

ELECTRODEPOSITION AND PERFORMANCE OF TUNGSTEN AND PANI-BASED ELECTROCHROMIC MATERIALS

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Abstract — Electrochromic (EC) materials reversibly change their optical properties with the application of electrical potentials. In application as smart windows, by modulating the amount of light passing through, EC windows contribute to lower energy consumption in maintaining temperatures in buildings. This study focused on electrochemical deposition (ECD) of the EC film, the main component of an EC device. This study (1) compared inorganic tungsten oxide (WO₃) and organic polyaniline (PANI) EC films; and (2) investigated the effect of the duration of ECD on the performance of the EC samples. WO₃ films were deposited with constant potential of -0.7V for durations of 200s, 500s, 800s, 1100s and 1400s. PANI films were deposited with galvanostatic current of 0.01A for durations of 60s, 80s, 100s, 120s and 140s. A directly proportional relationship was observed between deposition time and thickness of films for both WO₃ and PANI. With increasing thickness, the samples generally increased in contrast until an optimal thickness of 438nm for WO₃ and 131nm for PANI. Taking into account results of EC contrast, colouration and bleaching time, charge insertion and extraction potentials and colouration efficiency, WO₃-based samples were overall superior to PANI-based samples.

Keywords-electrochromic; smart windows; electrochemical deposition; WO₃; PANI; thickness; contrast; switching time; cyclic voltammetry; colouration efficiency.

1. Background and Purpose of Research

Electrochromic (EC) materials reversibly change their optical properties with the application of potential, thereby blocking waves of certain wavelengths from passing through. EC smart windows save 16% of peak electricity usage [1-3] via the modulation of light transmissions to regulate heat gain and electrical usage in maintaining temperatures within buildings [4]. This study seeks to optimise the performance of EC devices through comparisons between organic and inorganic EC materials assembled through electrochemical deposition (ECD) as ECD is a cost effective and accessible method of deposition [5,6].

1.1. Performance Factors

EC materials are usually assessed on their performance in the following aspects [7]: (i) Electrochromic Contrast is the difference in transmittance of the EC film between coloured and bleached states at wavelength of 633nm, where the contrast is most prominent. (ii) Switching Time, specifically colouration time and bleaching time, is the time taken to achieve 90% of the change in contrast – colouration refers to a decrease in the optical transmittance; bleaching refers to the opposite. (iii) Cyclic Voltammetry (CV) is used to evaluate the stability of the EC film [8]. Current is scanned linearly and repeatedly from one potential to another. The CV of a reversible redox reaction identifies the points of peak potential separation. (iv) Colouration Efficiency (CE) refers to the amount of change in the light absorbance of the

EC material for every charge per unit area applied (ΔQ). It is calculated by: $CE = \Delta \left[\log \left(\frac{T_b}{T_c} \right) \right] / \Delta Q$, where T_b and T_c refer to the transmittance values at bleached and coloured states respectively [8].

2. Hypothesis

This study compared and evaluated the performances of both WO₃ and PANI -based EC materials electrodeposited at varying parameters. As WO₃ is an inorganic material whereas PANI is an organic material, it was hypothesised that PANI samples have smaller electrochromic contrast, faster switching time, lower redox switching potentials and higher colouration efficiency [7].

3. Materials and Methods

Prior to this study, preliminary experiment on EC samples deposited with WO₃ on Indium Tin Oxide (ITO) glass revealed -0.7V to be the optimal ECD potential for WO₃, as shown in the appendix. In this study, samples were deposited with WO₃ and PANI respectively on Fluorine-doped Tin Oxide (FTO) glass, with 0.5M sulfuric acid (H₂SO₄) as electrolyte for functional testing [9].

3.1. Preparation of Electrolytes

To prepare the electrolyte for ECD of WO₃, 1.03g of Na₂WO₄ was dissolved in 200 ml DI water, and concentrated HClO₄ was added to lower the pH of the solution to 1.200 [8-9]. Following that, 0.0625g of 30% hydrogen peroxide (H₂O₂) was added to the solution, which was then stirred at 600rpm with a magnetic stirrer at room temperature for 24 hours before use. To prepare the electrolyte for ECD of PANI, 0.9ml of pure aniline was mixed with 100ml H₂SO₄ and stirred until fully dissolved. To perform the functional testing for the samples to evaluate their EC properties, concentrated H₂SO₄ was diluted to 0.5M and used as the electrolyte.

3.2. Electrodeposition Procedure

FTO-glass of thickness 1.1mm of size 2cm by 5cm were cleaned by ultrasonic sonication in acetone, isopropanol and deionised water. A strip of conductive copper tape was pasted along the width of the glass on the electrically conductive side. The glass slides were immersed in the electrolyte solution to a depth of 3.5cm. FTO on the glass served as the working electrode; a Pt plate was used as counter electrode; an Ag/AgCl electrode was used as a reference electrode. WO₃ was deposited at the optimal potential -0.7V via potentiostatic deposition, for time durations ranging from 200s to 1400s with intervals of 300s. Samples were labelled from W1 to W5 with increasing length of deposition. PANI was deposited via galvanostatic

deposition with a current output of 0.01A for time intervals ranging from 60s to 140s with intervals of 20s, with samples labelled from P6 to P10 with increasing length of deposition.

3.3. Characterisation

Prior to deposition, the sheet resistance of the FTO layer was measured by a Jandel model RM 3000 four-point probe at 3 random spots to ensure uniformity in electrical resistivity, as shown in the appendix. While the variable factor was the duration of deposition, the thickness of the EC film deposited has a more direct relationship with its performance, thus thickness was measured using an Alpha-step surface profiler. For the PANI samples, replicates were fabricated as tests for measurement of thickness and observation of morphology are both destructive to the integrity of the PANI film: P1 for P6, P2 for P7, P3 for P8, etc. To measure the contrast and switching time, the samples were placed in cuvettes filled with 0.5M H₂SO₄, into a UV-3600 UV-VIS-NIR Spectrophotometer. The transmittance was scanned over a wavelength range of 300.00nm to 900.00nm. Potentials of 0V, -0.7V and +0.3V were applied, where 0V results in the original post-ECD state; -0.7V, coloured state; and +0.3V, bleached state. Current was applied through the potentiostat for 70s before the start of data recording, for the samples to completely switch states. The wavelength of interest was narrowed down to 633 nm, the absorbance wavelength of Prussian blue. For calculation of contrast, the difference in transmittance at original and coloured states was calculated. The samples were cycled for 5 cycles by alternating between the colouration and bleaching voltage for 30s each to generate cyclic kinetics graphs to calculate colouration and bleaching time. To analyse charge intercalation characteristics of the film, a CV test was done for WO₃ samples over a scan range of -0.9V to +0.5V at scan rate of 15mV/s and for PANI samples over a scan range of -0.2V to 0.8V and scan rate of 15mV/s.

4 Results and Discussion

4.1. Crystal Structure and Morphology

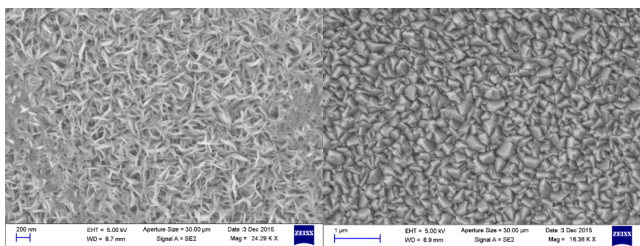


Figure 1a (left): W2 deposited at (-0.7V, 500s), coated with WO₃ to a thickness of 233nm;

Figure 1b (right): W5 deposited at (-0.7V, 1400s), coated with WO₃ to a thickness of 713nm

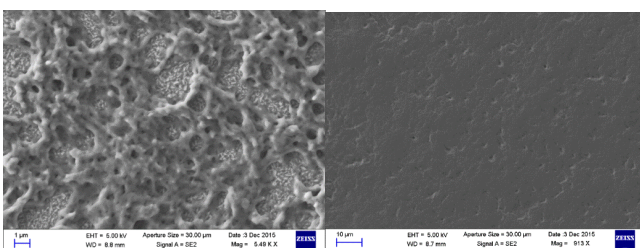


Figure 2a (left): P2 deposited at (0.01A, 80s), coated with PANI to a thickness of 78 nm;

Figure 2b (right): P3 deposited at (0.01A, 100s), coated with PANI to a thickness of 110nm

The SEM of W2 in Figure 1a shows even deposition of the spicule-like platelet structures characteristic of WO₃. The SEM of W5 in Figure 1b shows similar structures spread evenly across the surface. Noting that W5 has three fold of the deposition time for W2, the platelet structures of WO₃ have aggregated together, but cone-shaped structures still remain. The SEM of P2 shows fibrous structures that are deposited throughout the surface, although some parts are more concentrated with PANI. In Figure 2a, P2 signs of slight coarsening, as PANI fibres show signs of agglomeration [12]. In Figure 2b, with only 20s more of deposition, P5 is visibly coarsened to conformal film of PANI without visible nanofibers. The SEM indicates that WO₃ is a more stable material for ECD.

4.2. Optical Transmittance and Switching Time

The samples were deposited at various parameters as indicated below. From previous studies, -0.7V was found to be the most optimal voltage for ECD of WO₃-based samples via potentiostatic setting and from experimental data, -0.01A was found to be the most optimal current for ECD of PANI via galvanostatic setting, thus in this experiment, the respective settings were used to deposit for varying durations to investigate the effects of ECD time for W samples and P samples respectively.

| Sample | Deposition Parameter/ (V, s) | Thickness / (nm) | Coloration time/ (s) | Bleaching time/ (s) |
|--------|------------------------------|------------------|----------------------|---------------------|
| W1 | -0.7, 200 | 22 | 4.0 | 1.5 |
| W2 | -0.7, 500 | 233 | 4.2 | 3.0 |
| W3 | -0.7, 800 | 322 | 5.0 | 1.5 |
| W4 | -0.7, 1100 | 438 | 5.0 | 5.6 |
| W5 | -0.7, 1400 | 713 | 6.3 | 10.0 |
| Sample | Deposition Parameter/ (A, s) | Thickness / (nm) | Coloration time/ (s) | Bleaching time/ (s) |
| P6 | 0.01, 60 | 53 (P1) | 23.5 | 16.9 |
| P7 | 0.01, 80 | 78 (P2) | 3.0 | 18.5 |
| P8 | 0.01, 100 | 110 (P3) | 5.4 | 7.0 |
| P9 | 0.01, 120 | 131 (P4) | 4.5 | 7.5 |
| P10 | 0.01, 140 | 173 (P5) | 5.7 | 9.0 |

Table 1: Deposition parameters and results for thickness, coloration time and bleaching time for Sample W1 to W5 and P6 to P10.

The resistance of the conducting film affects the thickness and the uniformity of the deposition [13]. As such, 3 randomised readings of the resistance per square of the FTO glass slides were measured using a Jandel model RM 3000 four-point probe. The mean data is as displayed in Table 1 while the raw data is as listed in Table A2 in Appendix. There was no clear trend as to how thickness of the EC layer affected the switching speed of the PANI samples, but it is clear that for the WO₃ samples, as the thickness increased, the colouration time increased as well. Although conclusions could not be made within each type of sample, the switching time for WO₃ is generally shorter than that of PANI.

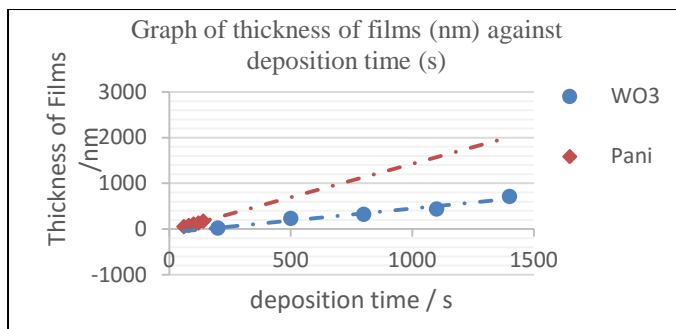


Figure 3a: Graph of thickness of film (nm) against deposition time of WO_3 films (s) of samples W1 to W5 and deposition time of PANI films (s) of samples P6 to P10.

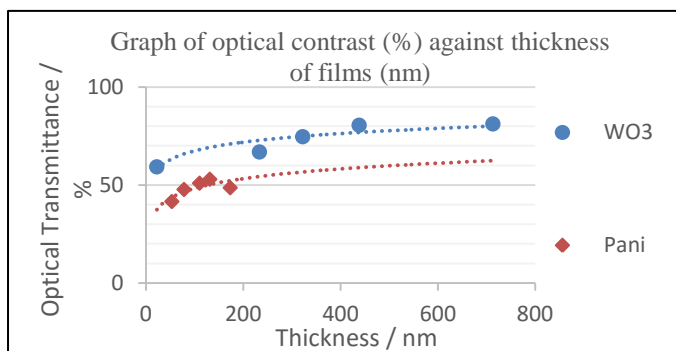


Figure 3b: Graph of optical contrast (%) against thickness of WO_3 films (nm) of samples W1 to W5 and thickness of PANI films (nm) of samples P6 to P10.

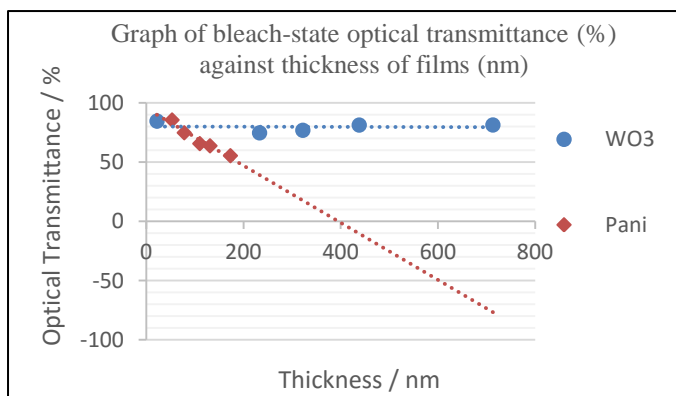


Figure 3c: Graph of bleach-state optical transmittance (%) against thickness of WO_3 films (nm) of samples W1 to W5 and thickness of PANI films (nm) of samples P6 to P10.

From Figure 3a, it can be established that an increase in deposition time invariably caused a proportional increase in thickness for both WO_3 and PANI deposits. From Figure 3b, for WO_3 , a thicker WO_3 layer resulted in greater EC contrast until W4, after which contrast started to plateau, whereas for PANI, the EC contrast of generally increased with thickness, until an optimal thickness of 131nm (P9), after which contrast visibly dropped. From Figure 3c, it is evident that increase in thickness of WO_3 layer did not significantly impact visibility: W1 to W5 have similar optical transmittance values of around 75% to 85% in the off state. On the other hand, visibility through PANI in the bleached state was increasingly compromised by increase in thickness, whereby the optical transmittance of PANI in the bleached state decreased steadily by 30.16% from P6 (85.55%) to P10 (55.39%).

4.3. Cyclic Voltammetry

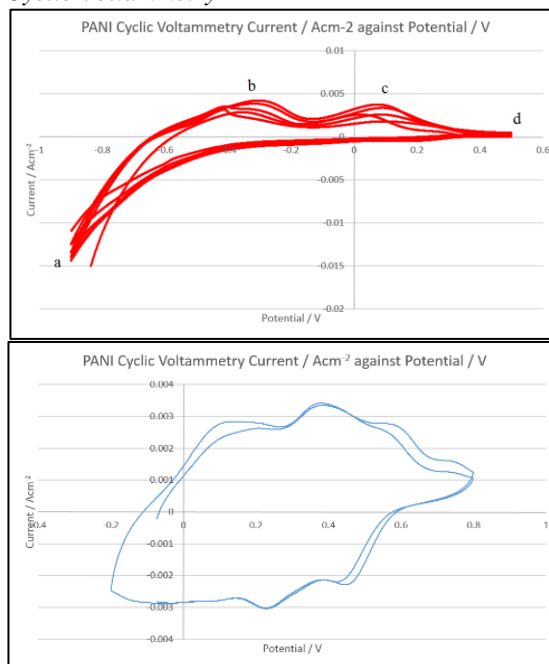


Figure 4a (left): CV of W1 in 0.5M H_2SO_4 ; Figure 4b (right): CV of P6 in 0.5M H_2SO_4

In Figure 4a, the positive scan from (a) the initial potential to (d) the switching potential allowed for oxidation to occur, while negative scan from (d) to (a) allowed for reduction and colouration to occur. The CV test identifies (b) and (c) to be the anodic peak potentials, and (a) as the cathodic peak potential where most of the oxidation and reduction reactions take place respectively. In Figure 4b, the CV test indicates that PANI is in fully reduced white leucoemeraldine state below 0.3V and oxidizes to blue-green emeraldine state as it approaches 0.3V. As the potential sweeping continued towards the potential of 0.8V, it starts to oxidize further to the violet pernigraniline state.

| | | Cathodic | Anodic |
|-----------|---|----------|-----------|
| Sample W1 | Peaks: | -0.900V | +0.091V |
| | Current density / (mA/cm^2) | -0.01503 | +0.003721 |
| Sample P6 | Peaks: | +0.226V | +0.378V |
| | Current density / (mA/cm^2) | -0.00302 | +0.00341 |

Table 2: The calculation of charge density of sample W1 and P6 (where area of film is 7.0 cm^2)

The cathodic or anodic current density is proportional to the amount of H^+ intercalated into or de-intercalated from WO_3 , respectively. The WO_3 film's charge insertion and extraction density is accounted for respectively by the peak current density values of the CV of -0.01503 and +0.003721 mA/cm^2 for W1 and -0.00302 and +0.00341 for P6, as shown in Table 2, indicating the speed of intercalation and de-intercalation processes for EC behaviour. There is a reduction in charge insertion and extraction in PANI as compared to WO_3 . However, as compared from Figures 4a and 4b, the magnitude of potential required to carry out the redox reaction is significantly lower for PANI at 0.2V compared to WO_3 at 0.9V.

4.4. Colouration Efficiency (CE)

| | Parameters | Cathodic | Anodic |
|-----------|--|----------|-----------|
| Sample W1 | Current density / (mA/cm ²) | -0.01503 | +0.003721 |
| | Charge density / (C / cm ²) | -0.06036 | +0.005582 |
| | Colouration efficiency / (cm ² / C) | 16.567 | |
| Sample P6 | Current density / (mA/cm ²) | -0.00302 | +0.00341 |
| | Charge density / (C / cm ²) | -0.05109 | +0.08029 |
| | Colouration efficiency / (cm ² / C) | 12.191 | |

Table 3: Comparison of between samples W1 and P6.

The CE values of the samples with the thinnest films in the respective batches (W1 and P6) were tabulated. The CE values, coupled with the current density values of W1 indicate that its optical modulation requires 73.6% of the charge insertion and extraction quantities for P6 per unit area for comparatively greater contrast (142.6% of that of PANI). A lower charge insertion or extraction rate can enhance cyclic stability. Therefore, WO₃-based samples (represented by W1) are expected to have better stability and higher colouration efficiency as compared to the PANI-based counterparts (represented by P6) for samples with similar contrast.

4.5. Considerations

The functions of a smart window necessitate highest possible transmittance of the EC in bleached state and the largest possible contrast with the coloured state, to create substantial differences between modes. WO₃ has shown itself to be superior to PANI in transparency when bleached, and opacity when coloured [14]. However, PANI is superior in that it exists in different oxidation states which allow it to transition between colourless, green-blue and violet, hence making it attractive to consumers. It is good to note that our results have shown that samples have high bleached transmittance and switching speeds.

5. Conclusion

WO₃ samples deposited at -0.7V generally had increased contrast as the deposition time (and thickness) of EC film increased, but above 438 nm (W4), the increase in thickness of WO₃ layer did not have a significant effect on contrast. For PANI samples, an increase in thickness of PANI layer caused an increase in contrast until an optimal of 131nm (P9). However, with increasing thickness, the overall bleached state transmittance of WO₃-based samples remained relatively constant while that of PANI-based samples decreased significantly. It was difficult to tell how the thickness of the PANI layer affected its switching time, but it is clear that as the thickness of WO₃ samples increased, the colouration time increased as well. The representative WO₃ sample (W1) had higher contrast and higher colouration efficiency compared to the representative PANI sample (P6). Hence, taking into account all performance factors considered in our study, it can be concluded that WO₃-based samples are overall superior to those of PANI.

6. Future Work

The durability and lifetime of PANI and WO₃ could be further investigated by subjecting samples of similar thickness and deposition method to conditions with higher pH, concentrations of solutions, elevated temperatures, or ultraviolet light. We hypothesize that these conditions, especially ultraviolet light or elevated temperatures which mimic actual conditions for smart windows application, would have a drastic detrimental effect on the contrast and lifetime of the ECs, and hence recommend that research into protection against such conditions be conducted to produce more durable, long-lasting ECDs.

7. References

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8. Appendix

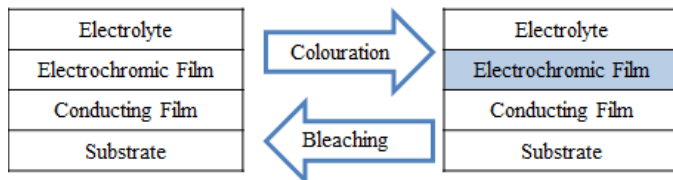


Figure A1: The assembly of our EC set ups, which are standard single electrochromic EC devices [7].

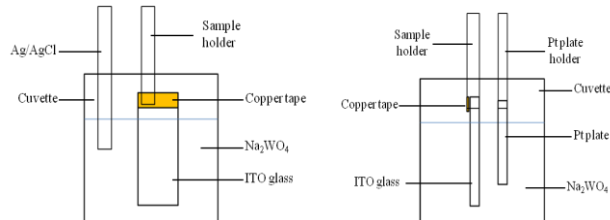


Figure A2a (left): Front view of ECD setup for EC samples (counter electrode Pt plate not in view);

Figure A2b (right): Side view (reference electrode Ag/AgCl not in view)

| Sample | Resistance/ (Ω/cm^2) | | | | Standard deviation |
|------------|--|--|--|--|--------------------|
| | 1 st reading/ (Ω/cm^2) | 2 nd reading/ (Ω/cm^2) | 3 rd reading/ (Ω/cm^2) | Mean resistance/ (Ω/cm^2) | |
| 1 | 10.56 | 10.58 | 10.49 | 10.54 | 0.04726 |
| 2 | 10.56 | 10.50 | 10.75 | 10.60 | 0.1305 |
| 3 | 10.42 | 10.40 | 10.54 | 10.45 | 0.07572 |
| 4 | 10.56 | 10.50 | 10.49 | 10.52 | 0.03786 |
| 5 | 10.63 | 10.56 | 10.60 | 10.60 | 0.03512 |
| W1 | 10.48 | 10.12 | 10.10 | 10.23 | 0.2139 |
| W2 | 11.46 | 10.21 | 11.24 | 10.97 | 0.6673 |
| W3 | 11.01 | 10.36 | 10.28 | 10.55 | 0.4004 |
| W4 | 10.61 | 10.52 | 10.58 | 10.57 | 0.04583 |
| W5 | 11.26 | 10.94 | 10.71 | 10.97 | 0.2762 |
| P1 | 11.00 | 10.79 | 10.53 | 10.77 | 0.2354 |
| P2 | 10.65 | 10.74 | 10.59 | 10.66 | 0.07550 |
| P3 | 10.47 | 10.39 | 10.83 | 10.56 | 0.2344 |
| P4 | 10.29 | 10.44 | 10.48 | 10.40 | 0.1002 |
| P5 | 11.67 | 11.41 | 11.61 | 11.56 | 0.1361 |
| P6 | 11.92 | 11.79 | 11.74 | 11.82 | 0.09292 |
| P7 | 12.73 | 12.77 | 12.63 | 12.71 | 0.07211 |
| P8 | 10.18 | 10.19 | 10.23 | 10.20 | 0.02646 |
| P9 | 12.24 | 11.93 | 11.02 | 11.73 | 0.6341 |
| P10 | 12.27 | 12.23 | 12.38 | 12.29 | 0.07767 |

Table A2: Table of the compilation of resistance values of the FTO layer on glass substrate.

| S/N | Potential / (V) | Time / (s) | Thickness / (nm) | Contrast (ΔT) / (%) | Bleached transmittance / (%) |
|-----|-----------------|------------|------------------|-------------------------------|------------------------------|
| 1 | -0.5 | 700 | - | 35.779 | 72.485 |
| 2 | -0.6 | 700 | - | 36.067 | 65.458 |
| 3 | -0.7 | 700 | - | 43.160 | 63.624 |
| 4 | -0.8 | 700 | - | 42.682 | 57.425 |
| 5 | -0.9 | 700 | - | 34.536 | 66.586 |
| S/N | Potential / (V) | Time / (s) | Thickness / (nm) | Contrast (ΔT) / (%) | Bleached transmittance / (%) |
| W1 | -0.7 | 200 | 22 | 59.250 | 84.585 |
| W2 | -0.7 | 500 | 233 | 66.846 | 74.685 |
| W3 | -0.7 | 800 | 322 | 74.632 | 76.846 |
| W4 | -0.7 | 1100 | 438 | 80.499 | 81.259 |
| W5 | -0.7 | 1400 | 713 | 81.160 | 81.327 |
| S/N | Potential / (V) | Time / (s) | Thickness / (nm) | Contrast (ΔT) / (%) | Bleached transmittance / (%) |
| P6 | 0.01 | 60 | 53 (P1) | 41.542 | 85.555 |
| P7 | 0.01 | 80 | 78 (P2) | 47.696 | 74.756 |
| P8 | 0.01 | 100 | 110 (P3) | 50.902 | 65.599 |
| P9 | 0.01 | 120 | 131 (P4) | 52.913 | 63.733 |
| P10 | 0.01 | 140 | 173 (P5) | 48.571 | 55.391 |

Table A1: Table of raw optical transmittance data corresponding to deposition parameters. First 5 rows of data are results of preliminary experiment while the next 2 sets are of samples in this study.