Color switching in $V_3O_7 \times H_2O$ films cycled in Li and Na based electrolytes: novel vanadium oxide based electrochromic materials

Issam Mjejri, Aline Rougier

► To cite this version:

Issam Mjejri, Aline Rougier. Color switching in $V_3O_7 \times H_2O$ films cycled in Li and Na based electrolytes: novel vanadium oxide based electrochromic materials. *Journal of Materials Chemistry C*, 2020, 8 (11), pp.3631-3638. 10.1039/C9TC06753A . hal-02561412

HAL Id: hal-02561412

<https://hal.science/hal-02561412>

Submitted on 5 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

ARTICLE

Color Switch in $V_3O_7 \cdot H_2O$ cycled in Li and Na based electrolytes: novel vanadium oxide based electrochromic material

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Issam MJEJRI and Aline ROUGIER*

Vanadium oxides exhibiting various V/O stoichiometries, are considered as ones of the most promising chromogenic materials for energy purposes. Commonly addressed are the thermochromic properties of VO_2 and the electrochromic ones of V_2O_5 . In this work, we report a robust synthetic methodology that provides access to stoichiometry-control of the final powder. Namely, the hydrothermal route is used to synthesize the pure vanadium oxyhydroxide with mixed valence state (V^{5+} and V^{4+}) of $V_3O_7 \cdot H_2O$ ($H_2V_3O_8$) formula. Upon synthesis of the powder, the influence of the reducing agent on structure, morphology and crystallite sized is investigated. The electrochromic properties of the doctor bladed $V_3O_7 \cdot H_2O$ thick film ($\approx 1.2 \mu m$) in Li- and Na-based electrolytes, show in both cases a good reversibility and nice color switch in between reduced and oxidized states. Preliminary investigations of the EC mechanism allow to identify faradaic and capacitive contributions for this oxide showing switching times of only few seconds.

I. Introduction

Owing to the increasing demand of our connected society for electronic devices with multicolor switch, chromogenic materials, able to adapt their optical properties to an external stimulus, have received increasing attention in recent years.¹⁻⁵ Among the various stimuli, electrochromism, corresponding to reversible optical changes under applied voltage, appears nicely suitable for answering a wide range of demands requiring controlled by the external user.⁶⁻⁸ Nowadays numerous electrochromic applications including protective sunglasses, smart windows, reflective displays, anti-glare mirrors, and adaptive camouflage for the military assets, etc have entered our daily life.⁹⁻¹² From materials points of view, among inorganic electrochromic materials transition metal oxides (WO_3 , MoO_3 , TiO_2 , IrO_2 , V_2O_5 , NiO)¹³ have been extensively studied since the discovery by Deb in the late sixties of the color switch of evaporated WO_3 layers.¹⁴ Till today, tungsten trioxide remains the center part of most of the applications; as a consequence the range of available colors and brightness are limited. In recent years, in our group, we have been particularly investigated the multichromism of vanadium oxides allowing to reach colors unachievable with the other well-known EC oxides.¹⁵⁻¹⁷ The vanadium element exists in several oxidation states, namely V^{3+} , V^{4+} , and V^{5+} leading to numerous phases of which stoichiometry may be difficult to control.¹⁸ The most stable one, V_2O_5 , has been reported for its excellent performance in the battery field thanks in particular to its layered structure.^{19,20} VO_2

is a well-known thermochromic material of high interest as it exhibits a transition temperature not too far from RT (namely $T_c = 68^\circ C$) associated with a structural transition from a monoclinic to a rutile phase.^{21,22} Nevertheless, the stabilization of the monoclinic low temperature phase is still a challenge for the synthesis community. Next to single valence oxides, mixed valence oxides usually offer enhanced performances linked for instance to higher electronic conductivity.²³ For example, $V_3O_7 \cdot H_2O$ with mixed valence (V^{5+}/V^{4+}) has been investigated for novel material in lithium ion batteries and super capacitors.^{24,25} The synthesis of $V_3O_7 \cdot H_2O$ was first reported by Théobald and Cabala using the hydrothermal route²⁶ and the structural model was first described by Oka et al.²⁷ If $V_3O_7 \cdot H_2O$ is one of the most attractive vanadium oxide hydrates due to its potential application in various fields it is known that the electrochemical performance of this oxide depends on the synthesis process and the morphology. Indeed, the synthesis of 1D nanostructure is more prone to charge transport than the bulk crystalline structures. Up to now, the various applications appear no to take advantage of another property of this vanadium oxide that is its potential to modify its color. In 2019, Cristopher et al. reported the EC properties of the non-hydrated phase from V_3O_7 thin films deposited by spray pyrolysis aiming at smart windows application.²⁸ Herein, the electrochromic properties of the oxyhydroxide $V_3O_7 \cdot H_2O$ are investigated. In addition, we introduce a facile strategy that lead to synthesize $V_3O_7 \cdot H_2O$ nanobelts by using V_2O_5 as vanadium source and 4-aminophenol which acts as a reducing and structure directing agent. The effect of the molar ratio on the structural and morphological properties of the final oxyhydroxide is particularly discussed.

This paper is structured as follows: the hydrothermal synthesis of the hydrated vanadium oxide with mixed valence is first explored and then the pure powders are characterized by different physico-chemical techniques. Finally, the electrochromic performance of the

CNRS, ICMCB-UMR 5026, F-33600 Pessac Université de Bordeaux, ICMCB-UMR 5026, F-33600 Pessac, France..

*corresponding author : aline.rougier@icmcb.cnrs.fr

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

$V_3O_7 \cdot H_2O$ in lithium and sodium based ionic liquid electrolytes are presented and preliminary mechanism is introduced.

II. Experimental part

2.1. Hydrothermal Synthesis of $V_3O_7 \cdot H_2O$ Powder and Characterization.

All the chemical reagents were purchased from Acros Organics and used without further purification. Vanadium oxide (V_2O_5) was used as vanadium source and 4-aminophenol as template. In a typical synthesis, V_2O_5 (0.166 g), $H_2NC_6H_4OH$ (0.05 g) and distilled water (5 mL) were mixed. Reactants were introduced in this order and stirred few minutes before introducing the resulting suspension in a Teflon-lined steel autoclave and the temperature set at 180°C for 48 hrs (Figure 1). The pH of the solution remained close to pH=7 during the whole synthesis. The obtained green powder was washed with acetone to remove organic residues then dried at 80°C to lead to a green powder, which suggests that V^{5+} ions have been partially reduced to V^{4+} through the decomposition of the organic compound (Figure 1). The powder structure was characterized by X-ray diffraction analysis on a X'Pert Pro Panalytical diffractometer with $\text{CuK}\alpha$ radiation ($k = 1.5418 \text{ \AA}$). The XRD measurements were carried out by applying a step scanning method (2h range from 5° to 55°), the scan rate was 0.017°s^{-1} and the step time was 1 s. Scanning electron microscopy (SEM) measurements were recorded on a JEOL JSM-840 (operating at 15 kV) microscope. X-ray photoelectron spectroscopy (XPS) experiments were performed using a Shimadzu ESCALAB at room temperature.

Fig. 1 Hydrothermal synthesis of the $V_3O_7 \cdot H_2O$ powders.

2.2. Film preparation and Characterization

$V_3O_7 \cdot H_2O$ films were deposited by the doctor blading method from homemade powder, synthesized by the hydrothermal process. First, 2.5 g of powder was dispersed into 5 mL of ethanol. The resulting dilute was stirred for 1 h at room temperature, and after, aliquots of the as-prepared colloidal $V_3O_7 \cdot H_2O$ solution were deposited on the ITO-coated ($\text{In}_2\text{O}_3:\text{Sn}$) glass (commercialized by SOLEM with a resistance of $30 \Omega \square^{-1}$). The thickness of the $V_3O_7 \cdot H_2O$ films, measured using a Dektak mechanical profilometer, was about $1180 \text{ nm} \pm 60 \text{ nm}$ and the active area was $2 \text{ cm} \times 1 \text{ cm}$. For the identification of the crystal phases of the films before cycling, X-ray diffraction (XRD, Philips PW 1820, PANalytical X'Pert instrument, 2θ range from 5° to 40° and $\text{Cu K}\alpha_{\lambda} = 0.154056 \text{ nm}$) was used. The morphology of the layers before cycling was investigated using a JEOL JSM-840 (operating at 15 kV) microscope.

2.3. Electrochromic Measurements

Electrochemical measurements were carried out in a three-electrode cell configuration using a Bio Logic SP50 potentiostat/galvanostat apparatus and $V_3O_7 \cdot H_2O$ films on ITO/glass as working electrodes. The counter electrode and reference electrode consisted of a platinum foil and saturated calomel electrode (SCE; $E_{\text{SCE}} = 0.234 \text{ V/ENH}$), respectively. The operating voltage was controlled between -1.2 V and $+1.9 \text{ V}$ at 20 mV/s in both lithium- and sodium-based electrolytes, namely, 0.3 M lithium bis-trifluoromethanesulfonimide (LiTFSI, Solvionic, purity >99.99%) in 1-Etyl-3-methylimidazolium bis (trifluoromethane-sulfonyl)-imide (EMITFSI) and sodium bis-trifluoromethanesulfonimide (NaTFSI, Solvionic, purity >99.99%) in 1-Etyl-3-methylimidazolium bis (trifluoromethane-sulfonyl)-imide (EMITFSI). The chronoamperometric cycles of the $V_3O_7 \cdot H_2O/\text{LiTFSI-EMITFSI/Pt}$ were performed at $-1.2\text{V}/60\text{s}$ and $1.9\text{V}/60\text{s}$. All the electrochemical measurements were carried out at room temperature. The diffuse reflectance of $V_3O_7 \cdot H_2O$ films, recorded *ex situ* after application of various potentials, was measured using a Varian Cary 5000 UV-vis-NIR spectrophotometer.

III. Results and Discussion

III.1. $V_3O_7 \cdot H_2O$ powders

The phase and composition of the resulting products synthesized at (180°C , 48 hrs) for different molar ratios (R) of 4-aminophenol to V_2O_5 (a) 1:1, (b) 0.9:1, 0.7:1 (c), 0.5:1 (d), 0.4:1 (e), 0.3:1 (f), 0.2:1 (g), 0.1:1 (h) and 0.05:1 (i), were determined by X-ray powder diffraction (XRD) (Figure 2). The crystalline phases for vanadium oxides are discriminatory at different molar ratios. For the molar ratios $R = 1:1$, $R = 0.9:1$, $R = 0.7:1$, $R = 0.5:1$ and $R = 0.4:1$, the XRD patterns reveal the presence of very intense peaks characteristic of the $\text{VO}_2(\text{B})$ (JCPDS#81-2392) crystalline phase. For a molar ratio equal to 0.3:1, the XRD pattern highlights the presence of the VO_2 phase with some characteristic peaks of the hydrated phase $V_3O_7 \cdot H_2O$. However, for the $R = 0.2:1$, $R = 0.1:1$, $R = 0.05:1$ ratio, the characteristic peaks of VO_2 fully disappear and all diffraction peaks are identified to the orthorhombic crystalline phase $V_3O_7 \cdot H_2O$ (space group: Pnam) (JCPDS#85 2401). No peaks of any other phases or impurities are detected. Based on the XRD results, it can be concluded that the amount of reducing agent allows to control the vanadium valence state. Indeed, for $R = 1:1$, a VO_2 pure phase is synthesized while a decrease in the molar ratio to $R = 0.05:1$ leads to vanadium oxyhydroxide with mixed valence states.

The average crystallite size was calculated using the Scherrer's formula: ²⁹

$$L = 0.89\lambda / \beta \cos \theta \quad (\text{eq1})$$

Where L is the average crystallite size in nm, $\lambda = 0.154056 \text{ nm}$, β is the full width at the half maximum, and θ is the diffraction angle. The average crystallite size value of the different oxides synthesized at different molar ratio: (a) 1:1, (b) 0.9:1, 0.7:1 (c), 0.5:1 (d), 0.4:1 (e), 0.3:1 (f), 0.2:1 (g), 0.1:1 (h) and 0.05:1 (i), calculated from four of the main peaks of the XRD pattern, decreases from about 175 nm to 70 nm (Supporting information Table S1).

With the modulation of the R ratio, there is an evolution of the powder from black ($R = 1:1$) to greyish black ($R = 0.3:1$) and green ($R = 0.05$).

Fig. 2 XRD patterns of the samples synthesized at different molar ratio 4-aminophenol: V_2O_5 (a) 1:1, (b) 0.9:1, 0.7:1 (c), 0.5:1 (d), 0.4:1 (e), 0.3:1 (f), 0.2:1 (g), 0.1:1 (h) and 0.05:1 (i).

The morphology of the two pure phases VO_2 and $V_3O_7 \cdot H_2O$ synthesized with $R=1:1$ and $R=0.05:1$ respectively is shown in Figure 3. SEM images of the as-synthesized VO_2 (b) powder consist of uniform nanorods about 2–10 nm in length, 20–50 nm in width (Figure 3 a and b). For a molar ratio $R = 0.05:1$, the hydrated phase $V_3O_7 \cdot H_2O$ morphology (Figure 3 c and d) is homogenous with uniform belts of about 5–20 nm in length.

Fig. 3 SEM images of VO_2 (a, b) and $V_3O_7 \cdot H_2O$ powders (c, d).

In the following, we focus our attention on the $V_3O_7 \cdot H_2O$ phase. Figure 4 shows the core level XPS spectrum of $V_3O_7 \cdot H_2O$ as well as the fitted-curves of the $V2p_{3/2}$ peak. The $V2p_{3/2}$ peak is divided into two components with the one centered in higher binding energy ascribed to the higher oxidation state. In this study, the peak centered at 518.2 eV is attributed to the V^{5+} state, while the peak centered at 516.3 eV is for the V^{4+} oxidation state.^{28,30} The determination of the two proportions for the V^{5+}/V^{4+} ratio summarized in Table 1, is in favor of the V^{5+} ion in agreement with the $V_3O_7 \cdot H_2O$ formula.

Table 1. V^{5+} and V^{4+} Quantification Deduced from XPS Study (100% corresponds to the normalization of the strongest Contribution)

	$V^{5+}(\%)$	$V^{4+}(\%)$	V^{5+}/V^{4+}
$V_3O_7 \cdot H_2O$	100	70	1.42

Fig. 4 High-resolution XPS spectra of $V2p_{3/2}$ of the as-synthesized $V_3O_7 \cdot H_2O$ powder.

III.2. Structure and morphology of the $V_3O_7 \cdot H_2O$ film

The XRD pattern of the doctor bladed $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ film shows in first approximation similar features as the powder (Figures 5 and 1 (i)). Indeed, the d-spacing values of all diffraction peaks match the ones of the orthorhombic crystalline phase (JCPDS#85 2401). No major change in XRD peak position compared to $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ powders and no peaks of any other phase or impurity are detected after deposition on ITO substrate, demonstrating a good stability of $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ NPs synthesized by the hydrothermal method using these deposition conditions.

The SEM analysis of the $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ thick film (Figure 5b) shows that the doctor blading deposition leads to porous films of uniform particles with smooth surfaces being relatively dense.

Fig. 5 XRD patterns of the $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ films doctor bladed on ITO/glass substrate (a) and corresponding SEM images (b), film thickness is $1180 \text{ nm} \pm 60 \text{ nm}$.

III.3. Electrochromic properties of $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ films

III.3.1. Cycling at 10 mV/s in Li-based electrolyte

Figure 6 shows the electrochemical activity of the $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ thick films cycled in lithium-based ionic liquid. The CVs were recorded at 10 mV/s from 1st to 500th cycles at room temperature in the potential range of -1.2 to 1.9 V, in a three electrodes cell using ionic liquid based (0.3 M) LiTFSI in EMITFSI as a supporting electrolyte and Saturated Calomel Electrode as reference electrode (SCE). The CVs shapes consist of several peaks illustrating several redox reactions that could be associated in first approximation with Li^+ insertion-deinsertion process. The redox peak distribution appears different in between the cathodic and the anodic sweeps. Three well defined peaks located at 0.1 V, -0.1 V and -0.4 V are visible in reduction while broader peaks located at -0.1 V, 0.25 V and 0.35 V appear in oxidation. The multiple peaks present in Li^+ insertion/deinsertion process are attributed to the electrochemical redox reactions

involving V^{5+} to V^{4+} transformation. The CVs show a nice reversible behavior over 500 cycles with a slight increase of capacity of 2% after 500 cycles (Inset Figure 6). Upon cathodic and anodic sweeping, two-step electrochromism from green to blue to orange is highlighted (Figure 6b).

Fig. 6 The 5th (solid line) and the 500th (dash line) cyclic voltammograms for the $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ film cycled in LiTFSI in EMITFSI electrolyte with a 10 mV/s scan rate (a), charge capacity evolution with the number of cycles is presented in the inset. Visual appearance of $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ films in the reduced and oxidized states (b).

The diffuse reflectances in the range of 300–800 nm of the films in the as-deposited, reduced and oxidized states are presented in Figure 7. The $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ films switch reversibly between a reduced blue state (-1.2 V) and an oxidized orange state ($+1.9$ V) associated with reflectance values of less than 9% and of 38% at 590 nm, respectively, leading to an optical reflectance modulation, ΔR , of about 29%.

Fig. 7 *Ex situ* Diffuse reflectance spectra for the $V_3O_7 \cdot H_2O$ films cycled in Li-electrolyte/Pt vs SCE, in reduction at -1.2 V and re-oxidized at $+1.9$ V.

The response time is a key parameter of electrochromic behavior. Its determination was deduced from chronoamperometry measurements performed at -1.2 V and $+1.9$ V for 60 s. The CAs of the $V_3O_7 \cdot H_2O$ film show good reversibility, and fast switching time in between the redox processes. Both response times are in the same order, 4 s in oxidation and 5 s in reduction (Figure 8). Compared with the archetypal electrochromic material based vanadium oxide (V_2O_5) synthesized in our lab,¹⁷ it is found that V_2O_5 and $V_3O_7 \cdot H_2O$ are characterized by a distinguished multi-electrochromism but with a very fast kinetics in the case of $V_3O_7 \cdot H_2O$. For comparison, Tong et al,³¹ have synthesized a dense film based V_2O_5 with a switching time in oxidation and reduction of the order of 13.5 s and 13.1 s respectively. The fast kinetics observed in the vanadium hydrate film may be explained by the unique structure of $V_3O_7 \cdot H_2O$. Furthermore, $V_3O_7 \cdot H_2O$ contains mixed valences of V^{5+} and V^{4+} , which contributes to higher electronic conductivity and more active redox sites during the reduction and oxidation process.

Fig. 8 Chronoamperometric cycles of the $V_3O_7 \cdot H_2O$ /LiTFSI-EMITFSI/Pt vs SCE in the range -1.2 V/60s to 1.9 V/60s.

Another criteria of merit of the electrochromic materials and devices is the coloration efficiency, CE, which relates the change in optical density (OD) per unit charge density (Q). CE is calculated using the following formulas.³²

$$CE = \Delta OD / Q \quad (\text{eq 2})$$

Where $\Delta OD = \log(R_{ox}/R_{red})$, Q is the electronic charge injected into the electrochromic material per unit area, R_{red} is the reflectance in the reduced state, and R_{ox} is the reflectance in the oxidized state. The data from Figures 6 and 7 into eq 2 yields to a coloration efficiency of $24.4 \text{ cm}^2 \text{C}^{-1}$.

Such value may appear rather limited but it should be kept in mind that the goal of those systems are the color change and their further use in displays favouring the integration of opaque films.

III.3.2. Cycling at various scan rates in Li-based electrolyte

The CVs shape, based on several peaks triggers our attention on the involvement of more than one mechanism. To further investigate the process, films were cycled at various scan rates. As the scan rate increases from 2 to 50 mV/s (Figure S1), the cathodic and anodic peak currents simultaneously increase and the maximum of the peak positions move towards higher potentials. This trend illustrates a limited diffusion/insertion-extraction of the lithium ions into the material at high scan rates. Indeed, larger proportion of redox reactions occurring at the surface are expected with increase scan rates.

The complex CV shape raised the question of the existence of both capacitive and faradaic contributions and would the EC mechanism in $V_3O_7 \cdot H_2O$ better described as pseudo-capacitive, corresponding to a faradaic process involving surface or near surface redox reactions. The distinction between the faradaic and capacitive contributions in battery or electrochromic systems, has been recently discussed for different materials including TiO_2 , WO_3 and NiO .³³ Indeed, the current (i) at a fixed potential (V) can be quantitatively separated into

a diffusion contribution and a capacitive contribution as shown by the following equation:

$$i(V) = k_1 v + k_2 v^{1/2} \quad (\text{eq 3})$$

For analytical purposes, this equation is slightly rearranged to:

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2 \quad (\text{eq 4})$$

$k_1 v$ and $k_2 v^{1/2}$ correspond to the current contributions from the surface capacitive phenomena and the diffusion-controlled insertion process, respectively. Thus the determination of k_1 and k_2 , allows, at specific potentials, one to quantify the fraction of the current due to each of the two contributions. An increase in scan rate is associated with the disappearance of distinguishable peaks. For the scan rates of 2 and 50 mV/s, the curve $i = k_1 v = f(v)$, corresponding to the capacitive contribution and the black curve corresponding to the experimental curve are plotted $i(V) = k_1 v + k_2 v^{1/2} = f(v)$ (Figure 9). A large part of the current is attributed to surface phenomena even for a slow scan rate of 2 mV/s (Figure 9 a), usually favoring insertion phenomena. Indeed, at low scan rate the CV is illustrated by well-defined peaks. Figure 9e shows that at a scan rate of 50 mV/s the current is mainly associated with capacitive contribution.

Figure 9f displays the evolution of the capacitive and faradaic contributions of $V_3O_7 \cdot H_2O$ films as a function of the scan rate in Li based electrolyte. Up to 10 mV/s, the mechanism is dominated by the faradaic contribution that remains nevertheless below 60 % and quasi similar from 2 to 10 mV/s. This faradaic contribution could be schematized by the following equation:

The number of exchanged electrons (x) involved during each reduction/oxidized process was estimated using the following equation:

$$Q = F \cdot n_{(V_3O_7 \cdot H_2O)} \cdot x$$

Where Q is the electrochemical faradaic capacity, $F = 96500$ C, and n is number of moles. The x values calculated from $V_3O_7 \cdot H_2O$ thin films is about 2.1, this value is in agreement with earlier studies mostly dedicated to cycling of the $H_2V_3O_8$ oxide in lithium battery application.³⁴ A lithium insertion of 2.1 would correspond to a full reduction of the V^{5+} cations.

For scan rates over 10 mV/s, the current is in majority associated with a capacitive contribution as high as 70% for the 50 mV/s scan rate. The domination of the capacitive contributions for high scan was already observed in our group on anodically colored NiO thin films.³³

Fig. 9 Cyclic voltammograms of $V_3O_7 \cdot H_2O$ /LiTFSI-EMITFSI/Pt vs SCE as a function of the scan rate (a) 2 mV/s, (b) 5 mV/s, (c) 10 mV/s, (d) 20 mV/s and (e) 50 mV/s in a potential range -1.2V/1.9V. (f) Evolution of the capacitive and faradaic contributions of $V_3O_7 \cdot H_2O$ as function of the scan rate from 2 to 50 mV/s.

III.3.3. Cycling at 10 mV/s in Na-based electrolyte

Finally the effect of the cation size on the electrochromic properties of $V_3O_7 \cdot H_2O$ was investigated by comparing the EC behavior in a Li^+ -based electrolyte to the one in a Na^+ -containing electrolyte. The CVs of $V_3O_7 \cdot H_2O$ in Na based electrolyte in the -1 to +1.9 V range show a nice reversible behavior over 500 cycles (Figure 10) with however a loss of capacity of 8% after 500 cycles (inset Figure 10), illustrating a larger irreversibility than in Lithium based electrolyte (Figure 6). Besides, the smaller recorded capacity corresponds to color change of less intensity from orange to green while the more reduced state marked by a bluish color is barely reached.

Fig. 10 The 5th (solid line) and the 500th (dash line) cyclic voltammograms for the $V_3O_7 \cdot H_2O$ film cycled in NaTFSI in EMITFSI with a 10 mV/s scan rate (a), charge capacity evolution with the number of cycles is presented in the inset. Visual appearance of $V_3O_7 \cdot H_2O$ films in the reduced and oxidized states (b).

The reduced green state (-1V) and the oxidized orange state (+1.9V) are associated with reflectance values of R_{red} 8% and R_{ox} 18% at 590 nm (Figure 11), corresponding to reflectance modulation ΔR of 10%. In Na based electrolyte, the coloration efficiency calculated using eq.2 is $10.3 \text{ cm}^2\text{C}^{-1}$. This value remains lower than in the case of the Li based electrolyte for which we could assume a larger faradic contribution in agreement with larger cation size. Nevertheless further investigations are required as for NiO thin films, similar EC behavior was recorded independently of the cations in the electrolyte and even when cycling in electrolyte free of small cations (i.e. EMITFSI).

Fig. 11 Diffuse reflectance spectra for the $V_3O_7 \cdot H_2O$ films cycled *ex situ* in Na-electrolyte/Pt vs SCE, in reduction at -1 V and re-oxidized at +1.9 V.

IV. Conclusions

In respect of their multiple stoichiometries, vanadium oxides are of great interest for several applications in the field of energy and active displays. Herein, emphasizing the benefit of a simple synthesis method allowing a fine tuning of the stoichiometry, the mixed valence (V^{5+} and V^{4+}) $V_3O_7 \cdot H_2O$ phase was prepared. The electrochromic activity of thick opaque films, deposited by doctor blading, was associated with a reversible color modulation from orange to green/blue in both Na and Li electrolytes as a result of a combination of capacitive and faradic contributions. The demonstration of the EC property of the mixed valency vanadium oxide is a step forward in our investigation of the multi-electrochromism exhibited by the vanadium oxide family, aiming at addressing color modulation in displays applications.

Conflicts of interest

Notes The authors declare no competing financial interest.

Notes and references

1. K. Madasamy, D. Velayutham, V. Suryanarayanan, M. Kathiresan, K.-C. Ho, Viologen-based electrochromic materials and devices. *J. Mater. Chem. C*, 2019, 7, 4622-4637.
2. I. Mjejri, C. M. Doherty, M. Rubio-Martinez, G. L. Drisko, A. Rougier, Double-Sided Electrochromic Device Based on

- Metal–Organic Frameworks. *ACS Appl. Mater. Interfaces* 2017, 9, 39930–39934.
- 3 S. Hassab, D. E. Shen, A.M. Österholm, M. D. Rocha, G. Song, Y. Alesanco, A. Viñuales, A. Rougier, J. R. Reynolds, J. Padilla, A new standard method to calculate electrochromic switching time. *Sol. Energy Mater. Sol. Cells* 2018, 185, 54–60.
 - 4 C.W. Hu, Y. Yamada, K. Yoshimura, A. Takahashi, H. Watanabe, K. Tajima, T. Kawamoto, High contrast gaso-chromism of wet processable thin film with chromic and cata-lytic nanoparticles. *J. Mater. Chem. C*, 2018, 6, 4760–4764.
 - 5 C.G. Granqvist, P.C. Lansaker, N.R. Mlyuka, G.A. Niklasson, E., Avendano, Progress in chromogenics: New results for electrochromic and thermochromic materials and devices. *Sol. Energy Mater. Sol. Cells* 2009, 93, 2032–2039.
 - 6 A. A. Argun, P.H. Aubert, B. C. Thompson, I. Schwendeman, C.L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A.G. MacDiarmid, J.R. Reynolds, Multicolored Electrochromism in Polymers: Structures and Devices. *Chem. Mater.* 2004, 16, 4401–4412.
 - 7 A. Chaudhary, D. K. Pathak, S. Mishra, P. Yogi, P.R. Sagdeo, R. Kumar, Polythiophene -viologen bilayer for electro-trichromic device. *Sol. Energy Mater. Sol. Cells* 2018, 188, 249–254.
 - 8 Cai, G., Park, S., Cheng, X., Eh, A.L.-S., Lee, P.S. Inkjet-printed metal oxide nanoparticles on elastomer for strain-adaptive transmissive electrochromic energy storage systems, *Sc. and Tech. of Adv. Mater.* 2018, 19(1) 759–770.
 - 9 R. Tällberg, B. P. Jelle, R. Loonen, T. Gaoa, M. Hamdy, Comparison of the energy saving potential of adaptive and controllable smart windows: A state-of-the-art review and simulation studies of thermochromic, photochromic and electrochromic technologies. *Sol. Energy Mater. Sol. Cells* 2019, 200, 109828.
 - 10 K. Sauvet, L. Sauques, A. Rougier, IR electrochromic WO₃ thin films: From optimization to devices *Sol. Energy Mater. Sol. Cells* 2009, 93, 2045–2049.
 - 11 S. Koyuncu, F. B. Koyuncu, A new ITO-compatible side chain-functionalized multielectrochromic polymer for use in adaptive camouflage-like electrochromic devices. *Reactive and Functional Polymers* 2018, 131, 174–180.
 - 12 R. Brooke, E. Mittraka, S. Sardar, M. Sandberg, A. Sawatdee, M. Berggren, X. Crispin, M. P. Jonsson. Infrared electrochromic conducting polymer devices, *J. Mater. Chem. C*, 2017, 5, 5824–5830.
 - 13 Y. Ke, J. Chen, G. Lin, S. Wang, Y. Zhou, J. Yin, P. S. Lee, Y. Long, Smart Windows: Electro-, Thermo-, Mechano-, Photochromics, and Beyond, *Adv. Energy Mater.* 2019, 9, 1902066.
 - 14 S. K. Deb, Opportunities and challenges of electro-chromic phenomena in transition metal oxides. *Sol. Energy Mater. Sol. Cells* 1992, 25, 327–338.
 - 15 G. Salek, B. Bellanger, I. Mjejri, M. Gaudon, A. Rougier, Polyol synthesis of Ti-V₂O₅ nanoparticles and their use as electrochromic films. *Inorg. Chem.*, 2016, 55, 9838–9847.
 - 16 I. Mjejri, L. M. Mancieru, M. Gaudon, A. Rougier, F. Sediri, Nano-vanadium pentoxide films for electrochromic display. *Solid State Ionics* 2016, 292, 8–14.
 - 17 I. Mjejri, M. Gaudon, G. Song, C. Labrugère, A. Rougier, Crystallized V₂O₅ as Oxidized Phase for Unexpected Multicolor Electrochromism in V₂O₃ Thick Film. *ACS Appl. Energy Mater.* 2018, 1, 2721–2729.
 - 18 I. Mjejri, A. Rougier, M. Gaudon, Low-Cost and Facile Synthesis of the Vanadium Oxides V₂O₃, VO₂, and V₂O₅ and Their Magnetic, Thermochromic and Electrochromic Proper-ties. *Inorg. Chem.* 2017, 56, 1734–1741.
 - 19 L. Du, H. Lin, Z. Ma, Q. Wang, D. Li, Y. Shen, W. Zhang, K. Rui, J. Zhu, W. Huang, Using and recycling V₂O₅ as high performance anode materials for sustainable lithium ion battery. *J. Power Sources* 2019, 424, 158–164.
 - 20 H. Yang, G. Xu, X. Wei, J. Cao, L. Yang, P. K. Chu, Ultrafast hetero-assembly of monolithic interwoven V₂O₅ nanobelts/carbon nanotubes architectures for high-energy alkali-ion batteries. *J. Power Sources* 2018 395, 295–304.
 - 21 F. Xu, X. Cao, H. L. P. Jin, Recent advances in VO₂-based thermochromic composites for smart windows. *J.Mater. Chem. C*, 2018, 6, 1903–191.
 - 22 Q. Lu, C. Liu, N. Wang, S. Magdassi, D. Mandler, Y. Long, Periodic micro-patterned VO₂ thermochromic films by mesh printing. *J. Mater. Chem. C*, 2016, 4, 8385–8391.
 - 23 D. Wang, Q. Wei, J. Sheng, P. Hu, M. Yan, R. Sun, X. Xu, Q. An, L. Mai. Flexible additive free H₂V₃O₈ nanowire membrane cathode for sodium ion batteries. *Phys. Chem. Chem. Phys.*, 2016, 18, 12074–12079.
 - 24 M. Rastgoo-Deylami, M. S. Chae, S.T. Hong, H₂V₃O₈ as a High Energy Cathode Material for Nonaqueous Magnesium-Ion Batteries. *Chem. Mater.* 2018, 30, 7464–7472.
 - 25 H. Tang, N. Xu, C. Pei, F. Xiong, S. Tan, W. Luo, Q. An, L. Mai, H₂V₃O₈ Nanowires as High-Capacity Cathode Materials for Magnesium-Based Battery. *ACS Appl. Mater. Interfaces* 2017, 9, 28667–28673.
 - 26 F. Theobald, R. Cabala, Hydrate V₃O₇·H₂O. *C. Acad. Sci. C Chim.* 1970, 270, 2138.
 - 27 Y. Ka, T. Yao, N. Yamamoto, Structure determination of H₂V₃O₈ by powder X-ray diffraction. *J. Solid State Chem.* 1990, 89, 372–377.
 - 28 M. Cristopher, P. Karthick, R. Sivakumar, G. Gopalakrishnan, C. Sanjeeviraja, K. Jeyadheepan, On the preparation of Tri-vanadium hepta-oxide thin films for electrochromic applications, *Vacuum* 160 (2019) 238–245.
 - 29 A.W. Burton, K. Ong, T. Rea, I. Y. Chan, On the estimation of average crystallite size of zeolites from the Scherrer equation: A critical evaluation of its application to zeolites with one-dimensional pore systems. *Microporous and Mesoporous Materials* 2009, 117, 75–90.
 - 30 J. Swiatowska-Mrowiecka, V. Maurice, S. Zanna, L. Klein, P. Marcus, XPS study of Li ion intercalation in V₂O₅ thin films prepared by thermal oxidation of vanadium metal. *Electrochim. Acta* 2007, 52, 5644–5653.
 - 31 Z. Tong, J. Hao, K. Zhang, J. Zhao, B.L. Suc, Y. Li, Improved electrochromic performance and lithium diffusion coefficient in three-dimensionally ordered macroporous V₂O₅ films. *J. Mater. Chem. C*, 2014, 2, 3651–3658.
 - 32 Yan, C. Kang, W. Wang, J. Cui, M. Wang, X. Foo, C. Chee, K. J. Lee, P. S. Stretchable and Wearable Electro-chromic Devices. *ACS Nano*. 2014, 8, 316–322.
 - 33 M. Da Rocha, B. Dunn, A. Rougier, Faradaic and/or capacitive: Which contribution for electrochromism in NiO thin films cycled in various electrolytes? *Sol. Energy Mater. Sol. Cells* 2019, 201, 110114.
 - 34 J. Prado-Gonjal, B. Molero-Sánchez, D. Ávila-Brandé, E. Morán, J. C., Pérez-Flores, A. Kuhn, F. García-Alvarado, The intercalation chemistry of H₂V₃O₈ nanobelts synthesised by a green, fast and cost-effective procedure. *Journal of Power Sources* 2013, 232, 173–180.