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H^+- intercalation Electrochemical/Electrochromic Properties of V-Ce Mixed Oxide Thin Films

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Vanadium-Cerium mixed oxides have been proved as good electrodes for electrochromic devices because of their passive optical behavior coupled with good charge capacity. Thin films of vanadium - cerium mixed oxides were deposited at room temperature on ITO plates by varying the RF power from 100W to 200 W in steps of 50W by RF magnetron sputtering in a pure argon atmosphere. Two targets were prepared by pressing the powder mixture of V_2O_5 and CeO_2 taken in different molar ratios (1:1; 1:2). A three electrode electrochemical cell was designed with these mixed oxide thin films as the working electrode, platinum mesh as counter electrode and the saturated calomel as the reference electrode with 0.01M HCl solution diluted in distilled water as electrolyte. The variation in the electrochemical and optical properties of the prepared thin films with H^+ ion intercalation and de-intercalation with respect to the RF power during deposition and the molar ratios of V_2O_5 and CeO_2 in the target material are elaborately discussed in this study.

Keywords: V-Ce mixed oxide thin films; Non reactive sputtering; Electrochromism

1. INTRODUCTION

Though vanadium pentoxide as counter electrode in electrochromic devices exhibits high charge capacity and unique optical properties, it shows mixed anodic/cathodic electrochromism[1,2]. Because of high transparency in both oxidized and reduced state, CeO_2 can be used as a passive counter electrode[3-5] but it exhibits slow reaction kinetics and low charge capacity[6]. Thus vanadia-ceria mixed oxide thin films can be used as optically passive counter electrodes in electrochromic devices with good charge capacity at around 20mC cm^{-2} [7-9]. $CeVO_4$ with zircon type structure consists of VO_4 tetrahedra which share corners and edges with CeO_8 dodecahedra[10]. The extended chain of these dodecahedra with distorted VO_4 unit along the c-axis of the crystal structure is a well suited one for the insertion of H^+ ions. Due to the electronic conductivity exhibited by the valance band holes, $CeVO_4$ compound is selected as the efficient electrode material in electrochromic devices. The electrochromic reaction occurring in $CeVO_4$ thin films can be written as below:

$$Ce_yVO_z + xH^+ + xe^- \leftrightarrow H_xCe_yV_{1-x}O_z$$

$CeVO_4$ thin films as passive counter electrodes in electrochromic devices exhibit a small coloration efficiency of 0.1-0.5 $cm^2\ C^{-1}$. In our present work, the experimental details for preparing V-Ce mixed oxide thin films in different molar ratios and the electrochemical properties and spectral transmittance variations of the prepared thin films with respect to H^+ ion insertion and de-insertion were elaborately discussed.

2. EXPERIMENTAL PART

Table 1. Composition of V_2O_5 and CeO_2 in the target powders during sintering.

Sintering	V_2O_5:CeO_2= 1:1		V_2O_5:CeO_2= 1:2	
	$CeVO_4$	V_2O_5	$CeVO_4$	V_2O_5
I	76%	23%	71%	29%
II	80%	20%	79%	21%
III	89%	11%	85%	15%
IV	94%	6%	92%	8%
V	100%	---	100%	---

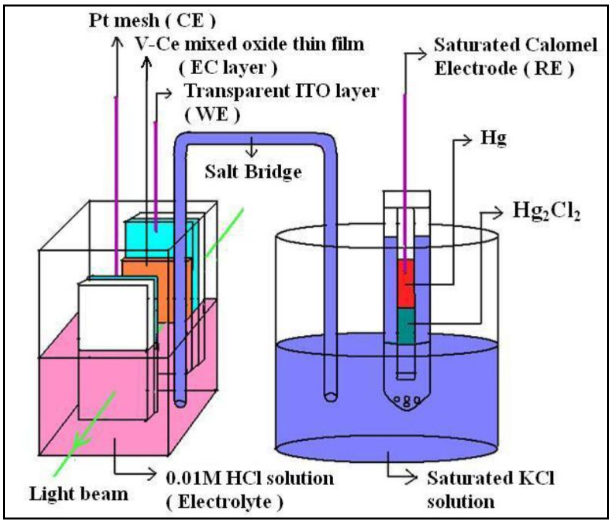

Figure 1. Schematic representation of in-situ cyclic voltammetry and UV-Vis-NIR spectrophotometer measurement setup.

The V-Ce mixed oxide thin films were deposited on transparent, conducting ITO glass substrates by RF magnetron sputtering in a pure argon atmosphere. Powder mixtures of V_2O_5 and CeO_2 in different molar ratios (V_2O_5:CeO_2= 1:1; 1:2) were sintered to 600°C for 5 hours. The mixture with

V_2O_5:CeO_2= 1:1 possessed 76% of $CeVO_4$ and 23% of V_2O_5 and there was no evidence of CeO_2 peaks which was revealed by studying the peaks formed in the XRD patterns whereas the powder mixture containing V_2O_5:CeO_2= 1:2 possessed 71% of $CeVO_4$ and 29% of V_2O_5 . To prepare a mixture free from unwanted phases, the powders were sintered again and again and after 5 trials, powder mixtures with pure $CeVO_4$ –W phase were obtained. The composition of phases in the target materials during the sintering process are listed out in Table 1.

Targets with 6mm thickness and 50mm diameter were obtained by pressing these mixtures in a pellatiser and were then sintered to 300° C for about 2 hrs. Before deposition, pre-sputtered vacuum was obtained in the chamber better than 10^{-5} mbar. Three sets of V-Ce mixed oxide thin films were deposited at room temperature by varying the RF power from 100W to 200W in steps of 50W under pure argon atmosphere. The following deposition parameters were kept constant for all samples preparation: 45 minutes deposition time, 1.33 x 10^{-2} mbar argon gas pressure and 6cm target-substrate spacing. Electrochemical cells were designed with the prepared thin films as working electrode, pure platinum mesh as counter electrode and saturated calomel as reference electrode. The electrolyte is a 0.01M HCl solution diluted in distilled water. The schematic diagram of the in-situ cyclic voltammetric arrangement along with the UV-Vis NIR spectrophotometer is shown in Fig. 1. The CV studies were performed by using a Model 600D Series electrochemical analyser/ workstation (CH instruments) in -1.6V to +1.6V voltage range with 10mV/s scan rate for 10 cycles. The voltage is represented with respect to Hg/Hg_2Cl_2 electrode in this work. Simultaneously the transmittance spectra of thin films were recorded by using a UV-Vis-NIR spectrophotometer (HR-2000, M/s Ocean Optics, USA) to study their electrochromic behavior.

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry

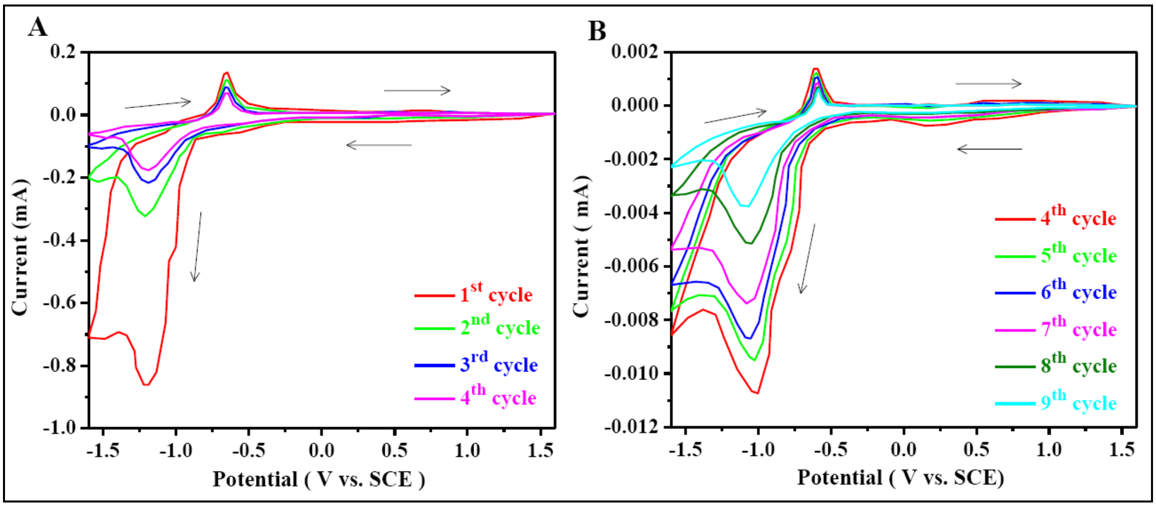

Figure 2. Cyclic voltammograms of V-Ce mixed oxide thin films (molar ratio 1:1; 150W deposition power) in **(A)** initial 3 cycles and **(B)** remaining 7 cycles.

In cyclic voltammetric studies (CV), 10 cycles of H^+ ion insertion and de-insertion inside the working electrode have been performed. Fig. 2A and 2B show the CV of V-Ce mixed oxide thin films prepared in molar ratio of 1:1 and deposited at 150W RF power. A large as well as a sharp cathodic peak appears during the first cycling at -1.25V vs. Hg/ Hg_2Cl_2 which implies that a large H^+ intercalation occurs and this peak has been shifted towards higher potential region and is centered at around -1V after fourth cycling. The corresponding anodic peak has been centered at -0.66V. These cathodic and anodic peaks are due to the redox process of the lower states of vanadium (V^{4+}/V^{3+})[11]. Also the shape of the CV implies that the cycling exhibits an irreversible charge capacity which may be due to the presence of amorphous cerium orthovanadates in the prepared thin films[12].After third insertion, the charge insertion has been reduced a lot which can be understood by viewing the corresponding CVs in Fig. 2B. This can be explained in this amorphous thin films as the probability of the H^+ ion to find the unoccupied site closer to the occupied ones decreases with insertion of more H^+ ions. The discharge potential decreases rapidly than the reduction potential when cycling increases and this is due to the capture of H^+ intercalated ions indefinitely in the thin film which may be enhanced by the amorphous nature of the mixed oxide thin films. Table 2 displays the diffusion co-efficient of H^+ ion which has been calculated from the Randles-Sevcik equation explained as follows:

$$i_p = 2.72 \times 10^5\, n^{3/2}\, A\, D^{1/2}\, C\, v^{1/2}$$

where

i_p = Maximum current which includes both i_{pc} and i_{pa}
n = Number of electrons participating in the redox process which is normally 1
A = Area of electrode
D = Diffusion co-efficient of H^+ ions
C = Concentration of active ions in the electrolyte solution
v = Scan rate

The H^+ ion diffusion co-efficient shows a monotonic decrease in value from 5.27×10^{-9} $cm^2\ s^{-1}$ to 6.48×10^{-14} $cm^2\ s^{-1}$ during the intercalation process when cycling continues. The high value of diffusion coefficient during initial cycling is due to the less density of the prepared amorphous thin films. The monotonic decrease in the value of diffusion co-efficient when cycling continues is due to the continuous decrease in the probability of finding the unoccupied site by the H^+ ions inside the amorphous sample as mentioned earlier. F. Varsano et.al. experienced a non monotonic variation in the diffusion coefficient of Li ion during intercalation in crystalline cerium-vanadium mixed oxide thin films prepared with molar ratio of 1:1 under reactive sputtering in which P_{O2} = 5 mTorr and so the non interacting lattice gas model could not be applied for those partially crystalline thin films[13]. The authors recorded the diffusion co-efficient value which varies with the intercalation level in a non monotonic way and its value ranges from 8×10^{-12} $cm^2\ s^{-1}$ to 5×10^{-13} $cm^2\ s^{-1}$ for intercalation level lying between 0 to 1. In our study, the diffusion co-efficient values during de-intercalation process decreases from 2.34×10^{-9} $cm^2\ s^{-1}$ to 2.12×10^{-14} $cm^2\ s^{-1}$ and the gradual decrease in these values with respect to those obtained for H^+ ion intercalation implies that some of the H^+ ions are trapped inside the sample when cycling process advances.

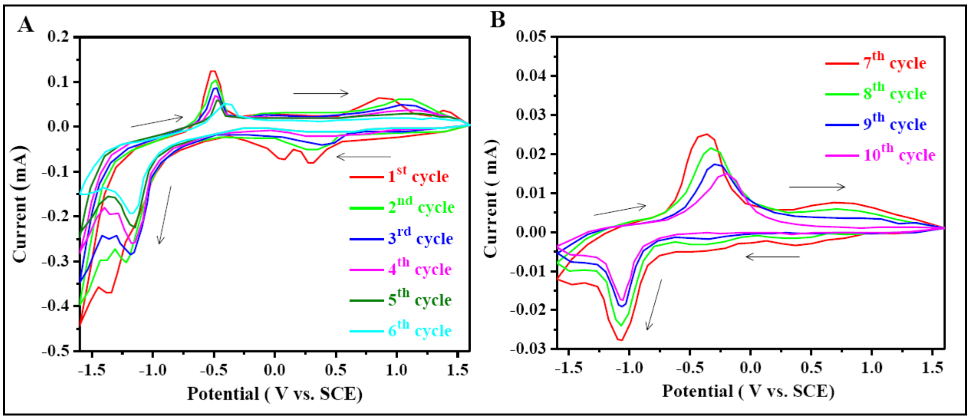

Figure 3. Cyclic voltammograms of V-Ce mixed oxide thin films (molar ratio 1:1; 200W deposition power) in **(A)** initial 6 cycles and **(B)** remaining 3 cycles.

Table 2. The electrochemical parameters of V-Ce mixed oxide thin films (molar ratio 1:1; 150W RF power).

No. of cycles	Cathodic peak i_{pc} (mA)	Anodic peak i_{pa} (mA)	Diffusion coefficient D (cm^2 s^{-1})	
			For i_{pc}	For i_{pa}
1	0.1996	0.1331	5.27×10^{-9}	2.34×10^{-9}
2	0.0884	0.0534	1.03×10^{-9}	3.77×10^{-10}
3	0.062	0.0532	5.08×10^{-10}	3.74×10^{-10}
4	0.0487	0.031	3.14×10^{-10}	1.27×10^{-10}
5	0.0036	0.001	1.71×10^{-12}	1.32×10^{-13}
6	0.0025	0.0006	8.26×10^{-13}	4.76×10^{-14}
7	0.0023	0.00055	7×10^{-13}	4×10^{-14}
8	0.0016	0.0005	3.39×10^{-13}	3.31×10^{-14}
9	0.0013	0.00046	2.23×10^{-13}	2.8×10^{-14}
10	0.0007	0.0004	6.48×10^{-14}	2.12×10^{-14}

Fig. 3 shows the cyclic voltammogram of V-Ce mixed oxide thin films in molar ratio of 1:1 and deposited at 200W RF power. The observed CV resembles that of $CeVO_4$-W structured thin films containing two electrochemically active regions, one in the higher potential range of 1.6V to -0.25V and the other in the lower potential range of -0.25V to -1.6V and the same CV pattern was recorded by I. Kozjek Skofic et.al. for V-Ce mixed oxide thin films prepared by sol-gel technique[11]. This explains that the H^+ intercalation occurs twice in the film structure during the first few cycles. The first reduction occurs at 0.28V and a small peak could be observed along with it at -0.06V which states that H^+ intercalation occurs at two different sites in the film structure at higher potential range during first cycling. The reason for the peak at around 0.28V is due to the reduction of V^{5+} to V^{4+} oxidation state. This peak was observed by F.Varsano et.al. in the CV of V-Ce mixed oxide thin films prepared with V/Ce = 2 by reactive sputtering in 150W RF power during Li^+ intercalation in which the thin film possessed mixed oxides of stoichiometric cerium vanadate and amorphous vanadium oxides[13]. F. Artuso et.al. prepared ternary Fe/Ce/V oxide thin films and the CV of thin films having lower Fe content resembled that of stoichiometric $CeVO_4$ thin films with two peaks at higher potential range at 2.8 and 3.2V while employing slow scan rate[14]. The chosen potential window was in the range of 1 to 4.3V vs. Li. The high potential peak is absent in the case of thin films prepared at 150W RF power which states that the role of V atoms in V_4^{-3} units is enhanced in thin films prepared at higher deposition power. F.Varsano et.al. also reported that the peaks at higher potential range were absent for mixed oxide thin films prepared in molar ratio of 1:1 with 150W RF power in non reactive sputtering when the cycling was undertaken in the potential range of 1-5V for Li intercalation. Also they observed this high potential redox peaks for thin films prepared with 20% of oxygen and 150W RF power during sputtering process in the same potential range[15]. The same authors observed two electrochemically active regions including the higher potential range for thin films prepared with Ce/V = 1:2 in 200W RF power prepared in reactive sputtering[16].

Table 3. The electrochemical parameters of V-Ce mixed oxide thin films (molar ratio 1:1; 200W RF power).

No. of cycles	Cathodic peak i_{pc} (mA)	Anodic peak i_{pa} (mA)	Diffusion coefficient D ($cm^2\ s^{-1}$)	
			For i_{pc}	For i_{pa}
1	0.04	0.012	2.12×10^{-10}	1.9×10^{-11}
	0.0367	0.0266	1.78×10^{-10}	9.36×10^{-11}
	0.1564	0.0867	3.23×10^{-9}	9.94×10^{-10}
2	0.0299	0.013	1.18×10^{-10}	2.23×10^{-11}
	0.103	0.0534	1.4×10^{-9}	3.77×10^{-10}
3	0.0234	0.0099	7.24×10^{-11}	1.3×10^{-11}
	0.0964	0.0399	1.23×10^{-9}	2.11×10^{-10}
4	0.0764	0.0299	7.72×10^{-10}	1.18×10^{-10}
5	0.066	0.0233	5.76×10^{-10}	7.18×10^{-11}
6	0.043	0.013	2.44×10^{-10}	2.23×10^{-11}
7	0.0109	0.0074	1.57×10^{-11}	7.24×10^{-12}
8	0.0083	0.0062	9.11×10^{-12}	5.08×10^{-12}
9	0.0078	0.0056	8.04×10^{-12}	4.15×10^{-12}
10	0.007	0.003	6.48×10^{-12}	1.19×10^{-12}

The two oxidation peaks corresponding to it are seen at 1.46V and 0.87V during the first cycle which converges in to a single peak in the second cycling itself and thereafter it is centered at 1.05V. These redox peaks disappear after 3rd cycle which informs that the V atoms involved in reduction are in complete V^{4+} state. The second reduction peak is centered at -1.38V which is due to the complete reduction of these V^{4+} state of vanadium into V^{3+} state. The corresponding oxidation peak is observed at -0.52V which also has been shifted slightly towards higher potential region when cycling continues and is located later at -1.13V. Though the charge capacity during intercalation process appears same in both thin films prepared at 150W and 200W RF power in the first few cycles, it clearly shows that thin films prepared at high RF power exhibit better charge insertion in prolonged cycling process. The calculated diffusion co-efficient of H^+ ion is tabulated in Table 3. During the intercalation process, the value of diffusion co-efficient decreases from 3.23 x 10^{-9} cm^2 s^{-1} to 6.48 x 10^{-12} cm^2 s^{-1} when cycling goes down to 10. Thus the charge insertion of H^+ ions inside these sample which are prepared at high RF power is larger than those prepared at lower RF power after 10 cycles of H^+ ion intercalation. This may be due to the improvement in the channel like growth of $CeVO_4$ structure in the sample with increase in RF power during deposition process. By sol-gel dip coating technique, U. Opara Krasovec et.al. deposited mixed oxide thin films having Ce/V ratio of 1:2 after heat treating for 4 h which possessed tetragonal $CeVO_4$-W phase along with vanadium phase similar to that of orthorhombic V_2O_5. Here the ion storage capacity was improved by the presence of $CeVO_4$-W phase [17]. The corresponding diffusion co-efficient values during de-intercalation process decreases from 9.94 x 10^{-10} cm^2 s^{-1} to 1.19 x 10^{-12} cm^2 s^{-1}. Thin films prepared at low RF power ie 100W couldn't show a stable CV and this may be due to the highly disordered form present in these thin films. Also the cycling voltage range of -1.6V to +1.6V may be a range taken out of the safe zone for such disordered thin films as the redox peaks may be suppressed fully even by the insertion of less amount of charge insertion.

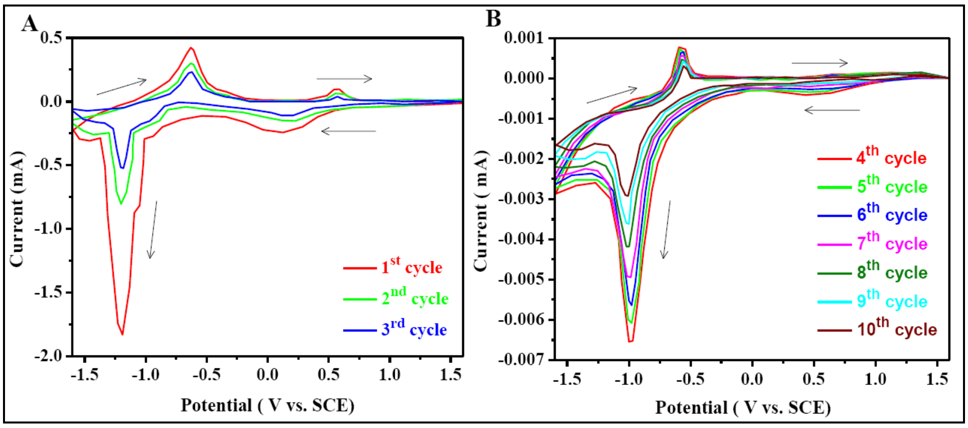

Figure 4. Cyclic voltammograms of V-Ce mixed oxide thin films (molar ratio 1:2; 100W deposition power) in **(A)** initial 3 cycles and **(B)** remaining 7 cycles.

The cyclic voltammogram of V-Ce mixed oxide thin films in molar ratio of 1:2 and prepared in 100W RF power is displayed in Fig. 4A and 4B. The CV diagram is similar to $CeVO_4$ phase exhibiting two potentially active regions. As in V-Ce mixed oxide thin films in molar ratio 1:2, the presence of $CeVO_4$ with the channel like structure helps improving the mobility of H^+ ions and electrons and so the charge insertion during the first three cycles are high compared to those of thin films with molar ratio 1:1. The sol-gel dip coated V-Ce mixed oxide thin films with Ce/V = 1 and heat treated for 4 h prepared by U. Opara Krasovec et.al. possessed $CeVO_4$-W alone which helped to improve their ion storage capacity[17]. The higher potential region lies in between 1.6V to -0.31V and the lower potential range is -0.31V to -1.6V.

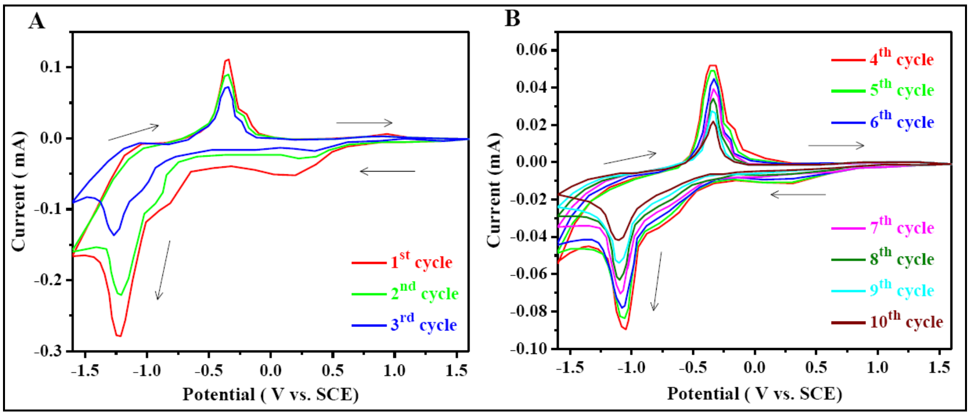

Figure 5. Cyclic voltammograms of V-Ce mixed oxide thin films (molar ratio 1:2; 150W deposition power) in **(A)** initial 3 cycles and **(B)** remaining 7 cycles.

The first reduction occurs at 0.13V and it is a broad peak corresponding to the reduction of V^{5+} state of vanadium into V^{4+} state. The oxidation peak corresponding to it is appeared at 0.56V. Further reduction occurs at -1.19V which is a sharp peak with high reduction of V^{4+} state in to V^{3+} state. The corresponding oxidation peak is seen at -0.63V and the unequal ratios of the two high reduction peaks with respect to their respective oxidation peaks imply that the inserted H^+ ions are irreversible and are intercalated inside the thin films. After 3rd cycle, a continuous decrease in the H^+ intercalation and de-intercalation is observed and the redox peaks at higher potential region also vanishes which is natural in the case of mixed oxide thin films prepared in pure argon atmosphere [15].

Table 4 shows the diffusion co-efficient of H^+ ion during intercalation and de-intercalation process. The value of diffusion co-efficient decreases from 7.57 x 10^{-8} cm^2 s^{-1} to 6.48 x 10^{-14} cm^2 s^{-1} during the intercalation process when cycling continues. Galvanostatic intermittent titration technique (GITT) has been adopted by G. Picardi et.al. to find the diffusion co-efficient value of mixed oxide thin films with molar ratio of 1:2 prepared by sol-gel dip coating technique[8]. When Li intercalation began in the prepared crystalline $CeVO_4$ thin films, the diffusion co-efficient value was 10^{-10} cm^2 s^{-1} which decreased to 10^{-13} cm^2 s^{-1} at the end of the insertion reaction. The comparatively high value of diffusion co-efficient in our study during the initial process implies that the amorphous vanadium states are available in the sample. The decrease in the probability of H^+ ion finding the unoccupied place inside the sample when cycling increases, is responsible for the gradual decrease in the value of diffusion co-efficient. The corresponding diffusion co-efficient values decreases as 2.88 x 10^{-9} cm^2 s^{-1} to 1.04 x 10^{-14} cm^2 s^{-1} during de-intercalation process and the high charge capacity and the stability even after 10 cycles make these thin films more appropriate to be used as working electrodes in ECDs than those prepared in molar ratio of 1:1. Better cycling durability was shown by V-Ce mixed oxide thin films with 38 at% of V than those with 55 at% of V prepared by Z. Crnjak Orel et.al. in sol-gel technique too[7].

Table 4. The electrochemical parameters of V-Ce mixed oxide thin films (molar ratio 1:2; 100W RF power).

No. of cycles	Cathodic peak i_{pc} (mA)	Anodic peak i_{pa} (mA)	Diffusion coefficient D ($cm^2\ s^{-1}$)	
			For i_{pc}	For i_{pa}
1	0.0738	0.0276	7.2×10^{-10}	1.01×10^{-10}
	0.7565	0.1476	7.57×10^{-8}	2.88×10^{-9}
2	0.0646	0.026	5.52×10^{-10}	8.94×10^{-11}
	0.4794	0.0738	3.04×10^{-8}	7.2×10^{-10}
3	0.0369	0.0185	1.8×10^{-10}	4.53×10^{-11}
	0.2397	0.073	7.6×10^{-9}	7.05×10^{-10}
4	0.0026	0.0006	8.94×10^{-13}	4.76×10^{-14}
5	0.0025	0.0005	8.26×10^{-13}	3.31×10^{-14}
6	0.0023	0.00045	7×10^{-13}	2.68×10^{-14}
7	0.0017	0.0004	3.82×10^{-13}	2.12×10^{-14}
8	0.0014	0.00034	2.59×10^{-13}	1.53×10^{-14}
9	0.0011	0.0003	1.6×10^{-13}	1.19×10^{-14}
10	0.0007	0.00028	6.48×10^{-14}	1.04×10^{-14}

Fig. 5A and 5B displays the CV of V-Ce mixed oxide thin films in molar ratio of 1:2 and prepared in 150W RF power. It also resembles that of the $CeVO_4$ thin films with prominent two electrochemically active regions ranging from 1.6V to -0.38V and -0.38V to -1.6V. The first region has one reduction and the corresponding oxidation peaks at -0.06V and 0.94V respectively which are due to the redox reaction of V^{5+} states in the vanadium atoms present in the prepared thin films. The lower potential region possess one reduction peak at -0.83V and the corresponding oxidation peak at -0.56V. The sharp reduction and oxidation peaks and the consistent charge intercalation inside the thin films even after 10th cycling imply that these thin films hold better electrochemical properties than thin films prepared at 100W RF power. This may be due to the formation of more $CeVO_4$ phases with channel like structure thereby helping the H^+ ions for easy insertion and de-insertion. The diffusion co-efficient of H^+ ion during intercalation and de-intercalation process is listed out in Table 5.

During the cycling process for 10 times, the value of diffusion co-efficient decreases as 2.05×10^{-9} $cm^2\ s^{-1}$ to 1.07×10^{-13} $cm^2\ s^{-1}$ in the intercalation process. The prolonged improvement in the cycling stability of these thin films states that these thin films exhibit better electrochemical properties than the previous one. The decrease in the corresponding diffusion co-efficient value is from 5.55×10^{-10} $cm^2\ s^{-1}$ to 1.07×10^{-13} $cm^2\ s^{-1}$ during de-intercalation process and the overall high diffusion co-efficient values of these samples prepared at high RF power than those prepared at 100W RF power implies that the high RF power during deposition helps to grow channel like structure of $CeVO_4$ in the thin film.

Table 5. The electrochemical parameters of V-Ce mixed oxide thin films (molar ratio 1:2; 150W RF power).

No. of cycles	Cathodic peak i_{pc} (mA)	Anodic peak i_{pa} (mA)	Diffusion coefficient D ($cm^2\ s^{-1}$)	
			For i_{pc}	For i_{pa}
1	0.0199 0.1246	0.0066 0.0648	5.24×10^{-11} 2.05×10^{-9}	5.76×10^{-12} 5.55×10^{-10}
2	0.005 0.0748	0.0033 0.0482	3.31×10^{-12} 7.4×10^{-10}	1.44×10^{-12} 3.07×10^{-10}
3	0.0382	0.0298	1.93×10^{-10}	1.17×10^{-10}
4	0.0329	0.0275	1.43×10^{-10}	1×10^{-10}
5	0.0295	0.0255	1.15×10^{-10}	8.6×10^{-11}
6	0.0245	0.0218	7.94×10^{-11}	6.28×10^{-11}
7	0.0217	0.0204	6.23×10^{-11}	5.5×10^{-11}
8	0.0182	0.0169	4.38×10^{-11}	3.78×10^{-11}
9	0.0126	0.014	2.1×10^{-11}	2.59×10^{-11}
10	0.0077	0.0009	1.07×10^{-13}	1.07×10^{-13}

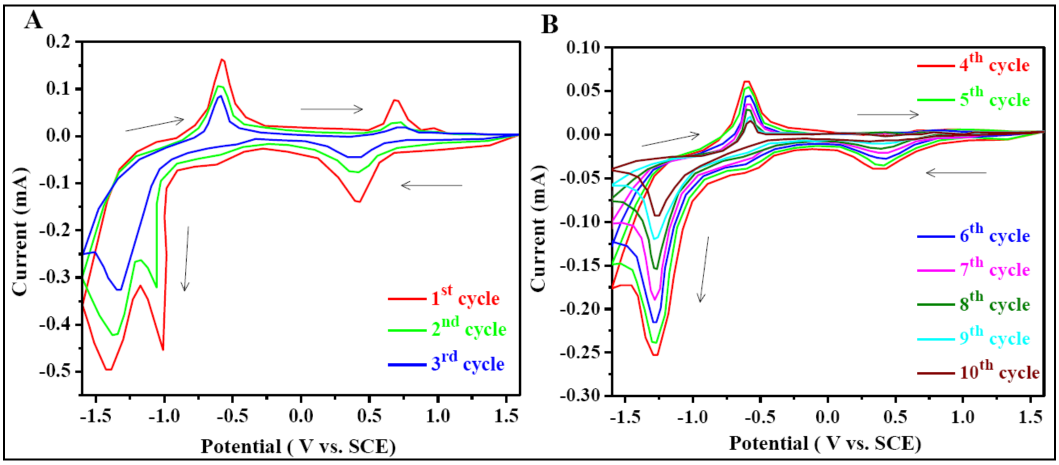

Figure 6. Cyclic voltammograms of V-Ce mixed oxide thin films (molar ratio 1:2; 200W deposition power) in **(A)** initial 3 cycles and **(B)** remaining 7 cycles.

The CV of V-Ce mixed oxide thin films in molar ratio of 1:2 and prepared in 200W RF power is shown in Fig. 6A and 6B. The prominent two electrochemically active regions separated by an inactive region are clearly visible in these high charge insertion and de-insertion process. The first electrochemically active region contains a reduction peak at 0.42V and the respective oxidation peak at 0.7V. In these thin films, this reduction peak is prominent which is due to the presence of more V^{5+} states than V^{4+} states in vanadium. The second region possess a sharp reduction peak centered at -1V and one oxidation peak corresponding to it at -0.56V. The reduction peak is due to the reduction of V^{4+} to V^{3+} and also in this case, the remaining V^{5+} to V^{4+} and then into V^{3+} state. The charge intercalation and de-intercalation continues effectively even upto the 10th cycle when compared to the previous cases with good cycling stability. The first oxidation peak is absent after 3rd cycle which states that the oxidation of V^{4+} into V^{5+} is limited and it is expectable as in a fully intercalated oxides, the oxidation states should be V^{3+} and Ce^{3+} states.

Table 6. The electrochemical parameters of V-Ce mixed oxide thin films (molar ratio 1:2; 200W RF power).

No. of cycles	Cathodic peak i_{pc} (mA)	Anodic peak i_{pa} (mA)	Diffusion coefficient D (cm^2 s^{-1})	
			For i_{pc}	For i_{pa}
1	0.0532	0.0385	3.74 x 10^{-10}	1.96 x 10^{-10}
	0.4378	0.0738	2.53 x 10^{-8}	7.2 x 10^{-10}
2	0.0259	0.0104	8.87 x 10^{-11}	1.43 x 10^{-11}
	0.2015	0.0594	5.37 x 10^{-9}	4.67 x 10^{-10}
3	0.017	0.0088	3.82 x 10^{-11}	1.02 x 10^{-11}
	0.1351	0.0554	2.41 x 10^{-9}	4.06 x 10^{-10}
4	0.015		2.98 x 10^{-11}	
	0.0782	0.0296	8.09 x 10^{-10}	1.16 x 10^{-10}
5	0.012		1.9 x 10^{-11}	
	0.0606	0.0251	4.86 x 10^{-10}	8.33 x 10^{-11}
6	0.0133		2.34 x 10^{-11}	
	0.069	0.0237	6.3 x 10^{-10}	7.43 x 10^{-11}
7	0.0107		1.51 x 10^{-11}	
	0.0528	0.0266	3.69 x 10^{-10}	9.36 x 10^{-11}
8	0.0076		7.64 x 10^{-12}	
	0.0398	0.0221	2.09 x 10^{-10}	6.46 x 10^{-11}
9	0.031	0.0118	1.27 x 10^{-10}	1.84 x 10^{-11}
10	0.0177	0.0103	4.14 x 10^{-11}	1.4 x 10^{-11}

The diffusion co-efficient of H^+ ion corresponding to the intercalation and de-intercalation process is given in Table 6. During the cycling process for 10 times, the value of diffusion co-efficient decreases as 2.53 x 10^{-8} cm^2 s^{-1} to 4.14 x 10^{-11} cm^2 s^{-1} in the intercalation process and the corresponding values for the de-intercalation process decrease as 7.2 x 10^{-10} cm^2 s^{-1} to 1.4 x 10^{-11} cm^2 s^{-1} which shows that the charge capacity as well as the stability even after 10 cycles is better than the previous samples. Thus the necessary electrochromic properties of the thin films are enhanced in thin films prepared at 200W RF power.

3.2 Optical properties

The in-situ optical transmittance characteristics of the V-Ce mixed oxide thin films prepared in molar ratio of 1:1 and deposited at 150W RF power in the wavelength range of 250nm to 900nm were measured with the help of UV-Vis-NIR spectrophotometer for all 10 cycles in the voltage range of -1.6V to +1.6V. The transmittance spectra during the first redox process of the sample are displayed in Fig. 7A and 7B. Charge intercalation leads to a decrease in transmittance over the whole visible range and the colour of the thin film has been changed from yellowish to grey. Irena Kozjek Skofic et.al.

reported the same change in colour of mixed oxide thin films prepared by sol-gel dip coating technique during charge intercalation[18]. The transmittance value of the as-deposited thin film in the visible region at 600nm is 96% and it has been reduced to 94.3% when intercalation begins for the first cycling. It has been reduced to 58% after completion of H^+ insertion. The high cathodic reduction in the visible region proves that in these thin films prepared at low RF power, the polaron absorption is high as the presence of CeO_8 dodecahedra which helped to separate the electrochemically active V_4^{-3} units is less due to the amorphous nature of these thin films. The V-Ce mixed oxide thin films prepared by U. Opara Krasovec et.al. in sol-gel route combined with the dip coating technique with Ce/V = 1:2 exhibited phases of tetragonal $CeVO_4$-W and vanadium in XRD patterns. The CV of these thin films also resembled that of tetragonal $CeVO_4$-W thin films and the presence of CeO_8 dodecahedra in those crystalline thin films helped to separate the electrochemically active V_4^{-3} units and so they observed a very low cathodic coloration which is not above 2%[17].

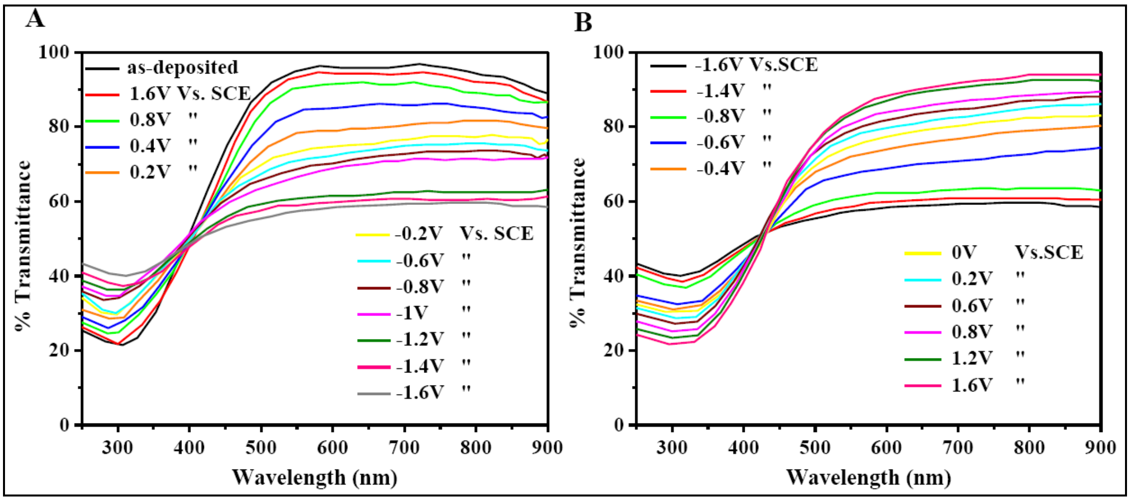

Figure 7. In-situ UV-Vis spectroelectrochemical response of V-Ce mixed oxide thin films (molar ratio 1:1; 150W deposition power) during first cycling at **(A)** H^+ ion insertion and **(B)** H^+ ion de-insertion.

By H^+ intercalation, the film transparency improves at lower wavelength and thus the film exhibits both anodic as well as cathodic coloration. F. Varsano et.al. prepared V-Ce mixed oxide thin films with Ce/V (1:2) target by reactive sputtering and they also observed the anodic-cathodic mixed behavior with respect to Li^+ ion intercalation[16]. The blue shift observed in the fundamental absorption edge due to the H^+ ion insertion is due to the anodic electrochromism and after de-insertion of H^+ ions, this edge does not regain its original as-deposited path which states that some of the H^+ ions are trapped inside the electrochromic thin films. The same result was stated by Z. Crnjak Orel et.al. for V-Ce mixed oxide thin films prepared with 55 at% and 38 at% of V which underwent Li^+ ion insertion[7]. E. Masetti et.al. studied the electrochromic properties of V-Ce mixed oxide thin films (molar ratio = 1:1) prepared under high oxygen pressure (P_{O2}/P_{Ar} = 1/6) in reactive sputtering and they also exhibited a shift in absorption edge towards UV region for Li insertion. Upto 10 cycles of charge insertion/ de-insertion, the irreversibility of inserted Li ions affected the optical properties of their thin films such as refractive index and extinction co-efficient[1]. The transmittance of the bleached thin films at the end of the first cycle of insertion and de-insertion is 88.5%. When cycling increases, the anodic electrochromism diminishes compared to the cathodic electrochromism seen in the visible region (not shown). The colour of the thin films after de-insertion is pale yellow. At the end of 10 cycles of intercalation and de-intercalation process, the average transmittance of the mixed oxide thin films is recorded as 59.4%.

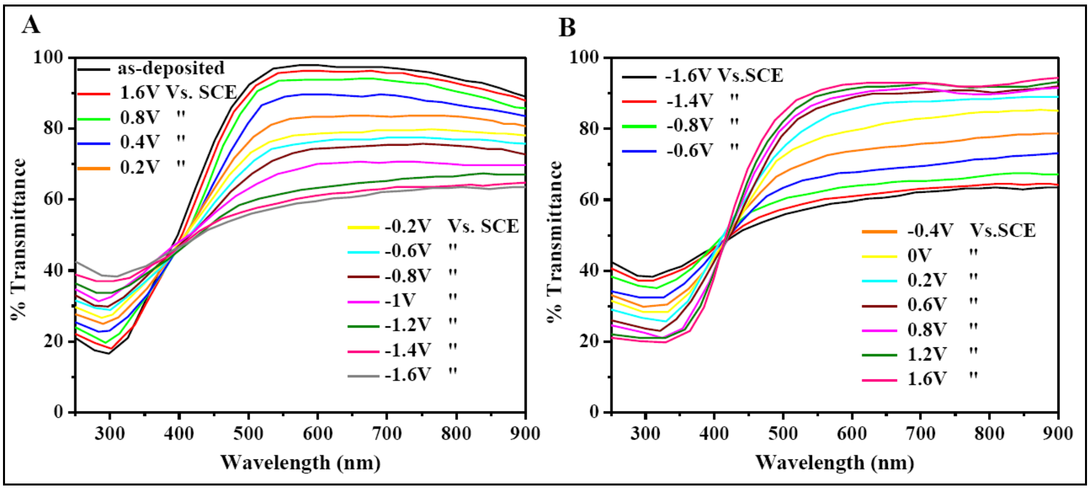

Figure 8. In-situ UV-Vis spectroelectrochemical response of V-Ce mixed oxide thin films (molar ratio 1:1; 200W deposition power) during first cycling at **(A)** H^+ ion insertion and **(B)** H^+ ion de-insertion.

The transmittance spectra of thin films prepared in molar ratio of 1:1 and deposited at 200W RF power during the first redox process are displayed in Fig. 8A and 8B. The color of the thin film changes from yellow to grey during intercalation. The cathodic electrochromism has been observed in the whole visible region of the spectra with decrease in transmittance by charge intercalation. In the first cycle of insertion, the transmittance value of the as-deposited thin film in the visible region at 600nm is 97.9% and during the starting of insertion of H^+ ions, it has been reduced to 96.4%. It has been reduced to 59.5% at the end of full H^+ insertion. Thus the intercalated transmittance is slightly improved by 1.5% for these thin films than the previous one. The decrease in transmittance at $\lambda >$ 450nm during H^+ ion intercalation is due to the polaron absorption[19]. Thin films show anodic electrochromism at low wavelength region ie $\lambda <$ 400nm by exhibiting an increase in the transmission and this increase in transmittance is attributed to the bandgap widening, a phenomenon shown by vanadium oxides during intercalation[17,19,20]. Thus the thin film exhibits both anodic as well as cathodic electrochromism. After the first cycle of redox process, the transmittance of the bleached thin films is 92.5% which is also higher than the thin films prepared at low RF power. When cycling increases, the cathodic coloration dominates the invisible anodic coloration occurring in the UV region. The de-inserted thin films are pale yellow in color. The average transmittance of the mixed oxide thin films is recorded as 67.9% after 10 cycles of intercalation and de-intercalation. This value is 8.5% higher than that obtained for thin films prepared at low RF power. The overall results indicate that the mixed oxide thin films prepared at high RF power exhibits good optical stability when subjected to redox process than those prepared at low RF power which may be due to the growth of $CeVO_4$ phase in the prepared thin films with increase in RF power as the channel like structure of $CeVO_4$ phase improves the mobility of H^+ ions and e^- easily inside the prepared thin films.

The transmittance spectra thin films prepared in molar ratio of 1:2 and deposited at 100W RF power for the first cycle are displayed in Fig. 9A and 9B. Similar to the thin films prepared in molar ratio of 1:1, these thin films exhibit both cathodic and anodic electrochromism during H^+ ion insertion[17]. The cathodic electrochromism is observed in the whole visible region of the spectra with decrease in transmittance by charge intercalation. The transmittance of the as-deposited thin films is 91.4% and at the beginning of charge insertion, the transmittance value is 90.6%. When the first cycle of insertion is over, the transmittance has been reduced to 37.1% which states that the mixed oxide thin films prepared at low RF power show high coloration during initial intercalation of charge. Anodic coloration is observed at lower wavelength region which may be due to the bandgap widening, a phenomenon exhibited by vanadium oxides during H^+ ion intercalation. Also the fundamental absorption edge suffers a blue shift with H^+ ion intercalation. This anodic electrochromism is rapidly decreasing even in the earlier cycles itself and the absorption edge moves back towards the longer wavelength region during ion de-intercalation process.

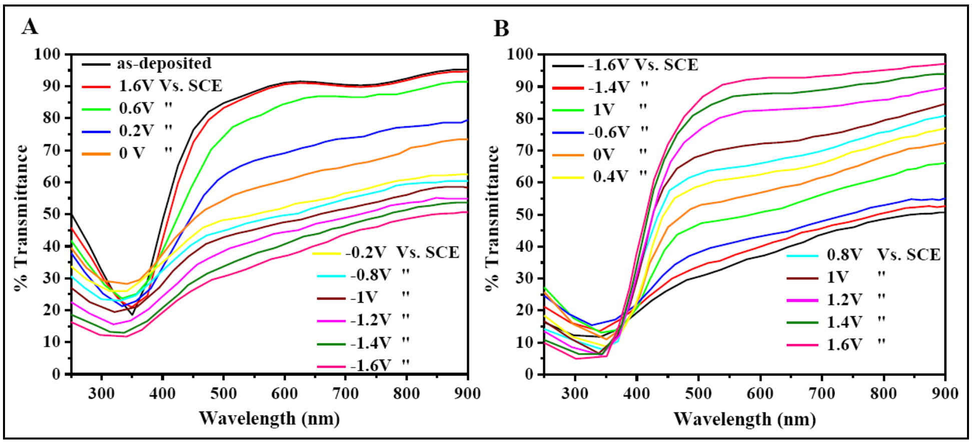

Figure 9. In-situ UV-Vis spectroelectrochemical response of V-Ce mixed oxide thin films (molar ratio 1:2; 100W deposition power) during first cycling at **(A)** H^+ ion insertion and **(B)** H^+ ion de-insertion.

After the first cycle of redox process, the transmittance of the bleached thin films is closer to that of the as-deposited thin films. Also this is the highest transmittance value of the bleached thin films when compared with those of thin films in molar ratio of 1:1. The color of the de-intercalated thin films is pale yellow and the average transmittance of the mixed oxide thin films is recorded as 76.7% after 10 cycles of intercalation and de-intercalation. This value is also 8.8% higher than that obtained for thin films in molar ratio of 1:1 prepared at 200W RF power. Z. Crnjak Orel et.al. also reported a 5% increase in the transmittance of V-Ce mixed oxide thin films having 38 at% of V than those having 55 at% of V prepared by sol-gel technique[7]. Also an increase in transmittance with increase in the content of CeO_2 in the prepared V-Ce mixed oxide thin films (71 at%, 55 at%, 38 at% and 32 at% of V) were observed by Z. Crnjak Orel [21]. Thus these mixed oxide thin films prepared in molar ratio of 1:2 behave as better optically passive working electrodes in ECD than those prepared in molar ratio of 1:1 because of the presence of more CeO_2 during preparation which is an optically passive element.

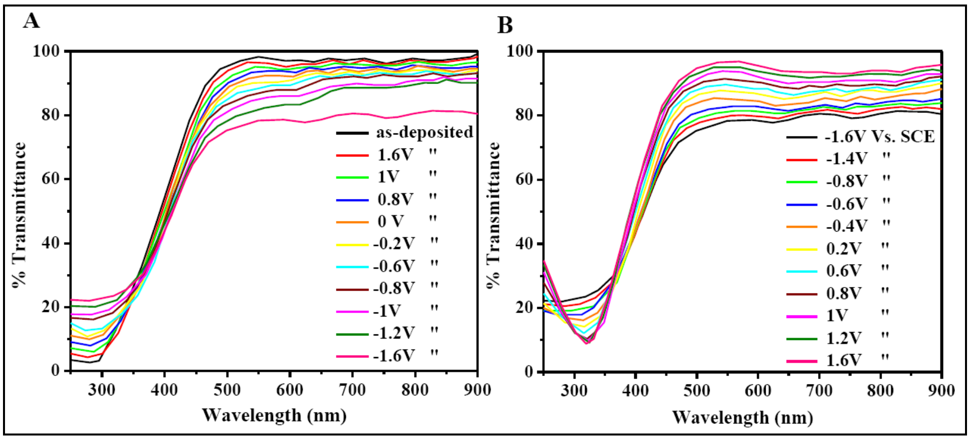

Figure 10. In-situ UV-Vis spectroelectrochemical response of V-Ce mixed oxide thin films (molar ratio 1:2; 150W deposition power) during first cycling at **(A)** H^+ ion insertion and **(B)** H^+ ion de-insertion.

Fig. 10A and 10B display the transmittance spectra of the V-Ce mixed oxide thin films prepared in molar ratio of 1:2 and deposited at 150W RF power for the first redox cycle. These thin films also exhibit both cathodic and anodic electrochromism during H^+ ion insertion. The transmittance of the as-deposited thin films is 97% and it has been reduced slightly to 95.5% when H^+ ion intercalation begins. After the first cycle of insertion is over, the transmittance has been reduced to 78.6% and this high value of transmittance after full insertion of H^+ ion in the 1st cycle is an indication of the optically passive nature of the thin films prepared at high RF power. After the first cycle of redox process, the transmittance of the bleached thin films is 95.3% and this high transparency after H^+ ion de-insertion makes these thin films suitable as passive working electrodes in ECD. The color of the de-intercalated thin films is pale yellow. The average transmittance of the mixed oxide thin films is recorded as 85.5% after 10 cycles of intercalation and de-intercalation which is 8.8% higher than those prepared at 100W RF power. The transmittance spectra of thin films prepared in molar ratio of 1:2 and deposited at 200W RF power for the first redox cycle are displayed in Fig. 11A and 11B. The color of the as-deposited thin films has been changed from yellow to grey when H^+ ions are intercalated. These thin films too exhibit both cathodic and anodic electrochromism during H^+ ion intercalation. The anodic electrochromism exhibited by these thin films is comparatively higher than all other samples and this may be due to the high bandgap widening which depends on the V/Ce molar ratio as well as the deposition parameter such as RF power. The dependence of certain optical parameters of the mixed oxide thin films prepared with high oxygen pressure (Ce/V = 1/6) such as extinction co-efficient and refractive index with respect to the amount of Li intercalation has been studied by E. Masetti et.al. and they observed an increase in the the optical bandgap and thereby an anodic coloration with increase in the amount of Li insertion[1]. The transmittance of the as-deposited thin films is high and is 97.3% which reduces to 95.1% when H^+ ion intercalation begins in the 1st cycle.

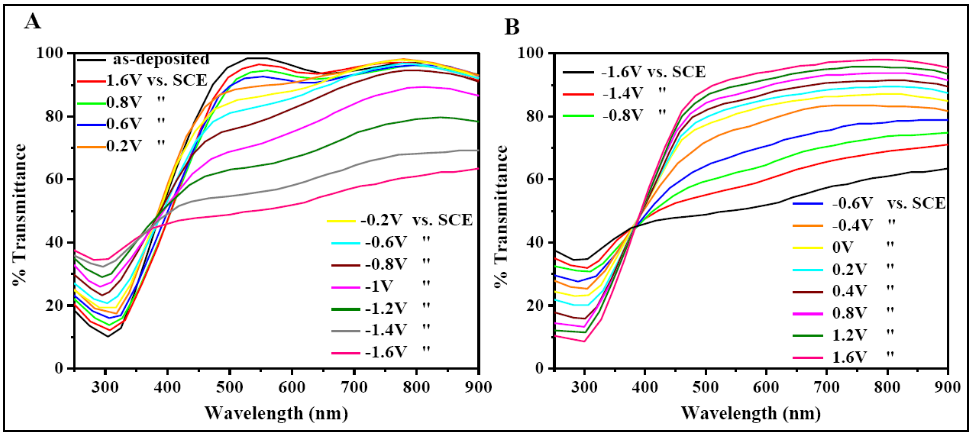

Figure 11. In-situ UV-Vis spectroelectrochemical response of V-Ce mixed oxide thin films (molar ratio1:2; 200W deposition power) during first cycling at **(A)** H^+ ion insertion and **(B)** H^+ ion de-insertion.

At the end of the 1st intercalation of H^+ ions inside the sample, the transmittance has been reduced to 52.3% . This implies that high charge insertion is allowed over the structure of the prepared mixed oxide thin films. A blue shift has been exhibited by the fundamental absorption edge with H^+ ion intercalation and it moves back towards the longer wavelength region during ion de-intercalation process. The de-inserted thin films do not retain the original transmittance value and this is due to the permanent insertion of H^+ ions inside the sample. The transmittance of the bleached thin films after the first cycle of redox process is 94.2% and this high transparency after H^+ ion insertion along with the good ion storage capacity makes these thin films suitable as passive working electrodes in ECD. The color of the de-intercalated thin films is pale yellow. After 10 cycles of intercalation and de-intercalation, the average transmittance value of the mixed oxide thin films is recorded as 88.6% which is 3.1% higher than those prepared at 150W RF power. When RF power during deposition is increased, more $CeVO_4$ phase with channel like structure grows in the prepared thin films and this is the reason for the above mentioned characters of these thin films as the channel like structure of $CeVO_4$ improves the mobility of the intercalated H^+ ions and e^-s.

4. CONCLUSIONS

In this paper, we have focused on the cyclic voltammetry and insitu transmittance characteristics of the V-Ce mixed oxide thin films deposited by varying RF power in non reactive RF magnetron sputtering. The presence of $CeVO_4$ in the prepared thin films with the channel structure helps to improve the charge insertion and it is enhanced in thin films prepared at high RF power. The high transmittance after H^+ ion de-insertion along with the good ion storage capacity makes thin films prepared in molar ratio of 1:2 more suitable as passive working electrodes in ECD than those prepared in molar ratio of 1:1 and the reason may be the presence of more CeO_2 during preparation which is an optically passive element.

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