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Preparation and properties of homogeneous V_2O_5–SiO_2 xerogel composite based on interpenetrating polymer network

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Abstract

In this paper, we report the conducting and electrochemical properties of a homogeneous V_2O_5–SiO_2 xerogel composite obtained from the simultaneous polymerization in both inorganic components (Si–O and V–O based polymers) forming an interpenetrating polymer network, where a mutual "solubility" due to cross-links and entanglements was observed. The presence of V_2O_5 inside the silica matrix has a strong effect on electrical conductivity; measurements showed room temperature conductivity almost 1000 times higher than what is found in the literature. In addition, the electrochemical behavior is quite similar to that found in V_2O_5 xerogel. Moreover, the effects of thermal treatment on the conducting and electrochemical properties were investigated. It was found that both properties were improved with no significant effect on V_2O_5 xerogel layered structure.
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1. Introduction

Oxide glasses containing transition metal oxide (TMO) have been the subject of increasing interest mainly due to the semiconducting properties that arise from electron hopping between two different valence states of the transition metal ions [1–8]. One of the materials that have been extensively investigated is V_2O_5/SiO_2. Apart from academic investigation [1–8], the technological applications in heterogeneous catalysis, optics, sensors and batteries have received special attention [9–15]. In order to achieve desirable performance of these materials it is important to obtain a uniform and homogeneous distribution of the transition metal ions through the silica matrix. In this context, several different synthetic procedures have been described in the literature. For example, vanadium can be introduced in large quantities in silica acting as a glass former; however, unfortunately the high viscosity of silica tends to produce heterogeneous materials characterized by phase separation [2,4,7]. Another possibility

is applying sol–gel method using alkoxides as starting reagents [3,5–9]. Nevertheless, there is still the problem with homogeneity because of the overall reaction kinetic [13]. In this context, the present study reports a new approach to produce vanadia–silica composite xerogel synthesized by the intimate mixing of inorganic polymers in the solid state [16–18]. In other words, a complex network involving two different inorganic polymers (Si–O and V–O based polymers) is stabilized by the formation of an interpenetrating polymer network, as the result of a mutual "solubility" due to cross-linking and entanglement of both components. The vanadia–silica xerogel films were investigated using electrochemical response as well as temperature-dependent conductivity measurements.

2. Experimental

2.1. Preparation of V_2O_5/SiO_2 xerogel film

Vanadium pentoxide gel, $V_2O_5 \cdot nH_2O$, was prepared by ion exchange method (ion-exchange resin Dowex-50X)

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from sodium metavanadate ($NaVO_3$, 99%, Fluka), as described elsewhere [19]. A pre-hydrolyzed solution was prepared by stirring for 1 h at room temperature (24°C) a solution containing: 1.12×10^{-2} mol of tetraethyl orthosilicate (TEOS, 99 + %, Aldrich), 1.12×10^{-2} mol of ethanol (99 + %, Merck), 1.0×10^{-8} mol of hydrochloric acid (99 + %, Merck) and 1.12×10^{-2} mol of water (purified using a Millipore Milli-Q System). Then, 0.19 mol of ethanol, 3.4×10^{-2} mol of water and 3.2×10^{-6} mol of HCl were added and stirred for 48 h at room temperature. Afterwards, 5.6×10^{-4} mol of vanadium pentoxide gel was added to 6.0 dm^{-3} of final solution (composition C1) and 2.8×10^{-4} mol vanadium pentoxide gel was added to 6.0 dm^{-3} of the final solution in order to obtain a second composite (composition C2). Both solutions were then stirred for 24 h at room temperature before deposition onto substrate. The V_2O_5/SiO_2 homogeneous xerogel composites in film form were obtained by dropping an amount of the final solution on a substrate (glass or ITO—indium tin oxide electrode), leading to a light red-orange film. The films were allowed to dry at room temperature for two days. Vanadium pentoxide xerogel composition was $V_2O_5 \cdot 1.8H_2O$ as determined by thermogravimetric analysis (TGA). The V_2O_5/SiO_2 xerogels formed have the following composition (atomic %) evaluated by energy dispersive X-ray spectrometry (EDX) technique:

Composition C1: V 22%; Si 78%.
Composition C2: V 11%; Si 89%.

2.2. Characterization and measurements

TGA was performed with a Thermal Analyst equipment model 2100-TA in air atmosphere. The TGA experiments were conducted from room temperature to 600°C at a linear heating rate of 10°C min^{-1}. The X-ray powder diffraction (PXRD) studies were carried out with a SIEMENS D5005 diffractometer using a graphite monochromator and Cu$K\alpha$ emission lines (1.541 Å, 40 kV, 40 mA). The samples, in film form, were deposited onto a glass plate and the data were collected at room temperature over the range $2° \leqslant 2\theta \leqslant 50°$ with a step of 0.020° EDX spectrometry data were obtained from a ZAF 4FLF LINK ANALYTICAL equipment. Fourier transform infrared (FTIR) spectra were recorded from pressed KBr pellets using a Bomem MB-100 FTIR spectrometer. Cyclic voltammetry (CV) experiments were carried out with an AUTOLAB (EcoChemie) model PGSTAT30 (GPES/FRA) potentiostat/galvanostat interfaced to a computer. The conventional three-electrode arrangement was used, consisting of a working electrode, the sample in film form supported on ITO electrode ($In_2(Sn)O_x$, $R_s \leqslant 20\,\Omega$, purchased from Delta Technogies), a platinum wire auxiliary electrode and saturated calomel electrode (SCE) as reference electrode containing 0.1 mol dm^{-3}

of supporting electrolyte ($LiClO_4$) in acetonitrile (chromatography grade, Aldrich). DC conductivity was measured as a function of temperature from 150 to 350 K. Measurements were done with samples in film form and were performed in an evacuated chamber using a DC bias of 1 V between silver electrodes.

3. Results and discussion

Fig. 1 shows a comparison of the TGA curves of the V_2O_5 xerogel ($V_2O_5 \cdot 1.8H_2O$), silica matrix and of the V_2O_5/SiO_2 xerogel composite. The curve for vanadium pentoxide xerogel shows two distinct stages of weight loss (Fig. 1a). The first weight loss (8.0%) extends to around 125°C attributed to the loss of intermolecular water. The second weight loss (3.0%) extends up to around 350°C related to the release of the strongly bounded water molecule. For temperature above 350°C there is the formation of crystalline vanadium pentoxide [20,21]. In contrast, the TGA curves for V_2O_5/SiO_2 xerogel composites (C1 and C2, shown in Figs. 1c and d, respectively) shows one step of weigh loss (approximately 19% for both compositions) up to 120°C, which can be attributed to the removal of weakly bound water and, probably, alcohol trapped in the pores of the xerogel composite. In addition, it also shows a continuous weigh loss (approximately 4% for both compositions) up to 500°C corresponding to the loss of more strongly bound water molecules and to decomposition of unreacted alkoxide groups. It should be noted that this behavior is quite similar to the behavior of silica matrix alone (Fig. 1b). However, there is an increase in the amount of water and ethanol present in the xerogel composite in comparison with silica and
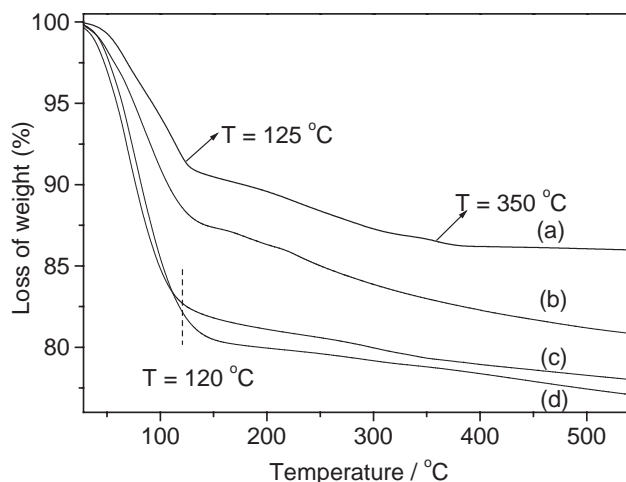

Fig. 1. Thermogravimetric curves of the vanadium pentoxide xerogel ($V_2O_5 \cdot 1.8H_2O$) (a), silica matrix (b), C1 xerogel composite (c) and C2 xerogel composite (d).

vanadium pentoxide xerogel. It seems that the V_2O_5 xerogel promoted the swelling capacity of the overall composite network, probably due to the increase of hydrophilic groups. Other possibility is the increase of porosity of the material that allowed the loading of water molecules even the retention of alcohol through hydrogen bonding.

In Fig. 2, typical powder X-ray diffraction patterns are shown for the both compositions of vanadia–silica xerogel and the xerogel of composition C1 after a thermal treatment at 150°C. The diffraction patterns of the vanadia-silica xerogels (Figs. 2a and b) exhibit 0 0 1 reflection characteristic of the vanadium pentoxide xerogel indicating the maintenance of the bi-dimensional structure [22–24]. The interlayer spacing observed for the V_2O_5/SiO_2 xerogels (*d*-spacing ≈ 1.4 nm) are slightly higher than that for vanadium pentoxide xerogel (*d*-spacing ≈ 1.20 nm) [22–24]. For the composition C1, a thermal treatment was carried out at 150°C during 15 min in order to evaluate the effect of water content on the structure (Fig. 1c). The shift of (001) peak to higher 2θ values was observed indicating a decrease of the interlayer spacing to 1.26 nm. The decrease of inter-lamelar spacing probably arises from the release of water and solvent molecules from interlamelar domain, in agreement with TGA. This result indicates the maintenance of the V_2O_5 xerogel lamellar structure (0 0 *l* reflections predominate) even after thermal treatment.

Unfortunately, infrared spectroscopy of V_2O_5/SiO_2 xerogel composite is dominated by SiO_2 framework vibrations, therefore it does not show clearly the characteristic vibrational modes from the vanadium pentoxide xerogel: 1012 cm^{-1} (V=O stretching); 763 cm^{-1} (V–O–V in-plane vibration); 515 cm^{-1} (V–O–V out-of-plane vibration) [25]. These bands are pre-sented as a shoulder (V=O stretching) or composite bands consisted of V–O–V and Si–O–Si vibrational modes. Nevertheless, characteristics vibrational bands assigned to SiO_2: 793 cm^{-1} (Si–O–Si) stretching vibration; 950 cm^{-1} (Si–O–Si and Si–OH vibrations); 1080 and 1210 cm^{-1} (Si–O–Si asymmetric stretching) are shown [26,27]. Again, we were not able to evaluate the existence of Si–O–V bond with confidence, thus further investigations are now in progress in order to clarify this point.

Electronic spectrum of V_2O_5/SiO_2 xerogel composite (Fig. 3) is dominated by intense absorption bands in the ultraviolet regions (248 and 376 nm) arising from vanadium(V)-oxide charge-transfer transition, which are nearly identical with those of vanadium pentoxide xerogel [19,24]. In addition to that, electron paramagnetic resonance (EPR) spectrum of the xerogel
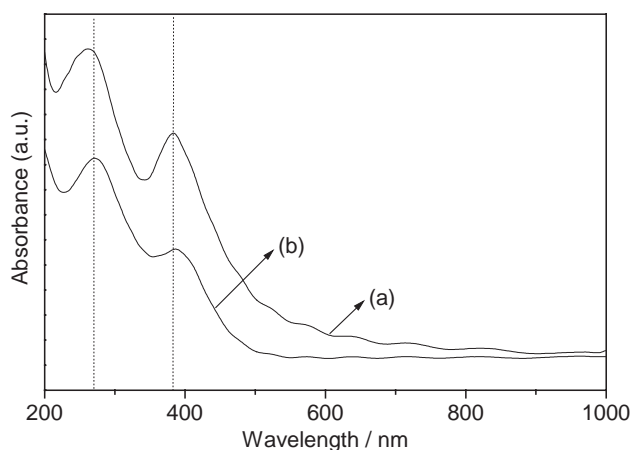

Fig. 3. UV/Vis spectra of the: vanadium pentoxide xerogel (a) and V_2O_5/SiO_2 xerogel composite (b).
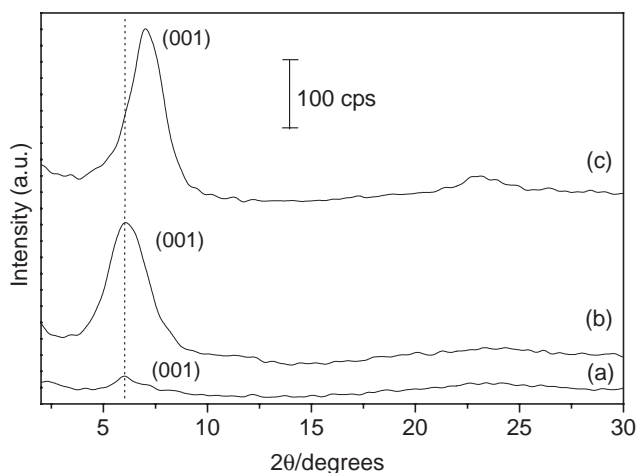

Fig. 2. Powder X-ray diffraction patterns of the C2 xerogel composite (a), C1 xerogel composite (b) and C1 xerogel composite after thermal treatment at 150°C (c).
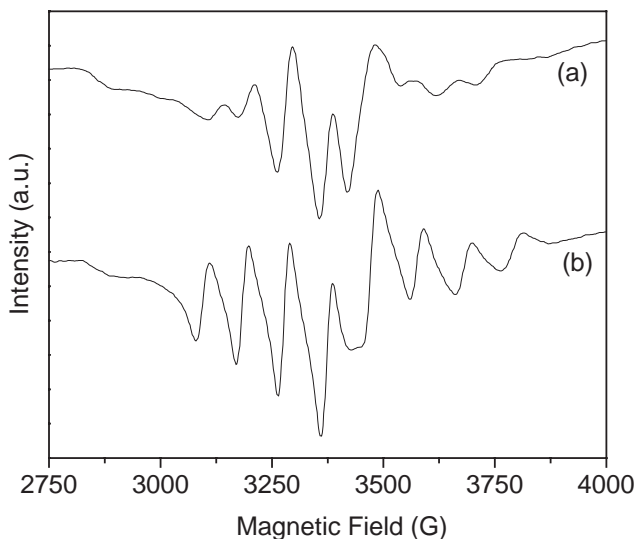

Fig. 4. EPR spectra of the: vanadium pentoxide xerogel (a) and V_2O_5/SiO_2 xerogel composite (b).

composite, shown in Fig. 4b, exhibits lines due to the hyperfine coupling of one unpaired electron with the nuclear spin (V^{IV}, $S = 1/2$, $I = 7/2$) in an axially distorted crystal field arisen from vanadium pentoxide xerogel (Fig. 4a) [24,28]. Thus, these results suggest that there was not any significant interaction between V_2O_5 and SiO_2 during the production of xerogel composite. Moreover, it seems that silica matrix practically does not affect the V_2O_5 structure and that vanadium (V) centers were not reduced to vanadium (IV), suggesting, therefore, a weak interaction between the inorganic polymers.

Fig. 5 shows the temperature dependence of conductivity in the range 370–240 K for V_2O_5/SiO_2 xerogel composite (composition C1) before and after thermal treatment at 150°C (Figs. 5b and c, respectively) and for vanadium pentoxide xerogel (Fig. 5a). One can observe that the conductivity decreases when the temperature falls, evidencing a thermally activated process. The measured conductivity at room temperature of vanadium pentoxide xerogel is 10–10^2 times higher than xerogel composite and its activation energy is slightly lower (values are shown in Fig. 5). This decrease of conductivity can be associated with the diminution of polymeric chain arisen from mechanical stress occurred during the polymerization of silica network. In addition, the thermal treatment of the xerogel composite sample has increased the electrical conductivity. Although V_2O_5/SiO_2 composite presents lower conductivity when compared with vanadium pentoxide xerogel, its conductivity is almost five orders of magnitude higher than other related systems [3,4]. The electrical conductivity in TMO can be explained by the electron hopping thermally activated between metallic centers in different oxidation states: hopping of unpaired electrons between V^{IV} and V^V ions that follows the small-polaron model [29,30]. In addition, such kind of gels can also be considered as hydrated oxides and the ionic contribution to overall conduction arises from hopping of protons

through the layered structure of vanadium pentoxide xerogel [31]. Apparently, the vanadium pentoxide xerogel is only embedded in the silica matrix preserving its overall structure and with little effects on its electronic properties, as verified by UV/Vis and EPR techniques. In the thermally treated sample, the rise in conductivity can be related to a higher degree of crystallinity of the sample provoked by temperature, as indicated by 0 0 1 peak that became more intense (Fig. 2c). It was expected that with the release of water molecules under rising temperature the conductivity would decrease. In other words, according to some authors the electrical conduction has the contribution of hopping of H^+ through the hydrogen bonds, i.e., it occurs only when the neighboring water molecule takes suitable orientation to form hydrogen bonding [31]. However, it seems that, despite of the release of water molecules, the electronic conduction dominated the overall conduction mechanism and that the higher crystallinity of V_2O_5 framework facilitated the hopping of small polarons between localized states. Another possibility to be considered is that with the release of water molecules the distance between adjacent V_2O_5 polymeric units become shorter contributing somewhat to the overall conductivity. In other words, if we consider that the V_2O_5 polymeric units are homogeneously distributed, and electrically isolated by SiO_2, decreasing the overall volume of the material will decrease also the average distance between conducting V_2O_5 polymeric units. This probably explains the higher conductivity when compared with other related systems [3,4], in which V^{IV} and V^V metallic centers are completely isolated.

The electrochemical properties of V_2O_5/SiO_2 xerogel composite were evaluated by cyclic voltammetry, as shown in Fig. 6. The voltammetric behavior is quite
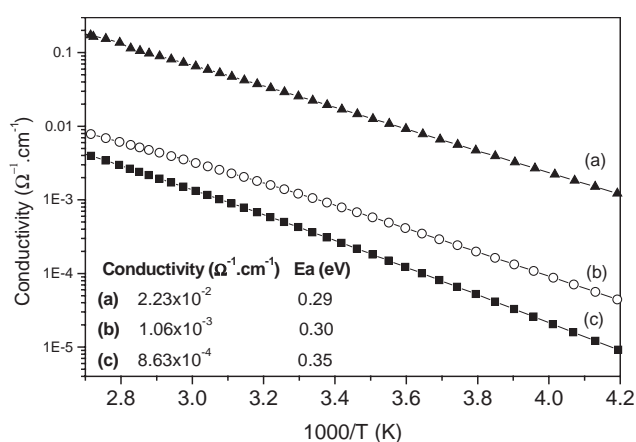

Fig. 5. Conductivity of V_2O_5 xerogel (a), V_2O_5/SiO_2 xerogel composite after thermal treatment (b) and before thermal treatment (c).
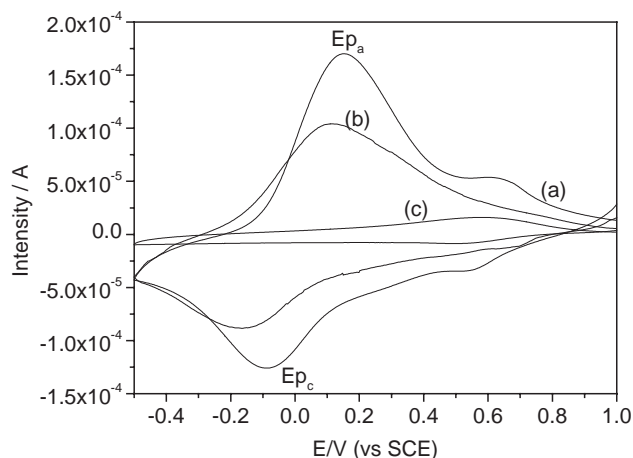
	Conductivity ($\Omega^{-1}.cm^{-1}$)	Ea (eV)
(a)	2.23×10^{-2}	0.29
(b)	1.06×10^{-3}	0.30
(c)	8.63×10^{-4}	0.35

Fig. 6. Cyclic voltammograms of the V_2O_5/SiO_2 xerogel composite in support electrolyte solution varying the cation species, $0.1\,mol\,L^{-1}$ $LiClO_4$ (a), $0.1\,mol\,L^{-1}$ $NaClO_4$ (b) and $0.1\,mol\,L^{-1}$ $TBAClO_4$ (c).

similar to that found for V_2O_5 xerogel [22,32,33]; showing reversible peaks ($V^{V/IV}$ redox pair: $xe^- + xLi^+ + V_2O_5 \cdot nH_2O \rightleftharpoons Li_xV_2O_5 \cdot nH_2O$, in acetonitrile solutions containing 0.1 M $LiClO_4$) in the potential range -0.50 to $+0.10$ V (SCE), as shown in Fig. 6a. In addition, the electrochemical response is dependent on support electrolyte solution varying the cation species (Figs. 6a–c). Probably, increasing the cation size the electrochemical process becomes irreversible. In order to achieve the electroneutrality, the reduction occurs simultaneously with insertion of cationic species into lamellar domain. Thus, with increasing the cation size as has been observed, the insertion process becomes more difficult resulting in a low rate of electronic transfer. Another interesting point is the fact that with the thermal treatment the current peak intensities increased, the width at half-maximum became narrower and the difference in peak potential values (ΔEp) was decreased (Fig. 7). In other words, the ΔEp value for process I changed from 240 mV for the V_2O_5/SiO_2 before thermal treatment to 190 mV for the sample after heating. Thus, a more electrochemically reversible system was attained in function of the release of water molecules. This fact can be explained by better electromigration of solvated lithium ions during the intercalation and de-intercalation processes. Probably, the release of weakly bounded water molecules results in a higher free volume within the interlamelar spacing that enable an easier intercalation and accommodation of the solvated ions [34]. In addition, it seems that the silica matrix offers structural stability allowing a satisfactory electrochemical response, which is desirable for lithium batteries [15]. At this point more experiments about the behavior of this xerogel composite as electrodes are still under investigation.
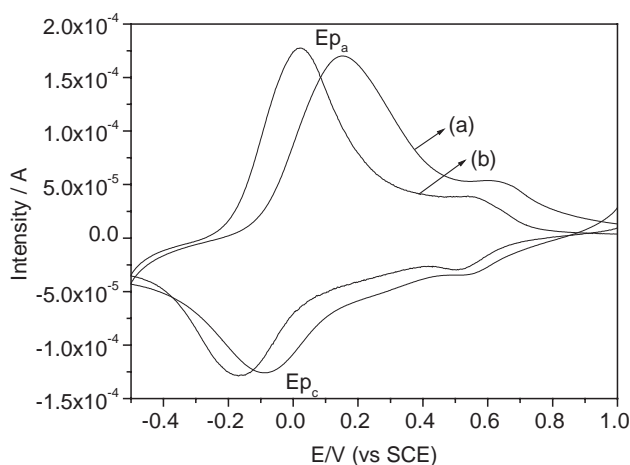
In face of electronic and electrochemical properties, presumably, the polymeric V_2O_5 chain coexists with silica polymer and it is homogeneously dispersed. Perhaps, Si–O–V linkages and interactions such as van der Waals and hydrogen bonding play an important role in mutual miscibility of both systems. Moreover, in the preparation of the material, the polycondensation of the silicon alkoxide was carried out in the presence of vanadium pentoxide gel; thus, generating Si–O–Si network interpenetrated with V–O–V and V–OH–V polymeric chains previously formed by oxolation and olation reactions [19,24]. Thus, this approach allowed the preparation of homogeneous bicomponent system in which the intimate mixing of inorganic polymers in the solid state are stabilized (as illustrated in Fig. 8) and lead to the maintenance electrochemical and electronic properties of vanadium pentoxide xerogel.

4. Conclusion

The incorporation of vanadium pentoxide xerogel into silica matrix by intimate mixing of two different inorganic polymers (Si–O and V–O based polymers) has yielded a homogeneous multi-component material. V_2O_5/SiO_2 xerogel composite presents conductivity almost five orders of magnitude higher than other related systems. In addition, the voltammetric behavior is quite similar to that found for V_2O_5 xerogel and is dependent on support electrolyte solution varying the cation species. Furthermore, it was found that both properties were improved with no significant effect on V_2O_5 xerogel layered structure. Overall, the experimental data evidence that the vanadium pentoxide xerogel embedded in silica retains its bi-dimensional structure as well as its electronic and electrochemical properties. Therefore, the synthetic approach applied in this study is extremely attractive due to its simplicity and can
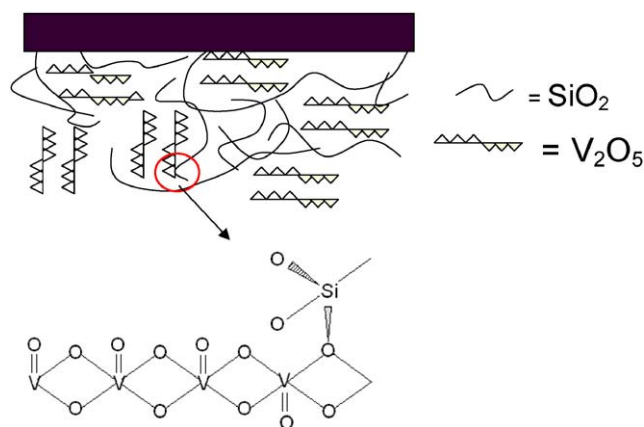

Fig. 7. Cyclic voltammograms of the V_2O_5/SiO_2 xerogel composite before and after the thermal treatment at 150°C in acetonitrile, 0.1 mol L^{-1} $LiClO_4$, in the potential range $+1.00$ V to -0.60 V (SCE) and $v = 100$ mV s^{-1}.

Fig. 8. Scheme of supposed structure of V_2O_5/SiO_2 xerogel composite.

provide new strategies for tailoring new materials for electrochromic devices, batteries and chemical sensing.

Acknowledgments

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