEDOT-PSS, polyaniline or viologens.

In this work, we propose a sustainable alternative to petroleum-based ink systems through the development of a bio-based binder. The ink matrix is formulated using different grades of nanocelluloses (CNF) and hydroxypropyl methylcellulose (HPMC). These cellulosic materials have previously demonstrated strong potential in printed electronics, either as substrates or as functional ink components (Agate et al., 2018; Hoeng et al., 2016). However, to the best of our knowledge, this is the first study combining these bio-based polymers with tungsten oxide particles for the formulation of electrochromic inks. The developed inks and the ensued printed layers will be characterized in terms of formulation stability, print quality, and electrochemical performance under operating conditions.

This electrochromic ink development project is part of a larger project that aims to develop each layer of the electrochromic dissipative using a bio-sourced and sustainable approach. The following figure illustrates all the stages (names work packages) of this extensive ongoing project.

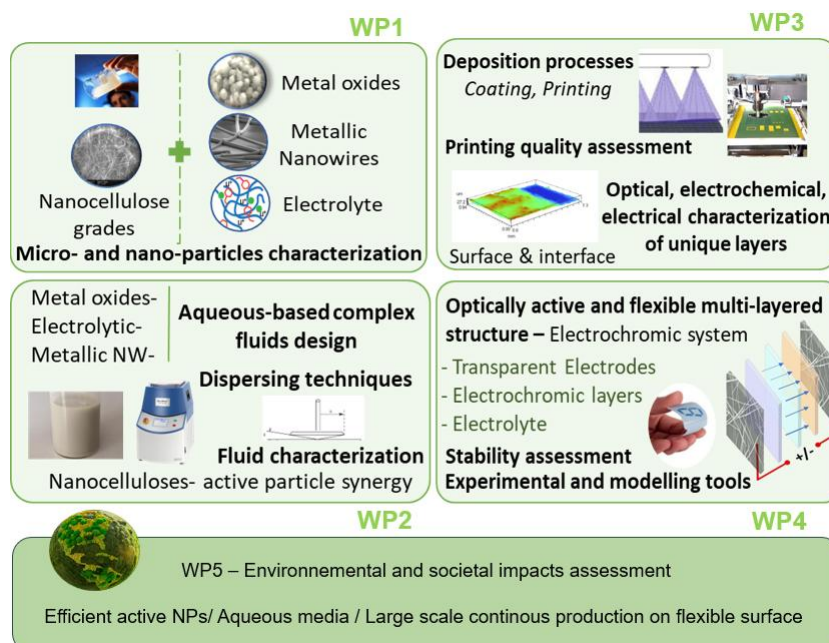


Figure 3: Work packages of the project

2. Materials and methods

2.1 Materials

Tungsten oxide was purchased from US Research Nanomaterials: nano powder with 60nm particles. An aqueous suspension of TEMPO-oxidized cellulose nanofibrils (CNFt) was purchased from Nippon Paper, Japan. An aqueous suspension of cellulose nanocrystals (CNC) was purchased from Université du Maine, USA. An aqueous suspension of cellulose nanofibrils (CNF) was purchased from Université du Maine, USA.

Hydroxypropyl methylcellulose (HPMC) was purchased from ThermoFisher Scientific, France with the following specifications: 27.0-30.0 %wt methoxy content and 7.0-12.0 %wt hydroxypropyl content. Distilled water was used for all experiments.

Polyethylene terephthalate (PET) coated with indium thin oxide (ITO) A4 sheets used as printing substrates were purchased from Gwent group (UK).

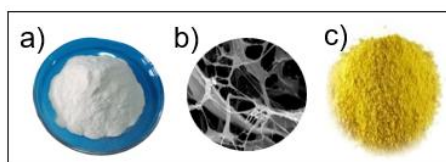


Figure 4: Materials image (a) HPMC, (b) CNFt, (c) tungsten oxide

2.2 Ink formulation

Firstly, an HPMC/CNFt suspension was prepared. The CNFt suspension was diluted to the chosen concentration (0.5 wt%) at neutral pH using distilled water and homogenized at room temperature with an Ultra-Turrax disperser (Thermofisher, France) at 4500 rpm during 30 to 60s. The suspension was then heated to 50°C using a hot plate with magnetic stirring. Once heated, the suspension was further mixed using the Ultra-Turrax, while HPMC powder was gradually added

until each powder portion was fully solubilized in the hot suspension. High shear-mixing was performed at 8000 rpm using the Ultra-Turrax disperser during 5 minutes. The final blends were stored in a fridge at 4°C for 24 to 48h prior to ink preparation.

Then, to obtain the final ink formulation, each component was weighted thanks to a precision balance and introduced into a beaker in the following order: HPMC/CNFt composite suspension, distilled water and tungsten oxide particles. The blend was homogenized at 1500 rpm for 4 minutes using a Speed mixer from Hauschild. The resulting ink was stored at room temperature for 24 to 48h prior to printing and/or characterization.

2.3 Colloidal stability assessment

5 wt% of tungsten oxide particles are added in distilled water with 0.5 wt% of nanocellulose in water and placed in test tube during days. Sedimentation is analysed thanks to Turbiscan device from Microtrac.

2.4 Flow behavior of the bio-based binder and ink rheology

Rheological measurements were performed using a rheometer (MCR 301) from Anton Paar. A parallel-plate geometry (CP50-1 mm) with a gap set of 1 mm was used at a controlled temperature of 20°C. Flow curve experiments were performed by increasing the shear rate from 0.1 to 100 s⁻¹ using a logarithmic ramp consisting of 40 steps, each with a duration of 60 s. The apparent viscosity was recorded as a function of shear rate. The thixotropy behaviour of the ink was evaluated through a three-step shear protocol: a low shear rate at 2 s⁻¹ applied for 150s, followed by a high shear rate of 1000 s⁻¹ for 45s, and finally a recovery step at 2 s⁻¹ for 150s. Each measurement was performed at least in duplicate.

2.5 Printing of stretchable inks by coating

The formulated inks were deposited onto ITO-coated PET substrates using a Baker film applicator from Elcometer mounted on an automated RK coater system from RK PRINT COAT INSTRUMENTS Ltd. The printed layers were dried at 30°C during 15 minutes.

2.6 Characterization of printed electrochromic layer by Scanning Electron Microscope (SEM)

A Quanta 200 Scanning Electron Microscope (SEM) provided by FEI (Hillsboro, Oregon, United-States) was used to take pictures at a smaller scale of printed electrochromic layer. It operated under high vacuum at 5.0 kV with a spot size of 5.0 in secondary electron mode. Around 5 pictures of each sample were taken and the most representative one is shown in the following work.

2.7 Behaviour of a printed layer: electrochemical characterization

The electrochemical behavior of the printed layers was investigated using a three-electrode electrochemical system. Measurements were performed with a potentiostat from Biologic, France, connected to an electrochemical cell kit from Sigma-Aldrich. A platinum plate was used as the counter-electrode. The electrolyte consisted of a liquid solution of LiClO₄ from Sigma-Aldrich dissolved in propylene carbonate from Roth.

3. Results and discussion

3.1 Colloidal stability of tungsten oxide suspensions

Prior to designing the bio-based binder formulation, several grades of nanocellulose were mixed with tungsten oxide particles in order to investigate the colloidal stability of the suspensions (Figure 5). Ensuring colloidal stability is essential for maintaining a homogeneous ink formulation over time and preventing aggregation and sedimentation of the electrochromic particles. This preliminary study aimed to evaluate the influence of nanocellulose morphology and surface charge on the stabilization of tungsten oxide particles. The graph shows the evolution of particles average value. Higher is the variation, higher is the sedimentation.

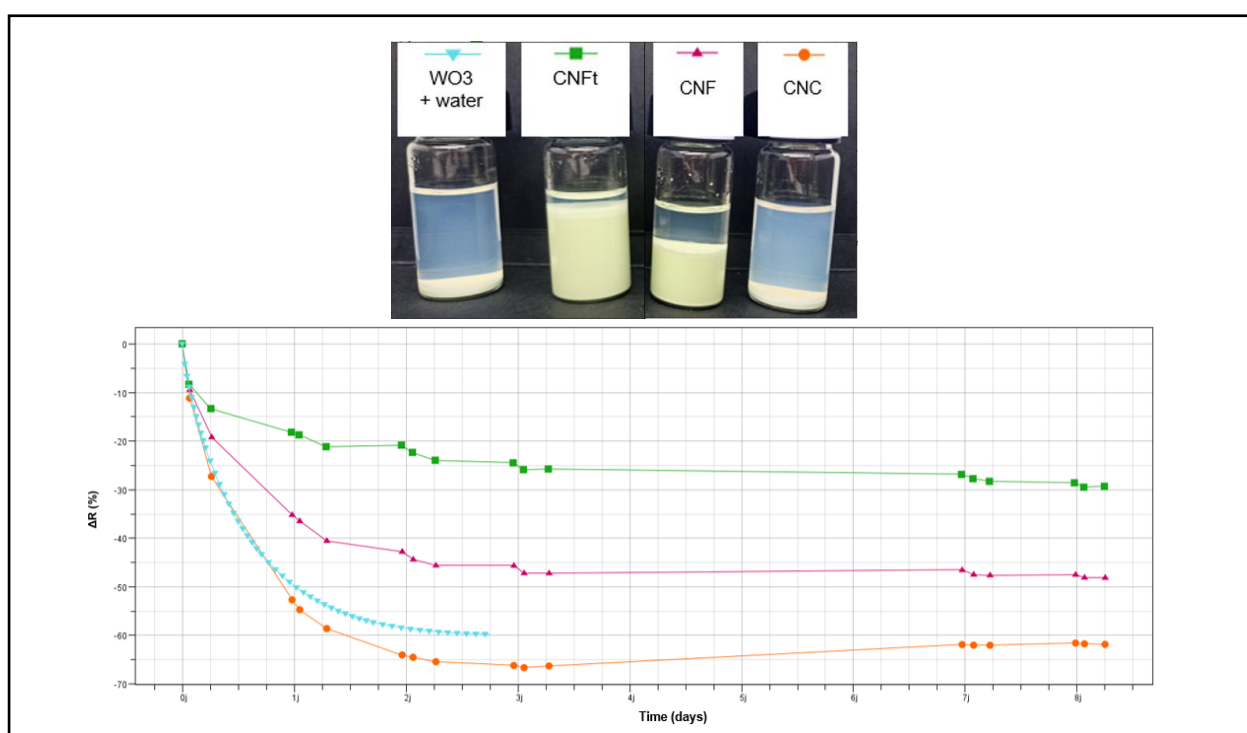


Figure 5: Colloidal stability of tungsten oxide suspensions depending on the nanocellulose grade

Tungsten oxide dispersed in distilled water exhibited poor colloidal stability and rapid sedimentation. The addition of nanocellulose significantly improved the stability of the suspensions. In particular, TEMPO-oxidized cellulose nanofibrils provided high stabilization. This behavior can be attributed to two main effects: first, the negatively charged carboxyl groups introduced during TEMPO oxidation promote electrostatic repulsion between particles, limiting aggregation. Second, the entangled fibrillar network formed by CNFt creates a three-dimensional structure that physically traps the particles, preventing sedimentation.

3.2 Bio-based binder formulation: blending CNFt and HPMC

The electrochromic inks developed in this work rely on a bio-based matrix composed of hydroxypropyl methylcellulose (HPMC) and TEMPO-oxidized cellulose nanofibrils (CNFt). The rheological properties of this composite system were investigated to assess the adequation for screen-printing ink formulation.

Rheological behaviours of biobased are extracted from Marie Goizet previous works, with authorization, while we wait for our own study to be done. Flow behavior was studied for several

ratios of HPMC/CNF_t, from 3:1 to 4:0. A pure solution of HPMC behaves almost as a Newtonian fluid, with a viscosity that remains nearly constant under shear. Introducing CNF_t in this solution, even at low concentrations, leads to a significant increase in viscosity and generates a shear-thinning behavior. This rheological behavior is particularly advantageous for screen-printing applications. Indeed, during printing, the ink initially rests on the screen and must remain sufficiently viscous to avoid flowing through the mesh openings. Then, the squeegee applies pressure, the ink experiences a high shear rate (Neidert et al., 2008), which reduces its viscosity and allows it to pass through the mesh onto the substrate. As shown in Figure 6, the viscosity of the HPMC/CNF_t composite decreases under shear, facilitating deposition while maintaining adequate viscosity at rest. Therefore, blending HPMC and CNF_t provides an efficient strategy to tune both viscosity and shear-thinning behavior in screen-printing inks.

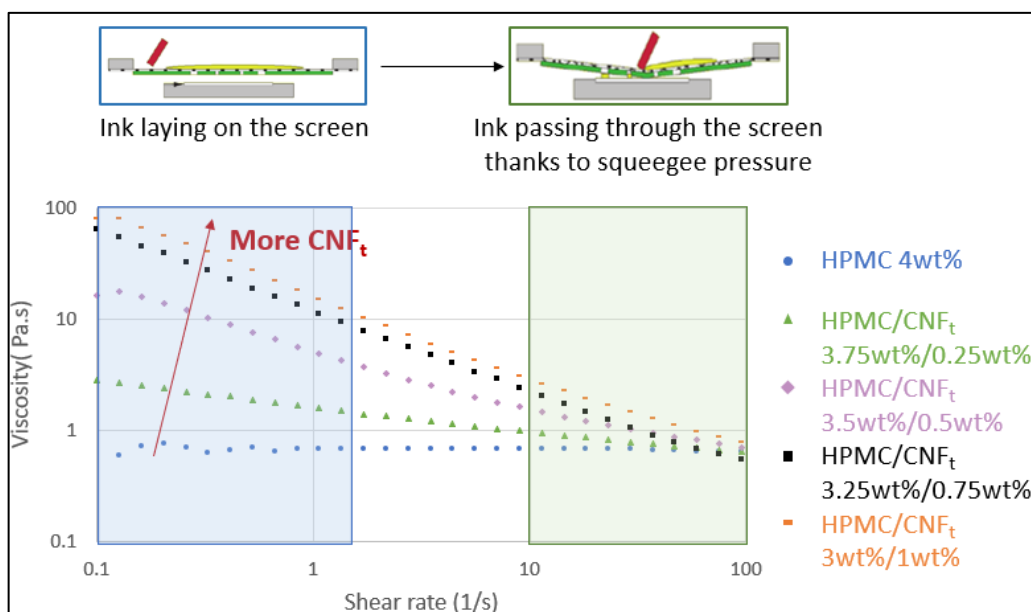


Figure 6: Flow curve measurements on HPMC/CNF_t suspensions at 4 wt% and connection with screen-printing process

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3.3 Electrochromic ink formulation

Electrochromic ink must meet the rheological requirements of the selected printing process. In the case of screen-printing, shear-thinning and thixotropic behaviours are specifically expected. In fact, a reduction in viscosity under shear facilitates the passage of the ink through the screen mesh, while viscosity recovery after deposition prevents excessive spreading on the substrate. Rheological measurements were therefore performed to evaluate the flow and recovery behavior of the electrochromic ink, based on 5 wt% of biosourced matrix and 5 wt% of tungsten oxide in distilled water.

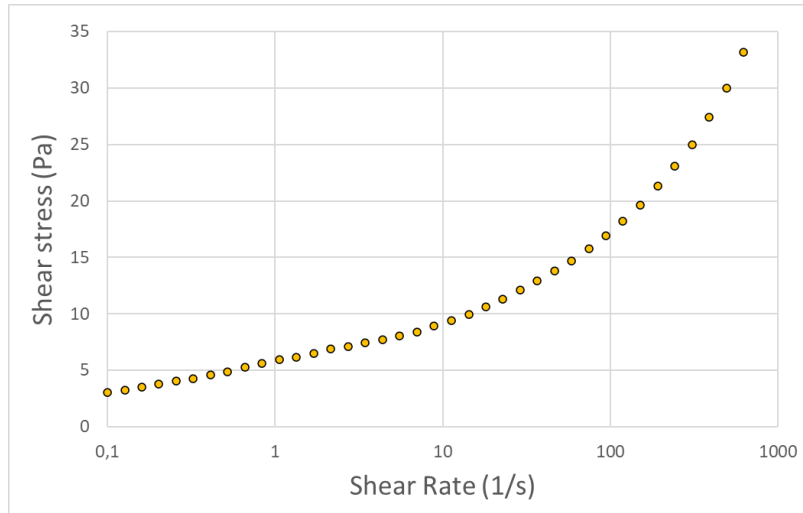


Figure 7: Shear rate evolution as a function of applied shear stress for the electrochromic ink

The electrochromic ink exhibits a pronounced shear-thinning behavior, confirming its suitability for screen-printing process, as shown on figure 7.

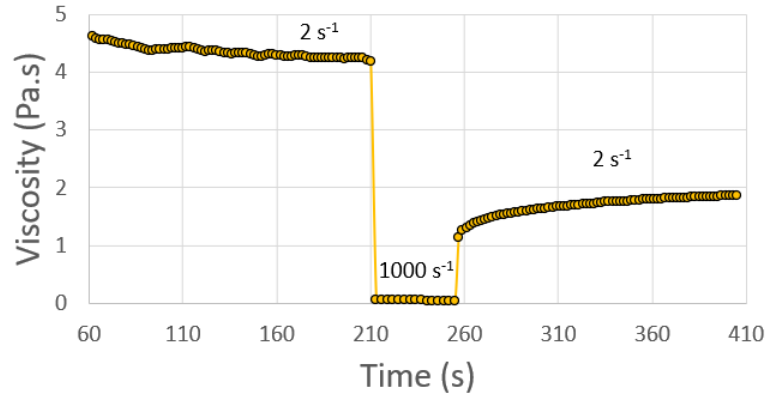


Figure 8: Thixotropic recovery test of the electrochromic ink

The thixotropic recovery was evaluated by comparing the viscosity before the application of a high shear rate and after a resting period under low shear, as shown on figure 8. A recovery rate of 81.5% was obtained, indicating that the ink rapidly restores its viscosity after deposition. This property is critical for ensuring good pattern fidelity and preventing ink spreading on the substrate.

3.4 Printed layer characterization and electrochemical performance

Preliminary coating test of the electrochromic ink resulted in homogeneous thin films with a thickness of approximately 25 μm . SEM images have been done onto surface and cross-section of the printed layer. Uniform particles repartition is observed with some aggregates, as shown on figure 9. Blending strategies are under study.

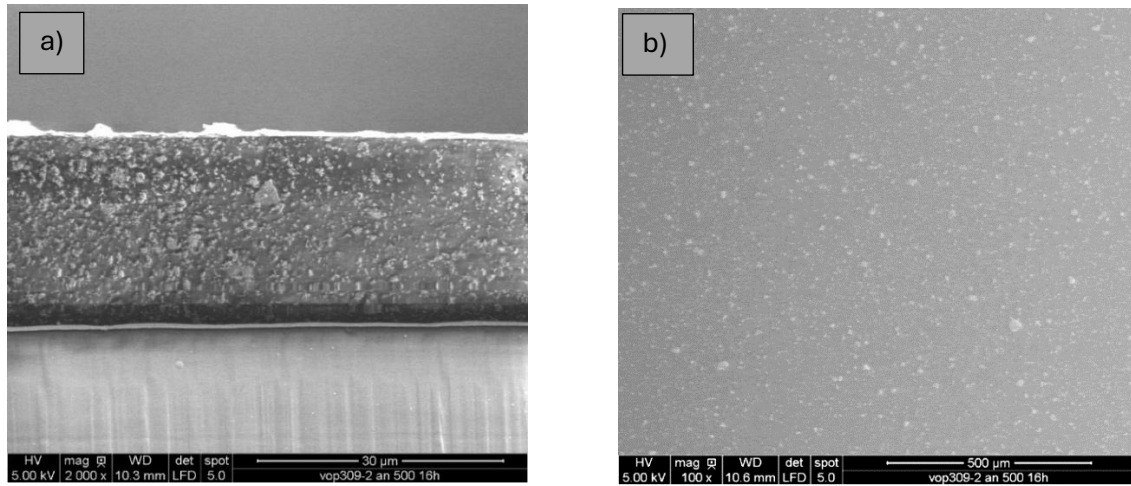


Figure 9: a) SE-SEM electrochromic layer cross-section, b) SE-SEM electrochromic layer surface

Electrochemical signal is obtained through cyclic voltammetry. Even if the signal remains low, (figure 10), it shows encouraging results. Optimizing the proportions of materials in the ink, as well as the thickness of the printed layer, will allow to obtained optimized performance.

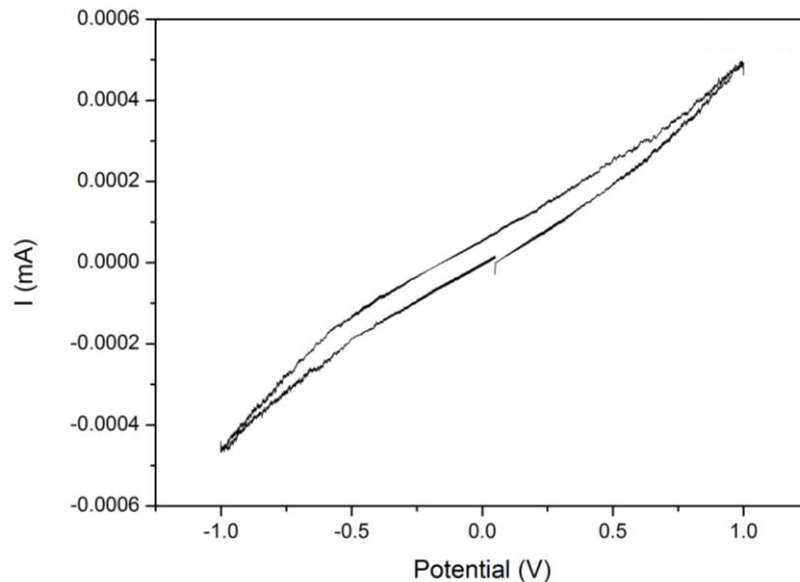


Figure 10: Cyclic voltammetry of printed electrochromic layer

4. Conclusions

This work demonstrates the feasibility of formulating bio-based electrochromic inks. The addition of TEMPO-oxidized cellulose nanofibrils significantly improves the colloidal stability of tungsten oxide suspensions, enabling the formulation of stable inks. A hybrid binder composed of HPMC/CNFt was developed providing both dispersing capability and suitable rheological properties for screen-printing. The resulting electrochromic ink exhibits the shear-thinning and thixotropic behaviors required for this printing technique. Homogeneous electrochromic films were successfully applied using a laboratory coater. Future works should focus on thickness layer reduction for enhancing the device as well as testing different mixing methods.

Acknowledgements

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