

## CHARACTERIZATION AND ELECTROCHROMIC PROPERTIES OF VANADIUM OXIDE THIN FILMS PREPARED VIA SPRAY PYROLYSIS

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Vanadium oxide thin films were grown on glass substrates using spray pyrolysis technique. The effects of substrate temperature, vanadium concentration in the initial solution and the solution spray rate on the nanostructural and the electrochromic properties of deposited films are investigated. Characterization and the electrochromic measurements were carried out using X-ray diffraction, scanning electron microscopy and cyclic voltammogram. XRD patterns showed that the prepared films have polycrystalline structure and are mostly mixed phases of orthorhombic  $\alpha$ - $V_2O_5$  along with minor  $\beta$ - $V_2O_5$  and  $V_4O_9$  tetragonal structures. The preferred orientation of the deposited films was found to be along [101] plane. The cyclic voltammogram results obtained for different samples showed that only the films with 0.2 M solution concentration, 5 ml/min solution spray rate and 450°C substrate temperature exhibit two-step electrochromic properties. The results show a correlation between cycle voltammogram, morphology and resistance of the films.

*Keywords:* Vanadium oxide; thin films; structural; electrical properties; cycle voltammogram.

### 1. Introduction

Vanadium oxides are a complex class of materials exhibiting various phases such as VO,  $V_2O_5$ ,  $V_2O_3$ ,  $V_4O_9$  and  $VO_2$ . Among these, vanadium pentoxide,  $V_2O_5$ , is the most stable with highest oxidation state,<sup>1,2</sup> having many interesting properties including special layered structure, wide optical band gap (2.44 eV), good chemical and thermal stabilities and excellent thermoelectric and electrochromic properties.

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Vanadium oxide thin films have been used in fabricating many solid state devices such as: high capacity lithium batteries, display systems, color filters, electrochromic devices (ECD), electronic and optical switches and gas sensors.<sup>3-5</sup>

Electrochromic materials with semiconducting nature are known for their interesting property of changeable optical characteristics under the action of an applied electric field. Recently, electrochromic devices based on lithium intercalation in transition metal oxides have been widely studied.<sup>6</sup> Also, vanadium oxide films have attracted considerable attention as a starting and/or host material for fabrication of electrochromic and electrochemical charge devices.<sup>7,8</sup> These applications depend on the deposition technique used to prepare the samples and also the properties associated to the crystallinity and morphology of the films.<sup>8,9</sup>

Vanadium pentoxide thin films have been prepared using various techniques including pulsed laser deposition (PLD),<sup>10</sup> electron beam evaporation,<sup>11</sup> sputtering,<sup>12,13</sup> sol-gel process<sup>3</sup> and spray pyrolysis.<sup>14</sup> Among these, spray pyrolysis is a rather simple and low cost technique which has the ability to coat large areas. Although the electrochromic properties of vanadium oxide thin films have previously been studied,<sup>9</sup> but up to our knowledge there are not many reports on the effect of different deposition parameters on electrochromic properties of vanadium oxide thin films prepared by spray pyrolysis. In this paper, we have investigated the electrochromic properties of vanadium oxide films prepared by this method, under various deposition conditions. The prepared samples were first characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and then their electrochromic properties were studied.

## **2. Experimental Methods**

### **2.1. Film deposition**

Vanadium oxide thin films were deposited on glass substrates by spray pyrolysis technique. For the electrochromic measurements, the films were deposited on fluorine oxide (FTO) coated glass substrates. First, certain amount of vanadium chloride ( $VCl_3$ ) was dissolved in distilled water to make the initial (precursor) solution. All the samples were deposited under a fixed nozzle to substrate distance. Compressed air of 3 atm pressure was used as the carrier. In order to determine the optimum deposition condition, various samples with different substrate temperatures of 300, 400, 450 and 500°C, different solution concentration of 0.05, 0.1, 0.15 and 0.2 M and solution spray rate of 3, 5, 7 and 10 ml/min were prepared; the details is reported elsewhere.<sup>15</sup> In order to investigate the effect of each parameter individually, the samples are considered in 3 groups namely: A, B and C. In each group, two of the parameters are maintained fixed at the optimum value and the other one changes slightly. The preparation conditions are listed briefly in Table 1. In group A, samples were prepared at two different substrate temperatures of 300°C and 450°C, with constant solution concentration and solution spray rate of 0.2 M and 5 ml/min, respectively. Samples in group B were prepared with two different solution concen-

Table 1. Preparative parameters of the vanadium oxide thin films deposited using different deposition parameters.

| Sample  | Precursor      | Nozzel-to-substrate distance (cm) | Air pressure (at) | Solvent         | Substrate temperature ( $^{\circ}\text{C}$ ) | Solution concentration (M) | Solution spray rate (ml/min) |
|---------|----------------|-----------------------------------|-------------------|-----------------|--|----------------------------|------------------------------|
| Group A | $\text{VCl}_3$ | 35                                | 3                 | Distilled water | 300 and 450                                  | 0.2                        | 5                            |
| Group B | $\text{VCl}_3$ | 35                                | 3                 | Distilled water | 450  | 0.2 and 0.3                | 5                            |
| Group C | $\text{VCl}_3$ | 35                                | 3                 | Distilled water | 450  | 0.2                        | 5 and 10                     |

trations of 0.2 and 0.3 molar, at constant substrate temperature ( $T_{\text{sub}} = 450^{\circ}\text{C}$ ) and solution spray rate (5 ml/min). In group C, the substrate temperature and solution concentration were kept at  $450^{\circ}\text{C}$  and 0.2 M, respectively and the solution spray rate were chosen as 5 and 10 ml/min.

## 2.2. Characterizations

The structure of the prepared films were studied by XRD (D8 Advance Bruker system with  $\text{Cu K}\alpha$ ,  $\lambda = 0.15406$  nm). The average crystallites size ( $D$ ) of the samples was estimated using the Scherrer's formula:<sup>16</sup>

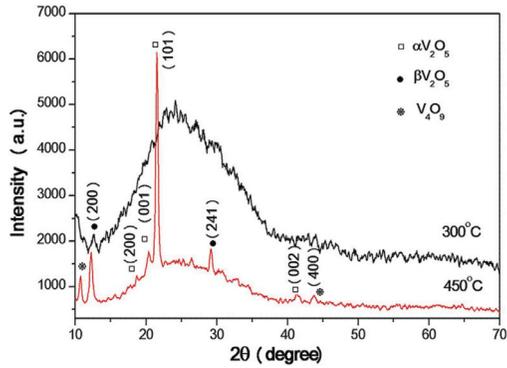
$$D = \frac{k\lambda}{\delta w \cos \theta}, \quad (1)$$

where  $\delta w$  is the full width at half maximum (FWHM) of the corresponding XRD peak,  $k$  is a constant ( $\sim 0.9$ ) and  $\theta$  is the Bragg angle. Surface morphology of the films was studied by SEM (VEGA TESCAN system). The sheet resistance ( $R_s$ ) of the samples was measured by two-point probe method with Al electrodes deposited by thermal evaporation in vacuum, using Edwards E-306A coating system. The electrochromic measurements were performed in a cell containing the vanadium oxide sample, a Pt counter electrode and an Ag/AgCl reference electrode, in a potential limit of  $-0.4$  V and  $+1.2$  V at scan rate of  $50$  mV  $\text{s}^{-1}$ . The used electrolyte was a solution of 1 M LiCl in distilled water.

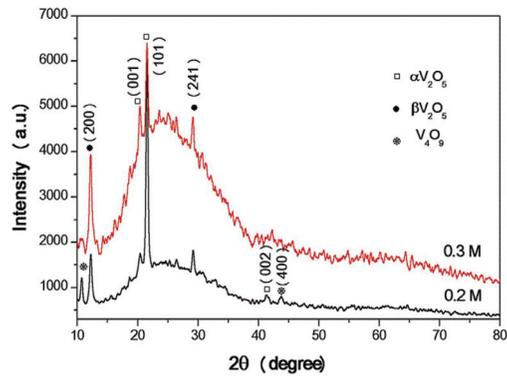
## 3. Results and Discussions

### 3.1. Structural properties

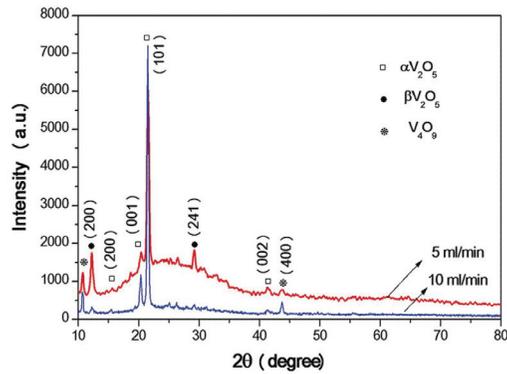
Figures 1(a)–1(c) show the XRD patterns of the vanadium oxide films prepared at two different substrate temperatures (group A), two different solution concentrations (group B) and two different solution spray rates (group C), respectively. Figure 1(a) shows the X-ray patterns of the films prepared at two different temperatures of  $300^{\circ}\text{C}$  and  $450^{\circ}\text{C}$ . As it can be seen, no clear peak is observed for the sample prepared at  $300^{\circ}\text{C}$  and the amorphous phase is revealed in the XRD pattern, while the structure of the sample made at  $T_{\text{sub}} = 450^{\circ}\text{C}$  is mainly orthorhombic  $\alpha\text{-V}_2\text{O}_5$  phase with minor tetragonal  $\beta\text{-V}_2\text{O}_5$  and  $\text{V}_4\text{O}_9$  phases. Therefore, one can say that increasing the substrate temperature from



(a)



(b)



(c)

Fig. 1. (a) XRD patterns of vanadium oxide films prepared at two different substrate temperatures constant vanadium concentration (0.2 M) and solution spray rate of 5 ml/min. (b) XRD patterns of vanadium oxide films deposited at two different solution concentrations at  $T_{\text{sub}} = 450^\circ\text{C}$  and 5 ml/min rate of solution spray. (c) XRD patterns of vanadium oxide films deposited at two various solution spray rates at  $T_{\text{sub}} = 450^\circ\text{C}$  and solution concentration 0.2 M.

Table 2. Summary of XRD parameters and crystallite size of all samples for (101) orientation.

| Sample   | $2\theta$ ( $^\circ$ ) | Lattice distance ( $\text{\AA}$ ) | FWHM ( $^\circ$ ) | Crystallite size (nm) | Identification with (hkl) value |
|--|------------------------|-----------------------------------|-------------------|-----------------------|---------------------------------|
| (A) The effect of substrate temperature (V-concentration = 0.1 M and solution spray rate = 10 ml/min)                |                        |                                   |                   |                       |                                 |
| 300 $^\circ$ C   | —                      | —                                 | —                 | —                     | —                               |
| 450 $^\circ$ C   | 21.52                  | 4.123                             | 0.294             | 29.19                 | Orthorhombic $V_2O_5$           |
| (B) The effect of V-concentration in solution ( $T_{\text{sub}} = 450^\circ\text{C}$ , solution spray rate 5 ml/min) |                        |                                   |                   |                       |                                 |
| 0.2 M  | 21.52                  | 4.123                             | 0.294             | 29.19                 | Orthorhombic $V_2O_5$           |
| 0.3 M  | 21.55                  | 4.123                             | 0.317             | 25                    | Orthorhombic $V_2O_5$           |
| (C) The effect of solution spray rate ( $T_{\text{sub}} = 450^\circ\text{C}$ , vanadium concentration 0.2 M)         |                        |                                   |                   |                       |                                 |
| 5 ml/min   | 21.52                  | 4.123                             | 0.294             | 29.19                 | Orthorhombic $V_2O_5$           |
| 10 ml/min  | 21.55                  | 4.130                             | 0.288             | 29.78                 | Orthorhombic $V_2O_5$           |

300 $^\circ$ C to 450 $^\circ$ C results in improvement of quality of the vanadium oxide films. The existence of different vanadium oxide minor phases has been also reported for  $V_2O_5$  thin films prepared by other methods as DC reactive magnetron sputtering.<sup>17</sup> Furthermore, from Fig. 1(a) one can say that the preferred orientation of the film deposited at  $T_{\text{sub}} = 450^\circ\text{C}$  is along [101] plane. Figure 1(b) shows the XRD pattern of the samples prepared at two different solution concentrations of 0.2 M and 0.3 M (group B). These results reveal that by increasing the solution concentration from 0.2 M to 0.3 M the relative intensity of [101] peak, corresponding to  $\alpha$ - $V_2O_5$  phase, has decreased, but  $\alpha$ - $V_2O_5$  [001] peak and [200] and [241] peaks related to  $\beta$ - $V_2O_5$  became more intense by solution concentration. It should be noted that the minor  $V_4O_9$  phase revealed in 0.2 M sample has almost disappeared in 0.3 M sample. XRD patterns of the samples prepared at two different solution spray rates (5 and 10 ml/min) are shown in Fig. 1(c), (group C). The patterns show that by increasing the solution spray rate from 5 to 10 ml/min, the relative intensity of [001] and [101] peaks corresponding to  $\alpha$ - $V_2O_5$  phase have increased. Moreover, it is observed that the amount of minor phase of  $V_4O_9$  detected in these films is less for lower solution spray rate. The information obtained from the XRD analysis is summarized in Table 2.

The scanning electron images of the prepared vanadium oxide films are shown in Fig. 2. The SEM image for sample prepared at  $T_{\text{sub}} = 300^\circ\text{C}$  [Fig. 2(a)] shows an uniform and featureless surface. It can be related to very small grains in the amorphous phase. By increasing the substrate temperature from 300 $^\circ$ C to 450 $^\circ$ C, the nano-sized platelet and granule shaped vanadium oxide are formed, Fig. 2(b). As shown in Figs. 2(b) and 2(c), by increasing the solution concentration from 0.2 M to 0.3 M the nanodisks are finally obtained. Figures 2(b) and 2(d) show that by increasing the solution spray rate from 5 to 10 ml/min flaky particles are formed.

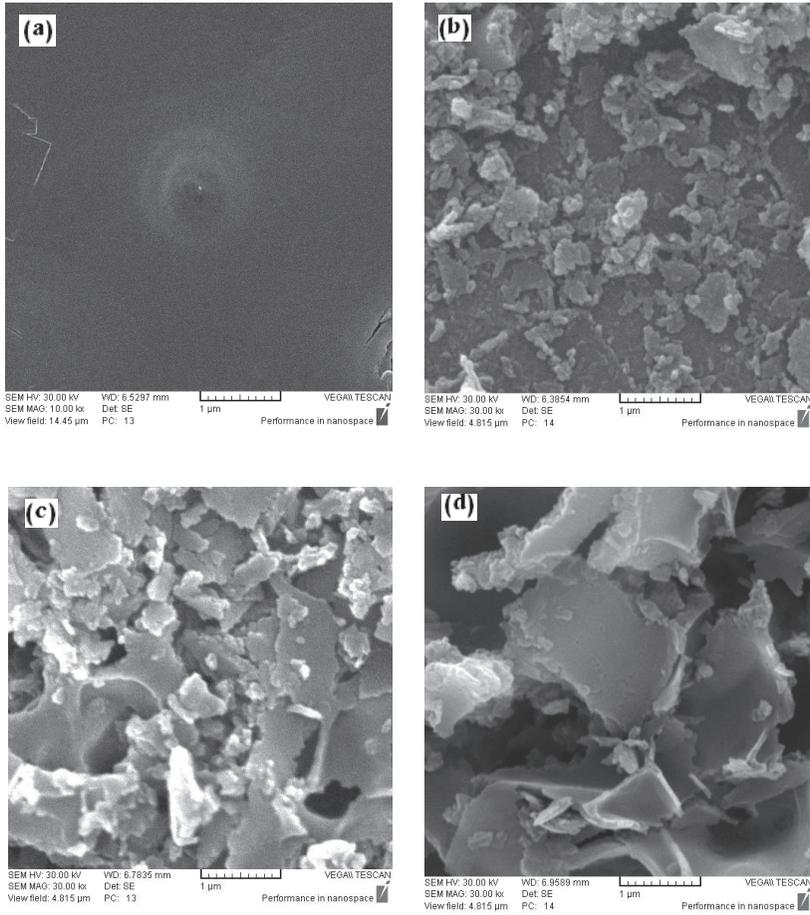


Fig. 2. (a)–(d) SEM images of vanadium oxide films: (a) prepared at  $T_{\text{sub}} = 300^{\circ}\text{C}$  with V-concentration 0.2 M and solution spray rate 5 ml/min, (b) prepared at  $T_{\text{sub}} = 450^{\circ}\text{C}$  with V-concentration 0.2 M and solution spray rate 5 ml/min, (c) deposited in 0.3 M V-concentration at  $T_{\text{sub}} = 450^{\circ}\text{C}$  and 5 ml/min solution spray rate and (d) deposited at 10ml/min solution spray rate at  $T_{\text{sub}} = 450^{\circ}\text{C}$  and V-concentration 0.2 M.

### 3.2. Electrical properties

The electrical measurements performed by two-point probe method show that the sheet resistance of the films decreases with increasing the substrate temperature and also solution spray rate. This can be related to growth in the grain size. By increasing the solution concentration, the sheet resistance of the films decreases. It can be due to the improvement of the stoichiometry of the samples. The results of the electrical measurements are summarized in Table 3. The thickness of the films, which were determined from the transmission data using the Puma software<sup>18</sup> are also given in Table 3.

Table 3. The electrical measurement results. (Thickness determination error is  $\sim \pm 5\%$ .)

| Sample           |                        |                     |                                    |                        |
|------------------|------------------------|---------------------|------------------------------------|------------------------|
| $T_{\text{sub}}$ | Solution concentration | Solution spray rate | $R_s$ ( $\text{K}\Omega/\square$ ) | Thickness ( $t$ ) (nm) |
| 300°C            | 0.2 M                  | 5 ml/min            | 1000                               | 320                    |
| 450°C            | 0.2 M                  | 5 ml/min            | 176                                | 233                    |
| 450°C            | 0.3 M                  | 5 ml/min            | 110                                | 278                    |
| 450°C            | 0.2 M                  | 10 ml/min           | 160                                | 220                    |

### 3.3. Electrochemical property

Figure 3 shows typical linear-sweep cyclic voltammograms (CVs) of vanadium oxide thin films prepared at various conditions. The CV curves of the 5th cycle of vanadium oxide films prepared with three layers at various conditions of temperature (group A), solution concentration (group B), solution spray rate (group C) in the potential windows between  $-0.4$  V and  $+1.2$  V versus an Ag are shown in Figs. 3(a)–3(c), respectively. The voltammograms recorded for group A samples are presented in Fig. 3(a). One anodic peak at  $+0.57$  V and one cathodic peak at  $+0.014$  V are presented in the CV curve for  $T_{\text{sub}} = 300^\circ\text{C}$ , which can be due to the existence of  $\text{V}^{+5}$  ions and  $\text{V}^{+4}$  ions, respectively. The color of the film with  $T_{\text{sub}} = 300^\circ\text{C}$  is originally pale yellow and then turns to blue because of reduction process occurrence which results in  $\text{V}^{+4}$  ions, in consistence with the vanadium pourbaix diagram. The film prepared at  $T_{\text{sub}} = 450^\circ\text{C}$  is different: it shows two well-defined reduction peaks at  $\sim -0.031$  V and  $\sim -0.27$  V and two oxidation peaks at  $\sim +0.048$  V and  $\sim +0.65$  V. While the as-deposited film is greenish yellow, on sweeping the potential downward and upward the CV curve shows two-step electrochromism, i.e. from yellow ( $\text{V}^{+5}$ ) it turns to blue ( $\text{V}^{4+}$ ) and then green ( $\text{V}^{+3}$ ) reversibly.

Similar behavior has been reported for other  $\text{V}_2\text{O}_5$  films prepared by thermal decomposition  $\text{TiO}_2/\text{Ti}$  in aqueous electrolytes.<sup>19</sup> As seen, the different nanostructure films of vanadium oxide with significantly different morphologies [Figs. 2(a) and 2(b)] have different CV curves. It is reasonable since the morphology or the total surface area of the nanostructure materials may affect the reaction rate in the electrochromic experiment. This relation between the morphology of the film and the electrochromic properties has been also observed for the vanadium oxide films prepared by thermal evaporation method.<sup>20</sup> The CV curve obtained for the film with  $T_{\text{sub}} = 450^\circ\text{C}$  shows more rapid rise in currents and the expanded area of the CV curve. It means that the electron transfer reaction kinetics for the electrode obtained with the  $T_{\text{sub}} = 450^\circ\text{C}$  condition is significantly more facile than the one with  $T_{\text{sub}} = 300^\circ\text{C}$ . It is said that this behavior can be partially related to the change in the compound of the samples as well as the different morphologies, and possibly to the decrease in the film resistance.<sup>21</sup> Figure 3(b) presents the CV curves of the samples of group B. As seen, the CV patterns show oxidation peaks at  $\sim +0.048$  V and

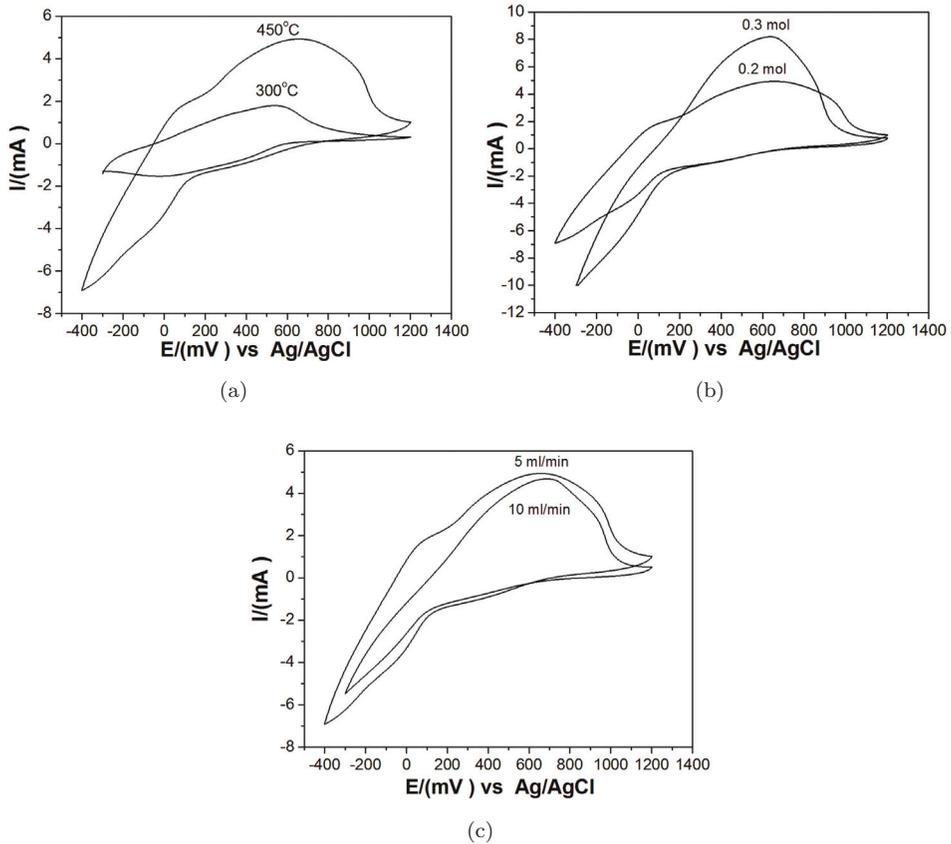


Fig. 3. (a) Cyclic voltammogram of vanadium oxide thin films prepared at two different substrate temperatures and constant vanadium concentration, 0.2 M and solution spray rate of 5 ml/min. The scan rate recorded at  $50 \text{ mV s}^{-1}$ . (b) Cyclic voltammogram of vanadium oxide thin films deposited at two different solution concentrations at  $T_{\text{sub}} = 450^\circ\text{C}$  and 5 ml/min rate of solution spray. The scan rate recorded at  $50 \text{ mV s}^{-1}$ . (c) Cyclic voltammogram of vanadium oxide thin films deposited at two various solution spray rates at  $T_{\text{sub}} = 450^\circ\text{C}$  and solution concentration 0.2 M. The scan rate recorded at  $50 \text{ mV s}^{-1}$ .

$\sim +0.65 \text{ V}$  for the film prepared with 0.2 M solution concentration and  $\sim +0.63 \text{ V}$  for 0.3 M sample, and reduction peaks at  $\sim -0.031 \text{ V}$  and  $\sim -0.27 \text{ V}$  for film prepared at 0.2 M solution concentration and  $\sim -0.058 \text{ V}$  for 0.3 M sample. These behaviors can be explained based on the Fig. 3(a) peaks: while the as-deposited films are yellow, the yellow becomes blue by decreasing the potential from  $+1.2 \text{ V}$  to  $-0.4 \text{ V}$ , in consistent with the one-step CV curve. Apparently it seems that the CV curves shapes are similar to each other; however their performances are relatively different from each other and as seen, the CV curve obtained for sample with 0.3 M solution concentration has one-step electrochromism and exhibit narrower and more intense characteristic anodic peak with respect to the 0.2 M sample. On the other hand, as mentioned above, the 0.3 M film has lower resistance. By this

observation one can conclude the direct relation between the shape of the cycle voltammograms and morphology in these samples. The voltammogram of group C samples presented in Fig. 3(c) show oxidation peaks at  $\sim+0.048$  and  $\sim+0.65$  V for film by 5 ml/min solution spray rate and 0.68 V for film by 10 ml/min solution spray rate and reduction peaks at  $\sim-0.031$  and  $\sim-0.274$  V for film by 5 ml/min solution spray rate and  $\sim-0.057$  V for film by 10 ml/min solution spray rate. The morphology of the samples is significantly different from each other [see Figs. 2(b)–2(d)], their CV curves are different. It means that the shapes of voltammograms are almost morphology-dependent. On the other hand, there is no considerable difference between the resistances of the films. This is an implicit confirmation of the relation of the CV curves shapes and the resistance of these films.

#### 4. Conclusion

In this paper, we reported the effects of deposition parameters on nanostructure and especially on electrochromic properties of vanadium oxide layers prepared by spray pyrolysis. The vanadium oxide samples prepared on glass substrates are mostly polycrystals of orthorhombic structure with [101] preferred orientation. Increasing the substrate temperature from 300°C to 450°C improves the crystalline quality of the prepared films and increasing the solution spray rate makes the  $\beta$ -V<sub>2</sub>O<sub>5</sub> phases nearly disappeared. The 0.3 M sample has both  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and  $\beta$ -V<sub>2</sub>O<sub>5</sub> phases. The morphology of the vanadium oxide layers can affect their electrochromic properties. The sample prepared at  $T_{\text{sub}} = 450^\circ\text{C}$ , 0.2 M solution concentration by 5 ml/min solution spray rate has two oxidation and reduction peaks, say a two-step electrochromism: the film is yellow (V<sup>5+</sup>) at  $\sim+0.65$  V, blue (V<sup>4+</sup>) around  $\sim+0.031$  V (V<sup>4+</sup>) and green (V<sup>+3</sup>) at  $\sim-0.274$  V, while the other samples have just one anodic and cathode peaks. The CV curves obtained from sample with 0.3 M solution concentration, 5 ml/min solution spray rate and  $T_{\text{sub}} = 450^\circ\text{C}$  exhibit narrower and more intense wave. This can be due to its higher electrical conductivity. At last, it can be concluded that the conductivity of the samples can facilitate the access for lithium ion intercalation and diffusion.

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