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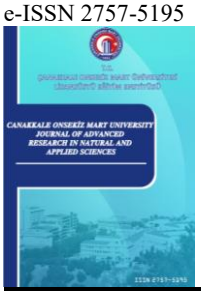

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Vanadium Oxide Based Electrochromic Energy Storage Devices via Facile Thin Film Preparation

Asuman Tuna[1], Sermet Koyuncu[1,2*]

[1]Department of Energy Resources and Management, Canakkale Onsekiz Mart University, Canakkale, Türkeye.
[2]Department of Chemical Engineering, Faculty of Engineering, Canakkale Onsekiz Mart University, Canakkale, Türkeye.

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Research Article

Abstract - The amount of energy utilized in our lives has significantly increased since the invention of electronic devices. Due to this increase in consumption, energy conservation and small-scale energy storage have become important. Smart glass technology is realized by using electrochromic devices prepared from thin films whose transmittance can be controlled under the influence of electric field. Most of the oxidized components of transition metals can be used in electrochromic devices. Vanadium, transition metal, is one of the rare compounds that show coloration in both anodic and cathodic layers. Vanadium Oxide thin films show phase change at different temperatures. With this feature, it shows anodic or cathodic differences in oxidation levels. In this study, V_2O_5 thin films were prepared by annealing at different thicknesses and temperatures with a spray coating device in order to measure the energy storage capacity of electrochromic devices. Prepared thin film samples were examined by atomic force microscopy (AFM) to determine their surface morphology. Optical and electrochemical properties of thin films were measured with UV-Vis spectrophotometer. Thin films were prepared for use in the anodic layer by coating PEDOT: PSS on the ITO/glass surface. Electrochromic devices were prepared by combining the anodic and cathodic layers with electrolyte gel by sandwich method. Durability and load capacity analyses of the prepared electrochromic devices were carried out.

Keywords *– Electrochromic devices, smart glasses, spray coating, thin films, vanadium oxide*

1. Introduction

The world quickly entered the age of technology with the invention of the transistor, which was acknowledged as the key component of electronics in the middle of the 20th century (Kastner, 1992). The rapid progress of this period, the beginning of which is not far away, has made technology much more accessible today. The fact that technology accompanies us in every aspect of our lives causes an increasing energy need day by day (Sumboja et. al., 2018). Considering the fossil resources with limited reserves and the developments in renewable energy resources, which have been studied frequently in recent years, two important points about energy stand out: the prevention of energy loss and the second is that the energy produced can be stored. The needs of cheaper cost, smaller volume energy production, storage, and power saving, which started with the introduction of electronic devices into our lives, have pushed scientists to work in this direction. Preventing energy loss plays an important role for long-term energy consumption. (Sorel et al., 2015). Most of the energy loss occurs due to building facades. In order to prevent these losses, glass technology with chromogenic (color changing) properties has been the focus of attention of many researchers. The most important feature of chromogenic materials is that in addition to being able to change color under an influence, this change is also

[1] skoyuncu@comu.edu.tr
[2] asumangula@gmail.com
*Corresponding Author

reversible. Chromogenic materials themselves do not produce energy (Zakirullin, 2020). Electrochromic structures, which are from a chromogenic material class, show the chromogen property under electric potential. Since the electrochromism was first defined in 1969, many scientists focused on working on low-cost electrochromic devices, and research on adapting these devices to daily life was accelerated (Chang et al. 2020). Many of the oxidized components of transition metals can be used in electrochromic devices (Zhang et al. 2020). However, there is a feature that distinguishes the oxide component of the vanadium transition metal from other transition metals. In transition metal oxide component materials, vanadium oxide components are one of the rare compounds that show coloration in both the anodic and cathodic layers (Kang et al., 2014). For this reason, it can be used in the active or counter layer in electrochromic material production studies, and it is frequently researched (Cai et al., 2016). Vanadium oxide components can form compounds at different oxidation levels from V^{+2} to V^{+5} and show a color change at each oxidation level. This behavior is an important feature for electrochromic devices (Mjejri et al., 2018).

The ability to store energy ensures that the produced energy can be used in case of need. Energy storage can be done in many different forms. The aim of energy storage systems is to store the highest energy in the lowest volume. In order to achieve this, the storage system must have a high storage capacity and a high charge/discharge time (Ibrahim, Ilinca, Perron, 2008). In this context, thin films can work as energy storage systems with high energy density and small volume, depending on the storage capacity of the material on which the film coating is performed. Transition metals show insulating properties and become conductive due to external factors such as magnetic field, electric field, heat and light. Vanadium, a transition metal, is an important source for electrochromic devices because it changes color under the influence of electric potential. Vanadium takes the values of V^{+2}, V^{+3}, V^{+4} and V^{+5} in its oxide components (Margoni et al, 2017). The fact that vanadium has a different color in each oxidation level makes vanadium an important working material for electrochromic devices (Table 1). The stable oxide components of vanadium are VO, V_2O_3, VO_2 and V_2O_5. It can be examining the oxide components in two separate groups as the V_nO_{2n-1} Magneli series and the $V_{2n}O_{5n-2}$ Wadsley series (Berezina et al, 2014). Each oxide form undergoes a phase change when it reaches the so-called critical temperature. This phase change can be in the form of a transition from semiconductor to conductive phase, or a reversible transition from the conductive phase to the semiconductor phase is also possible (Wu et al. 2008).

Table 1
Oxidation levels of V_2O_5

Oxidation Level	Ion	Color
+5	VO_3^- or VO_2^+	YELLOW
+4	VO^{2+}	BLUE
+3	V^{3+}	GREEN
+2	V^{2+}	PURPLE

Herein, the energy storage capability of electrochromic devices was evaluated by annealing V_2O_5 thin films at various thicknesses and temperatures using a spray coating device. AFM analysis was used to determine the surface morphology of prepared thin film samples. With a UV-Vis spectrophotometer, the optical and electrochemical characteristics of thin films were measured. ITO/glass surface was coated with PEDOT: PSS to create thin films for the anodic layer. By sandwiching the electrolyte gel with the anodic and cathodic layers, electrochromic devices were created. It was concluded that the V_2O_5 thin film prepared with a simple coating process is quite useful for electrochromic supercapacitor applications.

2. Materials and Methods

VCl_3 solutions at different concentrations were prepared and sprayed on the ITO/Glass surface from the same distance in the literature (Akl, 2006). VCl_3 solution at a concentration of 0.1 M was used in the study. Thin films were prepared by spraying the prepared solution on the ITO/Glass surface from distance of 20 cm with a spray gun device at a sub-base temperature of 100 ^oC. The prepared films were annealed at 300 ^oC. Apart from the prepared solution, there are the number of cycles and annealing temperature parameters that affect the test results. By changing these parameters, different thin films were obtained. The surface morphologies

of the obtained thin films were examined by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Using a Nanosurf Naio-AFM, the surface morphology of the polymer films was examined at ambient conditions and room temperature. This system was operated in the non-contact mode to capture topographic and phase images. Besides, the surface morphologies were also imaged by scanning electron microscopy (SEM, JEOL JSM-7100-F). By using a CH-Instrument CHI617D electrochemical workstation potentiostat-galvanostat system and a platinum disk (0.02 cm^2) as the working electrode, an Ag wire as the reference electrode, and a Pt wire as the counter electrode, electrochemical analyses were carried out (CE). The absorption spectra of V_2O_5 films under applied potential were taken into consideration through spectroelectrochemical measurements.

3. Results and Discussion

3.1. Surface Morphology of V_2O_5 thin Films

It is important that the surface has a rough structure in the prepared thin film samples. The high interaction surface between the electrolyte gel to be used in ECDs prepared using the sandwich system and the V_2O_5 thin film samples, which will be used as the cathode electrode, also increases the load holding capacity. For this reason, the surface roughness has been a decisive feature when examining the test results. In the spray coating device, ITO/Glass surfaces were coated with a thin film without annealing at different temperatures with 4, 6 and 8 cycles at 100 ºC substrate temperature (Kumar et al, 2008). Different samples were obtained by changing the number of cycles and temperature. The RMS values of the obtained samples are given in the table below. RMS values of the surface are measured by Atomic Force Microscope (Table 2).

Table 2
RMS Results of V_2O_5 thin films

V_2O_5 thin film	4 cycles	6 cycles	8 cycles
	RMS	RMS	RMS
Not annealed	4,21 nm	-	-
300	4,54 nm	8,43 nm	11,02 nm
350	4,73 nm	8,58 nm	11,27 nm

According to the results obtained, it was decided to use the thin film, which was prepared with 6 cycles and annealed at 300°C. AFM images of the V6_300 sample are given in Figure 1.

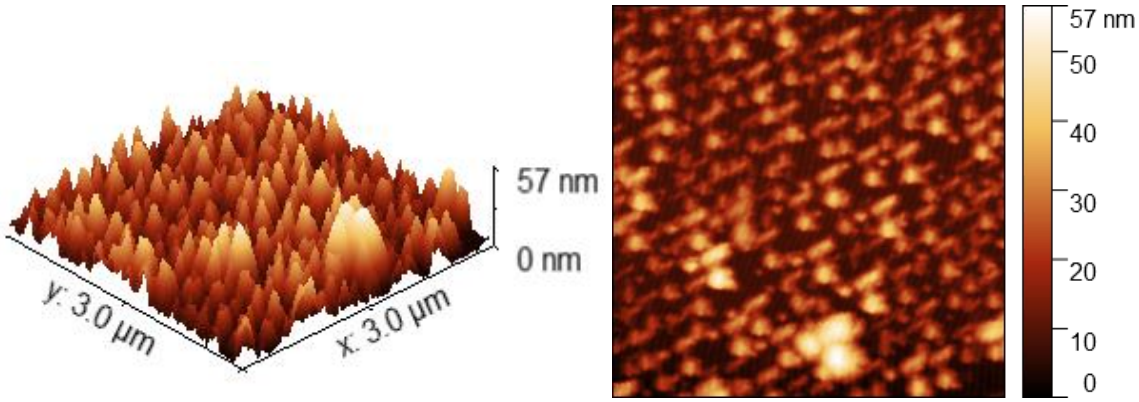

Figure 1. V6_300 V_2O_5 thin film

In addition, the surface morphology was examined by scanning electron microscopy. The SEM images of the V_2O_5 thin film coated in 6 cycles after annealing at 300 ºC are as follows. The rough structure of the surface is also observed in SEM images (Figure 2). The roughness on the surface occurs as agglomerations on top of each other. It was observed that precipitation occurred in the agglomerations formed in the 2 µm cross-section.

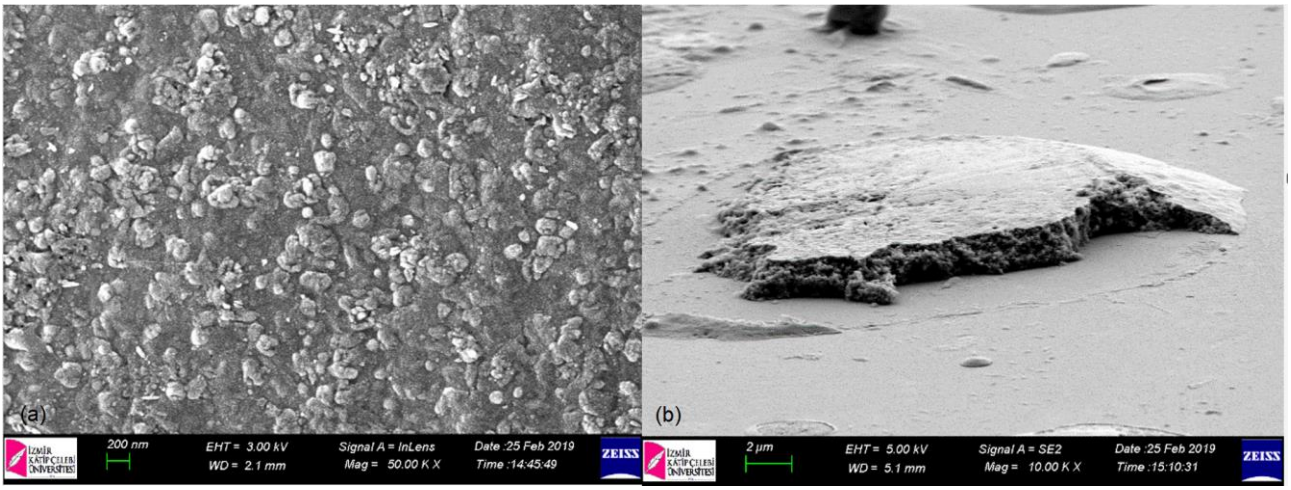

Figure 2. (a) SEM image of V6_300 V_2O_5 thin film (scale 200 nm) (b) SEM image of V6_300 V_2O_5 thin film (scale 2 µm).

3.2. Optical Properties of V_2O_5 thin Films

Optical characterization of V_2O_5 thin films, which were spray coated on the table at 100 ºC with the spray coating method, after annealing at 300 ºC, was made by UV-Vis absorption spectroscopy. Wavelength and absorbance/transmittance curves are given in Figure 3. It is seen that all the coated films have bands centered at 420 nm. In addition, as the film became thicker with the increase in the number of cycles, a significant increase was observed in the intensity in the absorption band and the related band also widened. Considering the optical band gap values calculated from the starting point of the lowest energy absorption band, the Eg value was calculated as 2.47 eV, 2.39 eV and 2.26 eV, respectively, depending on the increase in the film thickness (Abyazisani et al., 2015). These values are an important indicator of the semiconductor properties of the films. In addition, when the transmittance values at 400 nm are compared in the transmittance measurements, it is seen that the absorbance band, which decreases from 80% to 65%, ends, and that this value decreases from 98% to 85% above 500 nm. The results demonstrate that all thin films that have been created can be used directly in electrochromic devices.

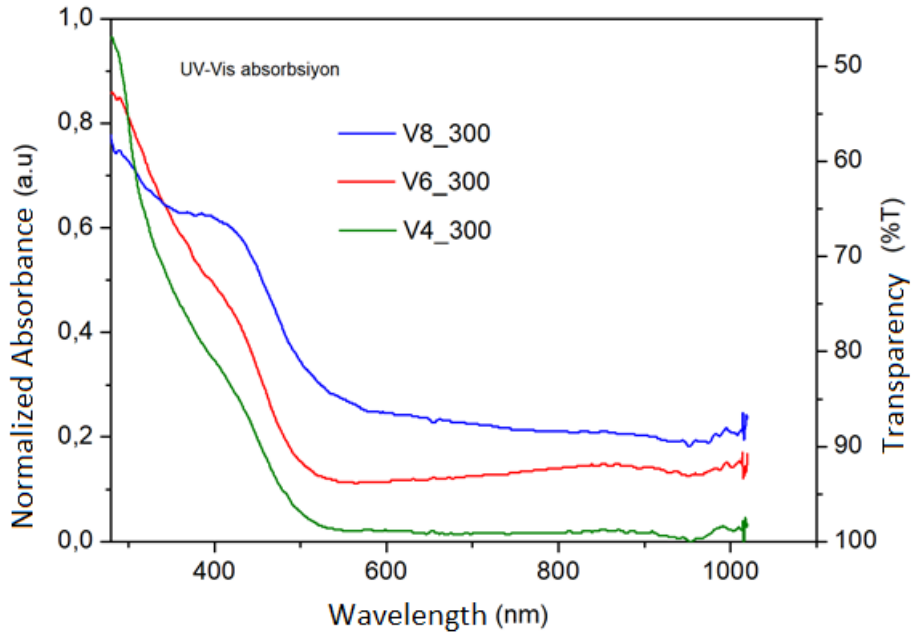

Figure 3. Absorbance spectrum of V_2O_5 thin film.

3.3. Electrochemical Properties

To determine the load holding capacity of the prepared thin films, cyclic voltammetry curves were obtained by applying potential on the thin film. Cyclic voltammetry graphs of 300 annealed V_2O_5 thin films prepared with 4, 6, 8 cycles of coating on 1 cm^2 area are shown in Figure 4. As in the literature, it is observed that the prepared thin films have two oxidation peaks (Mouratis et al. 2020). In the study, the load capacities of V4_300, V6_300, V8_300 thin films were measured as 2.89 x 10^{-2} C, 3.76 x 10^{-2} C, 4.94 x 10^{-2} C, respectively.

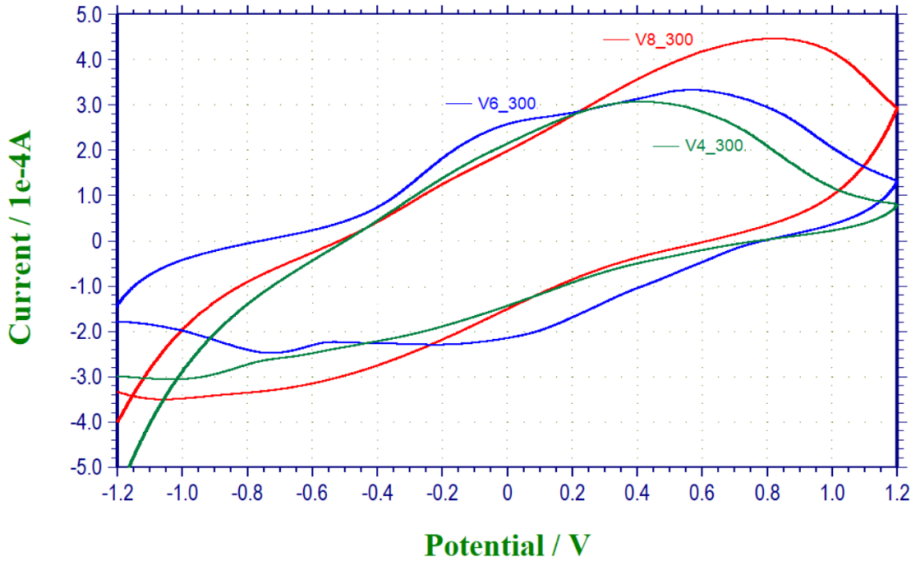

Figure 4. Cyclic voltammogram of V4_300, V6_300 and V8_300 thin films.

Cyclic voltammetry measurements were made to determine the load capacity of the prepared V_2O_5 electrochromic devices (EC). The V6_300 thin film is in the cathodic layer. In the anodic layer, an electrochromic device (EC) was prepared using PEDOT: PSS. The load holding capacity of the device prepared in 5 cm^2 active area was calculated as 0.154 C (Figure 5).

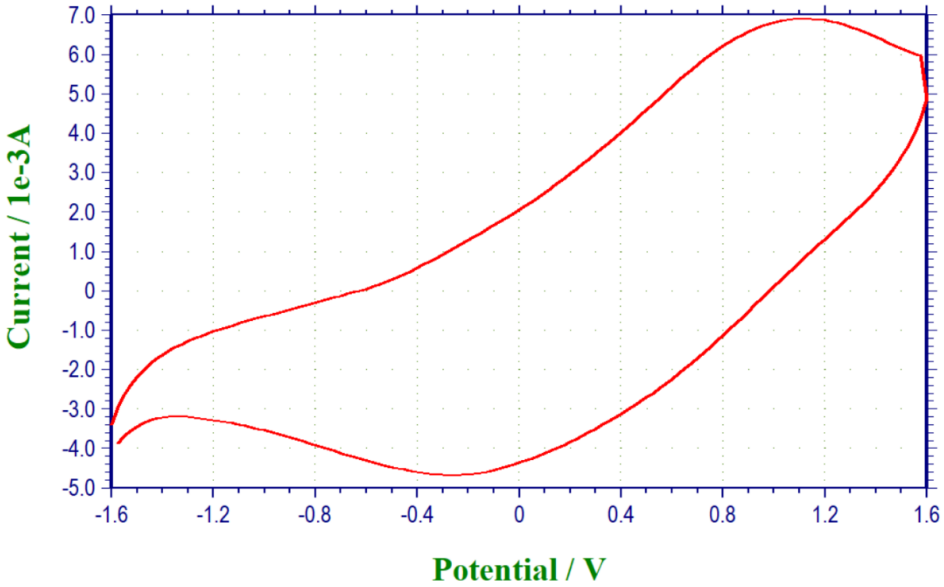

Figure 5. Cyclic voltammogram of V_2O_5 – PEDOT: PSS electrochromic device.

To measure the durability of the electrochromic device, -1.6 and 1.6V were applied at 10-second intervals. It was observed that the ECD prepared from V6_300 thin film maintained its stability at the rate of 98% at the end of 2000 cycles (Figure 6).

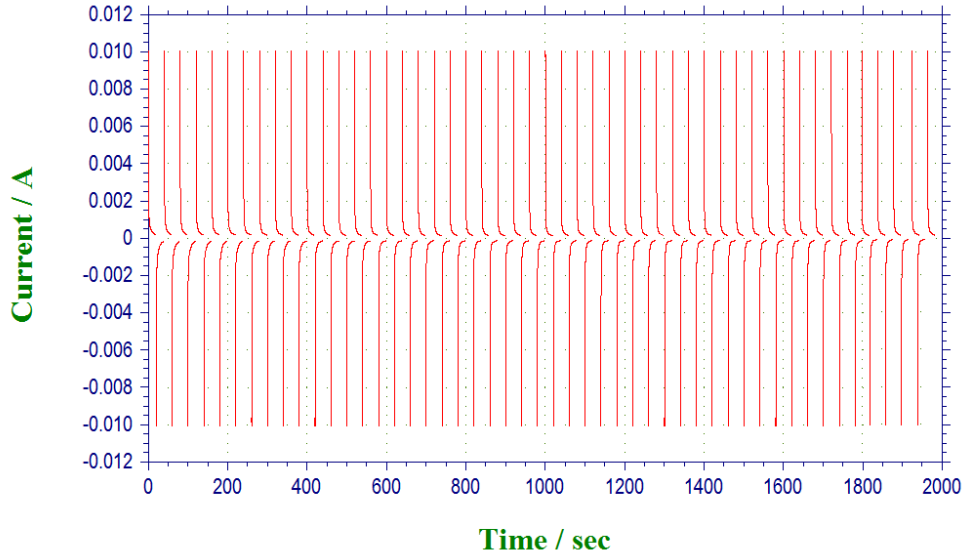

Figure 6. V6_300 sample V_2O_5- PEDOT: PSS Durability test graph of electrochromic device.

3.4. Spectroelectrochemical measurements

In the Spectro electrochemical characterization of the V6_300 thin film, which is one of the prepared V_2O_5 films, the measurement was performed in the range of -1.2-1.2 V. The most important feature of chromogenic materials is that they can change color, as well as this process is reversible. For this reason, spectroelectrochemical measurements were carried out in the range of -1.2-1.2 V, where the prepared V_2O_5 thin films showed reversible properties. It was observed that the color of the film changed from yellowish green to dark green depending on the applied potential (Figure 7). In the spectroelectrochemical characterization of the V6_300 thin film carried out between -1.2 V and 1.2 V, first, a strong absorption band of the thin film up to 500 nm at -1.2 V is observed. It was observed that the intensity of the 400 nm-centered band decreased partially as the potential continued to be applied. In addition, it is seen that the intensity of the 800 nm-centered bands covering 550 nm and the entire visible and near IR region has increased. It was observed that the color of the film changed from yellowish green to dark green depending on the applied potential (Surca, Drazic, Mihecic, 2020). As a result of the spectroelectrochemical measurements carried out between -1.6 V and 1.6 V for the prepared ECD, it is observed that the color of the transparent device turns dark blue because of the contribution of PEDOT: PSS to the coloration, with the application of positive potential and the increase in the intensity of all peaks above 400 nm. As a result of the experiments and studies carried out, it has been observed that the prepared ECDs behave like micro supercapacitors and have energy storage capacities (Hall and Bain, 2008).

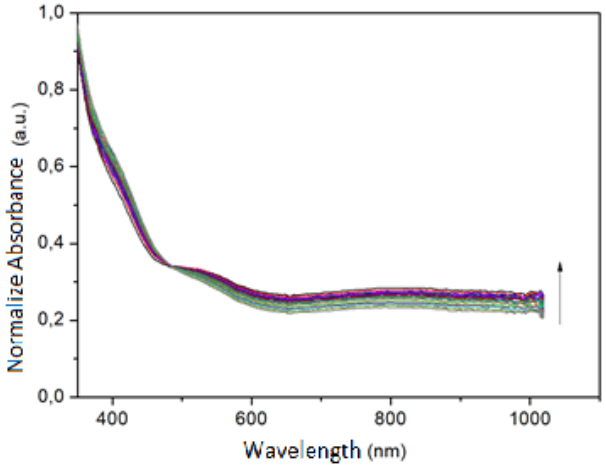

Figure 7. Spectroelectrochemical characterization of V6_300.

The electrochromic device is prepared in ITO-glass/V2O5//$LiClO_4$ gel electrolyte//PEDOT: PSS/ITO-glass architecture. The spectroelectrochemical behavior of PSS-based ECD was investigated in the range of -1.6-1.6 V. The prepared device shows reversible properties in the range of -1.6-1.6 V. It is observed that the color of the device, which is transparent, with the increase in the intensity of all peaks at 400 nm and above with the applied positive potential, turns into dark blue because of the contribution of PEDOT: PSS to the coloration (Figure 8). When the transmittance values at 400 nm of the samples prepared V4_300, V6_300, V8_300, respectively, were compared, it was observed that the transmittance values decreased from 80% to 65%. If the absorbance band is above 500 nm, it is seen that this value decreases from 98% to 85%. The obtained data show that all prepared thin film samples can be used in electrochromic devices. As a result of the CV electro-chemical measurements, it was observed that the cyclic voltammetry graphs of the electrochromic devices prepared with V_2O_5 thin films in the cathodic layer overlapped with the pseudo capacitors (Liu et al., 2017). When the cyclic voltammetry graphs were examined, it was determined that the thin film samples prepared in 1 cm^2 area performed oxidation in two stages under the positive potential. During this oxidation, the load capacities of V4_300, V6_300, V8_300 thin films were measured as 2.89 x 10^{-2} C, 3.76 x 10^{-2} C, 4.94 x 10^{-2} C, respectively. The load holding capacity of the ECD, which was prepared in an area of 5 cm2 using V6_300 in the cathodic layer and PEDOT: PSS in the anodic layer, was calculated as 0.154 C. It has been observed that the V6_300 – PEDOT: PSS EC device, which was prepared as a result of the stability tests, maintained its stability at the rate of 98% after 2000 cycles. This situation is very important in terms of charge-discharge durability, and it has shown that it can be used easily in this state in practice.

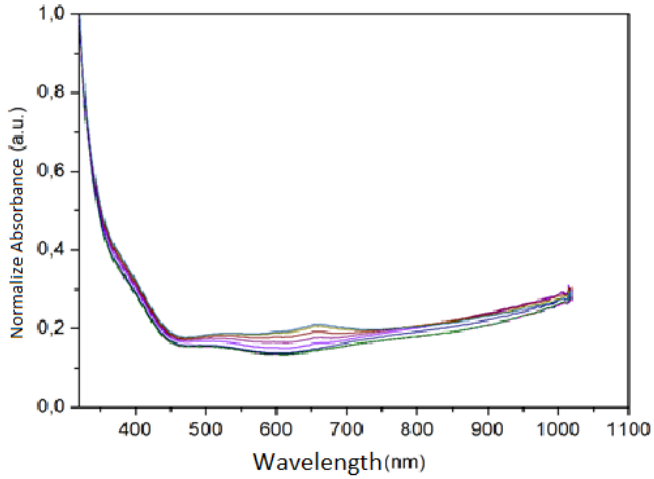

Figure 8. Absorbance spectrum of V_2O_5-PEDOT: PSS.

3.5. X-Ray Crystallography

The crystal structure drawn with the lattice parameters determined in the XRD results obtained for the V6_300 thin film is given in Figure 9. Blue balls represent Oxygen atoms and purple balls represent Vanadium atoms.

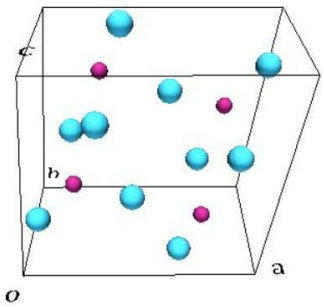

Figure 9. V6_300 thin-film crystalline structure

It showed a peak at 2θ 28º and 17º degrees in the V6_300 sample. Lattice parameters were determined as a (Å):11,285, b (Å):3,572, c (Å):4,114. The results obtained support the existence of V_2O_5.

4. Conclusion

In this study, the optimization of V_2O_5 thin films to be used in the cathodic layer in the ECDs prepared was studied. The energy storage capacities of ECDs prepared by using V_2O_5 thin films in the cathodic layer and PEDOT: PSS thin films in the anodic layer were investigated. Spray coating method was used to coat V_2O_5 thin films. VCl_3 was used as the precursor to be used in the coating device. Distilled water was used as the solvent. Morphological and optical characterizations of thin films were performed with the help of XRD, AFM, SEM and UV-Vis spectrometer measurement systems. As a result of XRD measurements, it was observed that all samples were in crystal structure in orthorhombic phase. The electrochromic device structure was formed by combining the prepared anodic and cathodic layers with the sandwich method. As a result of the experiments and studies carried out, it has been observed that the prepared ECDs behave like micro supercapacitors and have energy storage capacities.

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Author Contributions

Asuman Tuna: Conceived the analysis and performed statistical analysis.
Sermet Koyuncu: Collected data, performed the analysis and wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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