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Systematic optimization of chemical deposition conditions for synthesis of vanadium(V) oxide xerogels

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Abstract: We performed the optimization of conditions in chemical bath deposition using the design of experimental methodology. Factorial design (2^3) was used for finding the optimal conditions of preparing vanadium(V) oxide xerogel thin films with better electrochromic properties suitable for electrochemical applications. The thin films were prepared by acidification of NH_4VO_3 aqueous solution with chemical bath deposition. The factors and selected values we considered were as follows: the deposition time (10 and 20 min), the deposition temperature (70 and 80 °C), and the mass of ammonium metavanadate (0.3 and 0.5 g). UV-vis spectrometry was used for recording the transmittance variance, ΔT, as the property of interest for modeling in this work. Increasing the deposition temperature and time values led to an increase in the value of ΔT at 800 nm wavelength, but the mass of NH_4VO_3 showed the opposite effect. Modeling performed using a 2^3 factorial design showed that the concentration of the ammonium metavanadate was the single most important factor.

Key words: Optimization, factorial design, thin film, optical property, vanadium(V) oxide xerogel

1. Introduction

Vanadium(V) oxide xerogels ($V_2O_5 \cdot nH_2O$) with a layered structure gave rise to anisotropic coatings when deposited onto a substrate, with a variety of electronic, ionic, and electrochromic properties.[1,2] An attractive feature of $V_2O_5 \cdot nH_2O$ is that it can be easily produced from sol-gel synthetic routes at room temperature.[1–5] We have developed a chemical bath deposition (CBD) method for the preparation of electrochromic vanadium(V) oxide xerogels thin films using the synthetic approach of acidification of metavanadate aqueous solutions.[6,7] We found that the thin film thickness has a strong influence on the transmittance variance (ΔT) as deduced from the optical spectra of the reduced and oxidized states. The best result regarding the transmittance variance of 54% with composition $(NH_4)_{0.15}V_2O_5 \cdot 1.3H_2O$ and 55% with composition $(NH_4)_{0.3}V_2O_5 \cdot 1.25H_2O$ at 400 nm shows the potential of ammonium intercalated vanadium(V) oxide xerogel thin films for commercial application in electrochromic devices.[6,7]

Experimental design is a powerful tool for optimizing processes that is used to systematically examine different types of problems. It is expected that if experiments are performed randomly, the result obtained, most often, will depend on the experience of the person who performs them. Therefore, it is necessary to plan

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the experiments and it is reasonable to assume that the outcome of an experiment depends on the experimental conditions. This means that the result can be described as a function based on the experimental variables, $y = f(\mathrm{x})$. Although there are many different kinds of design, the factors vary independently of each other. The choice of factor levels is most important in a design. The factorial designs identify experiments at every combination of factor levels. There are L^k combinations of L levels of k factors. Experimental designs are written in terms of coded variables. For example, an experimental design that requires only two values of variable factor is usually given as a series of +1 and –1. The experimental space is defined inside these parameter values.[8–12]

Not only in live sciences and agricultural settings, but also in many areas of business, such as marketing and financial services, there has been dramatic growth in the use of designed experiments recently.[13] This interest in the design of experiments has led to much new research on the subject.[13] There are many papers in the literature in which experimental designs are used for optimization of conditions in different areas such as analytical chemistry,[14–17] organic chemistry,[18–20] pharmacy,[21–23] forensic toxicology,[24] environmental chemistry,[25] nanomaterials,[26] electrochemistry,[27] and thin film deposition.[28–30]

This paper reports the optimization of conditions and experimental design of a chemical bath deposition method for the production of $\mathrm{V_2O_5 \cdot \mathit{n}H_2O}$ xerogel thin films. The chemical bath deposition method is one of the simplest methods for deposition of thin films. Thin films of ammonium intercalated vanadium(V) oxide xerogels prepared by chemical bath deposition[6,7] yield good results in transmittance variance (ΔT) and show the potential for commercial application in electrochromic devices. We used a 2^3-full factorial design to study the influence of different conditions on the optical properties of vanadium(V) oxide xerogel thin films. In this way, we could obtain samples with better ΔT (transmittance variance) values. The variables we investigated were deposition time, temperature, and mass of $\mathrm{NH_4VO_3}$. In this paper the samples are denoted as VA0570, VA0580, VA0370, and VA0380. For example, VA0570 denotes the thin film obtained from solution containing 0.5 g of $\mathrm{NH_4VO_3}$ at 70 °C (the first two figures (05) refer to the amount of $\mathrm{NH_4VO_3}$, while the last two figures (70) refer to the temperature).

2. Results and discussion

The property of interest for modeling in this work is ΔT. Transmittance variance (ΔT) corresponds to the difference in transmittance between the reduced (T_{red}) and oxidized (T_{ox}) state of the thin films at preselected wavelength ($\Delta T = T_{reduced} - T_{oxidized}$). In this study transmittance variance was selected as a physical property that represents the electrochromic quality of the thin films.

The optical transmittance spectra of a set of thin films at potentials of -2.5 V and +2.5 V applied for 3 min are shown in Figure 1.

The transmittance variance values of $\mathrm{V_2O_5 \cdot \mathit{n}H_2O}$ thin films measured at 800 nm are presented in Table 1. The obtained results indicate that, generally, the transmittance variance values of 10 min deposited thin films at 800 nm are lower than those of the thin film prepared for 20 min (Table 1; Figure 1), with the exception of VA0580 thin films.

According to the results given in Table 1, there are deviations in the transmittance variance values between the first and the last experiment (spectrum). Our experience with thin films of vanadium(V) oxide xerogels shows that this kind of deviation is always present. The transmittance variance value of the thin film in the first record is always lower than the other ones. A certain number of reduction and oxidation cycles are needed to stabilize ΔT. This is in relation with Li ion intercalation/deintercalation processes and with the

different crystalline states of $Li_xV_2O_5$, (α, ε, δ phases), which depends on the lithium content,[2,4,5] obtained as a product of Li ion intercalation.

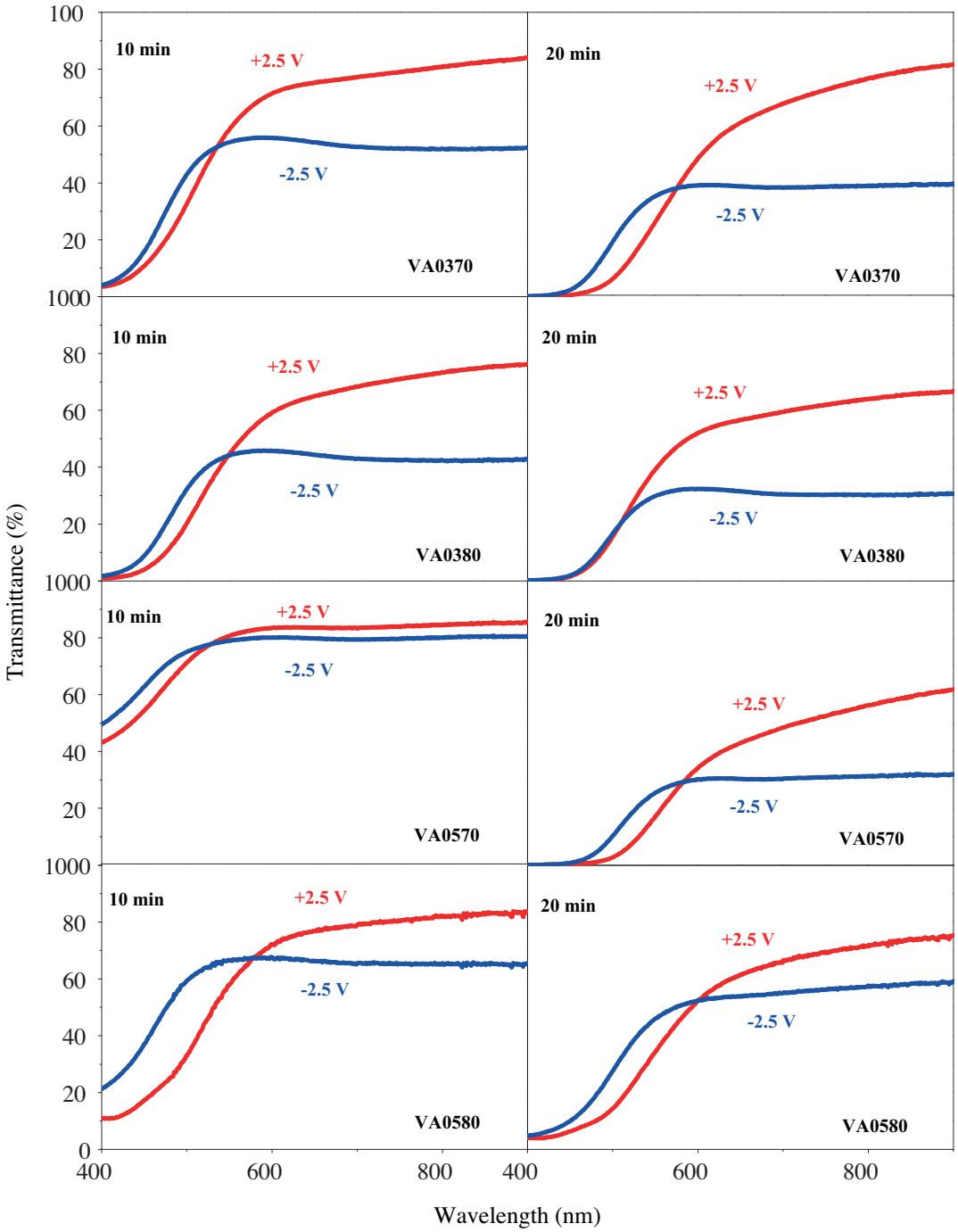

Figure 1. In situ optical transmittance spectra of VA0370, VA0380, VA0570, and VA0580 thin films prepared at different deposition times.

XRD patterns of the prepared samples are shown in Figure 2. The comparison with the patterns from the powder-diffraction file (PDF) database showed that there is a great similarity with the pattern of $V_2O_5 \cdot nH_2O$

xerogel (PDF 40-1296).[6,7] The structure of xerogel is found to be an assembly of double V_2O_5 sheets forming slabs that are stacked along the c-axis of a monoclinic unit cell.[3,31] The slabs are separated by water molecules. The basal distance between the layers depends on the amount of water and increases by a step of about 2.8 Å for each water layer: 11.55 Å for $n \approx 1.5$–1.6 and 8.75 Å for $n \approx 0.5$.[32] The first peak at 7.88° (001) shows the distance between the layers. This peak is more intense for the VA0370 (Figure 2g) and VA0570 (Figure 2e), or precipitates prepared at lower temperature (70 °C).

Our previous work,[6,7] with thin films and precipitates of vanadium(V) oxide xerogels showed that the

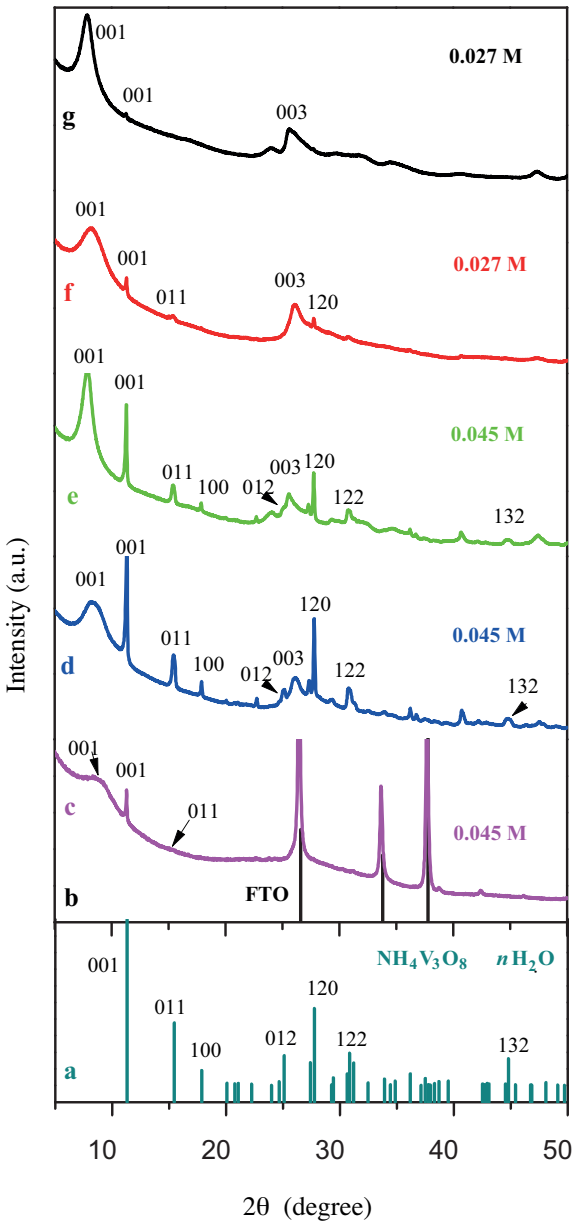

Figure 2. XRD patterns of: a) $NH_4V_3O_8 \cdot nH_2O$ (from PDF database) b) FTO (from PDF database); c) VA0580 (thin film prepared for 20 min deposition time); d) VA0580 (precipitate); e) VA0570 (precipitate); f) VA0380 (precipitate); g) VA0370 (precipitate).

Table 1. ΔT (%) of $V_2O_5 \cdot nH_2O$ thin films with different deposition time at wavelength of 800 nm.

Experiments	VA0370		VA0380		VA0570		VA0580	
	Deposition time (min)							
	10	20	10	20	10	20	10	20
1	23	25	26	31	2	18	14	7
2	23	25	28	31	3	18	14	7
3	27	33	30	33	3	23	15	10
4	28	38	31	34	4	23	16	11
5	28	38	31	35	4	23	17	14

precipitate and films have the same phase composition. However, XRD analyses of precipitates and thin films in this study showed that there are differences between the precipitate and thin film composition, namely the impurity phase, $NH_4V_3O_8 \cdot nH_2O$ (Figure 2a, PDF 41-0492), is present. This impurity phase appears in different amounts (Figure 2).

All of the prepared thin films (VA0570, VA0580, VA0370, and VA0380) exhibit two-step electrochromism with color changes from yellow to green and from green to blue. The observed reversible color changes are typical for electrochromic vanadium(V) oxide xerogels[1,2,5–7] and are related to the transition between two oxidation states only, V(V) (yellow) and V(IV) (blue). The green color arises by mixing yellow and blue due to the presence of the two vanadium oxidation states (Figure 3).

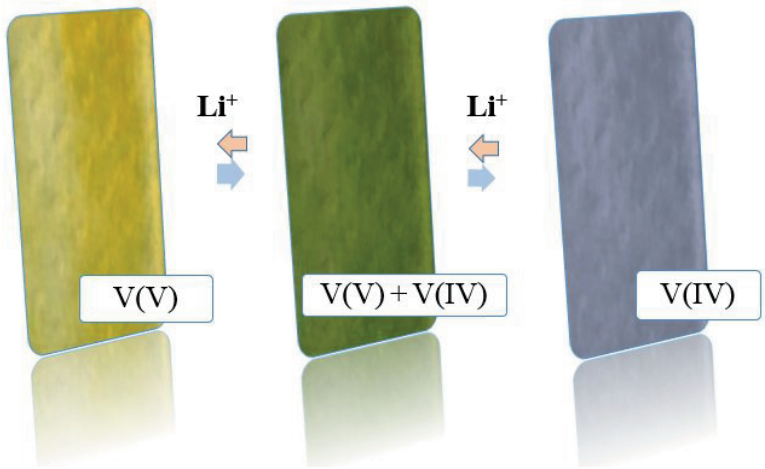

Figure 3. Graphical illustration of color changes of electrochromic $V_2O_5 \cdot nH_2O$ thin films at ± 2.5 V.

3. Optimization design

3.1. 2^3 full factorial design of experiments

Designed experiments allow the analyst to control the factors thought to be important in characterizing or explaining the response variables of the experiment.[13] When attempting to discover the important factors and then optimize a response by tuning these factors, experimental design (design of experiments (DoE)) is a powerful tool. It includes modeling using an empirical function, without need for detailed knowledge of the underlying physicochemical properties of the system.[12] For this purpose, a number of experiments is performed

in order to evaluate the influence of selected factors on the property of interest. The estimation of the parameters in the empirical function is performed on the basis of the measured values for the property of interest. In the case of a 2^3 full factorial design, experiments should be performed according to the scheme presented in Table 2. A graphical representation of this factorial design is presented in Figure 4.

Table 2. The 2^3 full factorial design for CBD method.

Experiments	Factors			Variables			Results
	x_1	x_2	x_3	Deposition time (min)	Temperature (°C)	Mass of NH_4VO_3 (g)	ΔT* (%)
1	–1	–1	–1	10	70	0.3	26
2	+1	–1	–1	20	70	0.3	32
3	–1	+1	–1	10	80	0.3	29
4	+1	+1	–1	20	80	0.3	33
5	–1	–1	+1	10	70	0.5	3
6	+1	–1	+1	20	70	0.5	21
7	–1	+1	+1	10	80	0.5	15
8	+1	+1	+1	20	80	0.5	10

*ΔT values are measured at 800 nm wavelength.

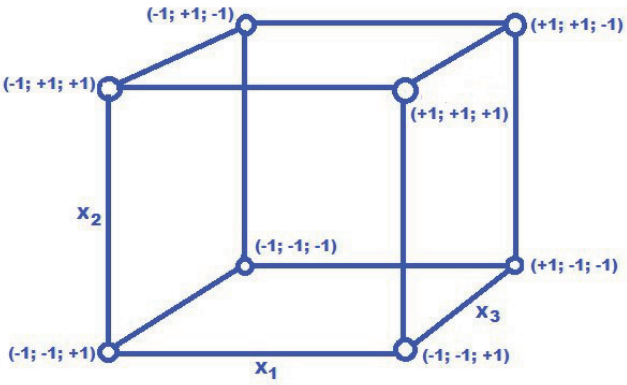

Figure 4. Graphical presentation of the 2^3 matrix.

In a factorial design the influences of all experimental variables and interaction effects are investigated. Full factorial designs have every possible combination of factors at the designated levels. There are n^k combinations of k factors at n levels, and fractional factorial designs are a specific subset of a full design. The factorial design will consist of 2^k experiments when the combinations of k factors are investigated at two levels. The levels of the factors are given by (–1) minus for low level and (+1) plus for high level.[9–11]

The general modeling function for the 2^3 factorial design, when interactions between the factors are present is

$$y = b_o + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3, \quad (1)$$

where b_0 is the mean value of responses of all the experiment; b_1, b_2, b_3, are coefficients that represent the effect of the different factors (x_1, x_2, and x_3); b_{12}, b_{13}, b_{23} are coefficients that represents binary interactions between the factors; and b_{123} represents the coefficient of interaction between all three factors.

3.1.1. Factors screening

The experiments together with the optimization process determine the optimal conditions for obtaining thin films of vanadium oxides with the best electrochromic properties, and also determine how different factors influence the obtained results. Earlier experiments performed in our laboratory have shown that variables influencing the deposition of $V_2O_5 \cdot nH_2O$ xerogel thin films are (1) deposition time, (2) temperature, and (3) concentration.[6,7]

As previously noted, the property of interest in this study is the assessment of the effect of these variables on ΔT of the obtained vanadium(V) oxide xerogel thin films. In determining the optimal conditions we used a full factor design with three variables at two levels (2^3). Based on our previous experience in the laboratory we decided that it is suitable to change the factors of interest in the following intervals:

- Deposition time – selected values for deposition time were 10 and 20 min;
- Temperature – selected values for temperature were 70 and 80 °C;
- Mass (which is proportional with the concentration) – selected values for mass of NH_3VO_3 were 0.3 and 0.5 g dissolved in 45 mL of deionized water (the concentrations of NH_3VO_3 were 0.027 M and 0.045 M, respectively).

Each experiment was repeated five times (Table 1). The average values for the measured property (transmittance variance) as well as the conditions under which the experiments were performed are presented in Table 2.

For our modeling purposes, the deposition time ($\boldsymbol{x}_1$), temperature ($\boldsymbol{x}_2$), and mass ($\boldsymbol{x}_3$) were replaced with values for the factors according to the full factorial design (Table 2).

3.1.2. Modeling of the response

Coefficients of the modeling function that was previously presented can be calculated easily if the values obtained for the modeled property are placed in a $\boldsymbol{y}$ vector, the matrix of the factor design is labeled with $\boldsymbol{D}$, while the unknown regression coefficients are stored in vector $\boldsymbol{b}$:

$$\mathbf{y} = \mathbf{Db} \tag{2}$$

The regression coefficients could be estimated using the following equation:

$$\mathbf{b} = 1/8\mathbf{D}^T\mathbf{y} \tag{3}$$

The estimated values for the coefficients are presented in Table 3. Only one of the effects is statistically significant. According to the results presented in this table, the concentration of NH_4VO_3 is the only influential variable. In general, it is expected that the deposition time and the temperature have positive effects on ΔT. As one can see in Table 3, the coefficients that represent the influence of these variables are positive. However, in this experiment, which was performed under the previously described conditions, the coefficients that describe the deposition time (b_1) and the temperature (b_2) were not statistically significant. Additionally, we concluded that none of the interaction factors (b_{12}, b_{23}, b_{13}, and b_{123}) had a significant influence on ΔT.

Table 3. Calculated effects for the 2^3 factorial design and their standard errors.

b_0 – Average (bias)	7.07 ± 1.27
Main effects	
b_1 – Deposition time	0.93 ± 1.27
b_2 – Temperature	0.21 ± 1.27
b_3 – Mass of NH_4VO_3	–2.93 ± 1.27
Two-factor interaction	
b_{12}	–1.10 ± 1.27
b_{13}	0.15 ± 1.27
b_{23}	–0.12 ± 1.27
Three-factor interaction	
b_{123}	–0.87 ± 1.27

4. Effect of variables on the modeled property of prepared thin films

The estimated values for the main effects are presented in Table 3. The effect of the interaction of the variables in the model defined by Eq. (1) for the 2^3 factorial design is also presented in Table 3. The estimated values for this model are accompanied by their standard errors.

A detailed examination of Table 3 showed that the coefficient b_3 (representing the influence of the concentration on ΔT) has significant influence on the results. Further, we will try to explain the importance of these terms on the obtained results.

The influence of concentration (b_3) – Table 3 shows that the concentration (b_3) has the largest influence on ΔT for the prepared vanadium(V) oxide thin films. The increase in the concentration lowers the values of the measured property. The way this parameter influences results can be easily estimated by looking at Tables 1 and 2. All solutions prepared with 0.5 g of ammonium metavanadate have lower values for ΔT compared to the experiments performed with the solution that contains 0.3 g of ammonium metavanadate. The XRD patterns of VA0370 (Figure 2g) and VA0380 (Figure 2f) exhibit several broad and weak peaks. The intensity of the first peak at 7.88° is much higher than that of the other terms (Figures 2f and 2g). When the mass of NH_4VO_3 is increased, the intensity of the peak (001) of the impurity phase is increased too (Figures 2d and 2e). The thin films synthesized from the CBD with high NH_4VO_3 concentration (Figure 2c) contain an electrochemically inactive impurity phase ($NH_4V_3O_8 \cdot nH_2O$).[33] According to the XRD patterns of prepared xerogel powders, an increase in the concentration of NH_4VO_3 (VA0570 and VA0580) causes an increase in the percentage of impurity phase ($NH_4V_3O_8 \cdot nH_2O$) (Figure 2). Most probably, this is the reason for the lower ΔT values of samples prepared from solutions with higher concentrations of NH_4VO_3 (Table 2; Figure 1). The best result of transmittance variance of thin films prepared from 0.3 g of NH_4VO_3 solution is around 33%, which is better compared to the thin films results prepared from 0.5 g of dissolved ammonium metavanadate solutions (ΔT= 21%).

The influence of temperature (b_2) *and deposition time* (b_1) – The values of b_2 (0.21) and b_1 (0.93) given in Table 3 show the effect of temperature and deposition time on the transmittance variance value of vanadium(V) oxide thin films. The results given in Table 2 show generally higher transmittance values for thin films prepared at 80 °C and for 20 min deposition time. The positive values of b_1 and b_2 indicate that the ΔT value generally increases with the increase in the deposition temperature and time (Figure 1). The influence of the deposition temperature and time compared to the influence of concentration is very low, although it shows

an opposite effect (b_3 = –2.93). The influence of the temperature parameter on the properties of $V_2O_5 \cdot nH_2O$ xerogels thin films compared with the influence of the deposition time is approximately 4 times weaker (b_1 = –0.93, b_2 = 0.21). These effects may be related to the morphological and microstructural[7] properties of vanadium(V) oxide xerogels. According to our previous work,[6,7] higher temperature means higher deposition rate. This can be related to the higher nucleation rate, which affects the morphological characteristics and film defect. The growth of grains and the decrease in defects due to the processes of recrystallization and dissolution during the longer deposition times contribute to optical changes, which lead to high transmittance values at larger wavelengths.[7,34,35] We can thus conclude that the morphological and structural changes at 80 °C and the 20 min deposition time improve the optical properties of thin films.

The obtained results, as a maximum value of transmittance variance (33%) at 800 nm, indicate that these thin films of vanadium(V) oxide xerogels are useful for the fabrication of multicolored electrochromic devices[36] and transparent counter electrodes in electrochromic devices.[37] Because of longer response times[7] they cannot be used for display devices, but they could be used for applications of electrochromic materials requiring longer response times, such as "smart windows".

In conclusion, 2^3 full factorial design methodology was used for the optimization of chemical bath deposition. Electrochromic thin films of vanadium(V) oxide xerogels show two-step electrochromism (yellow/green/blue). The deposition time (1), temperature (2), and the mass of ammonium metavanadate (3) were the analyzed factors. According to the visible spectroscopy analysis, the ΔT of the thin films prepared with higher concentration of NH_4VO_3 is considerably lower compared to the thin films prepared with lower concentration of NH_4VO_3, which is due to the presence of impurity phase $NH_4V_3O_8 \cdot nH_2O$. According to the statistical optimization results, concentration is the most significant factor. Hence, we concluded that generally for our purposes it is more convenient to prepare vanadium(V) oxide thin films with lower concentrations of ammonium metavanadate, longer deposition times, and higher temperatures. The obtained maximum value of transmittance variance (33%) makes these thin films attractive for many applications as multichromic devices.

5. Experiments

5.1. Synthesis of vanadium(V) oxide xerogels

The thin films of vanadium(V) oxide xerogels were synthesized by the chemical bath deposition method via acidification of aqueous solutions of NH_4VO_3 (Riedel-de Haen AG. Seelze, Hannover, Germany) with acetic acid (Aldrich) at different temperatures. All reagents used for these experiments were analytical pure substances. The solutions of ammonium metavanadate were prepared in laboratory beakers (100 mL) by dissolving the NH_4VO_3 (0.3 g or 0.5 g) in 45 mL of deionized water and heating at around 30–40 °C. The thin films were prepared on commercially available glass substrates of SnO_2:F (fluorine-doped tin oxide) possessing high optical transparency of 80% in the visible spectrum and electrical resistance of 10–20 Ω/cm^2. Before deposition the substrates were cleaned with detergent, alkaline solution, hydrochloric acid, hexane, and acetone and finally rinsed with deionized water and dried in air. The clean substrates were supported by the wall of the beaker. Then 50 mL of glacial acetic acid was added to each solution. With continuous stirring the solution was heated up to 70 °C or 80 °C. The beginning of the deposition reaction was observed as the yellow-orange opaque state of the solution. The color of the reaction system at the beginning of the reaction was yellow (for lower concentrations) and orange (for higher concentrations), but over time became orange brown, and at the end of the reaction turned bright brown. After the chosen deposition times (10 or 20 min), the thin

films of $V_2O_5 \cdot nH_2O$ xerogels were removed from the chemical bath, washed with ethanol, and dried at room temperature. The as-deposited films were yellow, varying from light yellow to deep yellow depending on the deposition time and concentration of NH_4VO_3 in the solution.

5.2. Characterization of vanadium(V) oxide xerogels

In-situ optical spectra of the thin films were recorded by a Varian Cary 50 Scan spectrophotometer in the range from 400 to 900 nm using 1 M $LiClO_4$ in propylene carbonate as electrolyte. The voltage varied from -2.5 to $+2.5$ V. The prepared films were placed in the electrochemical cell with electrolyte into which the substrates were immersed. Identification of the composition of prepared materials was performed with the XRD analyzing method. The XRD patterns of the precipitates were recorded by Rigaku Ultima IV X-ray diffractometer (CuKα radiation).

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