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Intercalation compounds based on vanadium(V) oxide xerogel

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Abstract. Data published during the last 15 years on the intercalation of metal and n-alkylammonium ions, organic molecules and organometallic complexes in vanadium(V) oxide xerogel are generalised and described systematically. The possible mechanisms of intercalation processes are considered. The possibility of using hybrid materials in electrochemical and optical devices and as precursors for the preparation of anhydrous and nanotubular forms of oxide compounds is discussed. The bibliography includes 159 references.

I. Introduction

In intercalation compounds (insertion compounds), ions or guest molecules are located in the crystallographic vacant sites of such host substances as, for instance, simple or complex oxides, sulfides, *etc*. Basically, these are layered compounds with sandwich-like structure or one-dimensional channel-like substances (tubulenes). Layered compounds possess higher intercalation capacities as compared with tubulenes. Currently, researchers are paying special attention to the intercalation compounds based on vanadium(V) oxide xerogel,[1] which manifests properties of both the original vanadium – oxygen matrix and the intercalated substances. A characteristic feature of these compounds is a quasi-one-dimensional structure and a turbostratic disorder of their layers. Both cations and organic molecules can easily be intercalated into this structure.

This property distinguishes the xerogel under consideration from crystalline V_2O_5, the three-dimensional lattice of which can be intercalated only by metal ions.[2] The high intercalation capacity of xerogel is explained by its nature (this is polyvanadium acid, *viz*., $H_2V_{12}O_{31} \cdot n\,H_2O$) and is ensured by the negative charge of the vanadium – oxygen layers, which is distributed along the V_2O_5 fibres.[3] Intercalation may occur owing to dipole absorption, ion-exchange or redox processes. In all cases, this results in a change in the interlayer distance, which corresponds to the insertion of one or several layers of an intercalant and does not change the structure of the xerogel itself. Solid solutions in which vanadium is replaced by hexa-, penta- or tetravalent ions can be obtained based on vanadium(V) oxide xerogel. These solid solutions have larger homogeneity regions than anhydrous complex oxides. Such solid solutions can easily be obtained in the form of films, superfine powders and nanocomposites using energy-saving environmentally friendly technologies. That is why they are promising for designing materials for various electrochemical and optical devices,[4] they can be used in the synthesis of catalysts and as precursors for anhydrous and nanotubular forms of oxide compounds.

Intercalation compounds are usually obtained by a sol – gel method in aqueous, organic or aqueous – organic media. For the large-scale synthesis of $V_2O_5 \cdot n\,H_2O$ xerogel, a vanadium(V) oxide melt is poured into water, the sol $V_2O_{5-\delta} \cdot n\,H_2O$ obtained is transformed with time into the gel which is dehydrated. By choosing the conditions for dehydration, it is possible to obtain xerogels with different specific surface areas.[5] An efficient method for the synthesis of intercalation compounds with the general composition $M_xV_{2-y}T_yO_{5+\delta} \cdot H_2O$ (M is a mono-, di- or trivalent cation, T = Mo, W, Cr, Ti) consists of dissolution of the corresponding oxides, hydrides or metals in hydrogen peroxide followed by decomposition of the peroxide compounds.[1]

By passing solutions of alkali metal metavanadates through a cation-exchange resin, a yellow solution of decavanadium acid $H_6V_{10}O_{28}$ is obtained, which becomes dark-red with time and transforms into the stable V_2O_5 gel.[5] Polymerisation is accompanied by partial ($\sim$1%) reduction of V^{5+} to V^{4+}. Intercalation compounds containing cations M^{z+} and different amounts of tetravalent vanadium in particular, can be obtained by hydrolysis of organovanadium compounds[6] and alkali-metal vanadates.[7] Intercalation compounds based on vanadium(V) oxide xerogel can possess both mainly ionic or electronic and mixed conductivity.[5] The ionic component is determined by the mobility of cations M^{z+} and depends on the relative humidity of air, while the electronic component depends on the content of tetravalent vanadium.

In the present review, special attention is given to the studies of the synthesis, structure and physicochemical properties of the intercalation compounds based on vanadium(V) oxide xerogel that have been carried out in recent years. In addition, a new class of these compounds, *viz*., VO_x-nanotubulenes with intercalated organic substances, is considered.

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II. Structure of intercalation compounds

Studies of the structure of intercalation compounds have been carried out on film samples of $V_2O_5 \cdot n\,H_2O$ xerogel, which is considered to be an insertion product of water molecules in vanadium(V) oxide.[8] The xerogel has a layered structure, which is deduced from the diffractograms of the $V_2O_5 \cdot n\,H_2O$ film (Fig. 1). The vanadium–oxygen layers are formed by tangled fibres and connected by water molecules. The interlayer distance (d) depends on the water content and equals 11.57 Å for the composition $V_2O_5 \cdot 1.6\,H_2O$ (phase I). On heating to 50 °C, this parameter changes only slightly ($d = 11.30 \pm 0.05$ Å). At ~100 °C, phase I gradually disappears and phase II ($V_2O_5 \cdot 0.5\,H_2O$) is formed. The formation of the latter is completed at 250 °C. The diffractograms of phase II also suggest a layered structure, but the interlayer distance equals 8.75 Å in this case. At temperatures above 350 °C, chemically bound water is removed and crystallisation of vanadiun(V) oxide occurs. It was found by electronography that the fibres are flat ribbons 1000 Å in length and 100 Å in width (Fig. 2). In the plane of the ribbon, their structure is analogous to that of orthorhombic V_2O_5 and is characterised by the following parameters: $a = 27.0$ and $b = 3.6$ Å. According to the IR spectroscopic analysis, the short-range ordering in $V_2O_5 \cdot n\,H_2O$ xerogel is similar to that in crystalline oxide. The main absorption bands of IR irradiation for the vanadium(V) oxide xerogel, *viz*., 1605, 1015, 910, 760 and 530 cm^{-1}, correspond to the following vibrations: $\delta(H-O-H)$, $\nu(V=O)$, $\delta(V-O\cdots H)$, $\delta(V-O-V)$ and $\delta(V-O)$.[2] Orthorhombic units constituting the ribbons do not lie in the common plane, but rather form a relief structure with an 'amplitude' of 2.8 Å. It was established by neutron and X-ray diffraction that the distance between the basal planes in $V_2O_5 \cdot nH_2O$ changes from 8.8 Å ($n = 0.1-0.5$) to 40 Å ($n = 18.5$ or higher) as the water content (n) increases. For $n \geqslant 5-6$, the parameter d_{001} increases in a stepwise manner by 3 Å, which corresponds approximately to the thickness of the interstitial water layer. Usual water freezes at the temperatures below 273 K by several degrees to form hexagonal ice crystals. In the xerogel, an interlayer distance of ~15 Å, caused by the presence of ordered bilayers of non-freezing water in the range $110 < T < 230$ K, was found by neutron diffraction technique. As the temperature increases to 270 K, the d_{001} value increases to 19 Å and the ordered state of the water layers is violated. The ordering of water in the hydrated layered systems is characteristic of not only $V_2O_5 \cdot n\,H_2O$ gel but also, for instance, clays.

The structure of the double vanadium–oxygen layer up to now has been controversial. According to one opinion (see, *e.g.*, Ref. 9), it consists of two $VO_{1.5}$ planes, with a distance of 2.8 Å between the planes (Fig. 3). Such a structure is similar to that of the δ-phase of oxide vanadium bronzes of the $M_xV_2O_5$ type (M = K, NH_4).[2] According to another opinion,[10] the V_2O_5 layers are 4.368 Å apart from one another and consist of one $VO_{1.5}$ plane. The axial-distorted tetragonal V_2O_5 pyramid in the $V_2O_5 \cdot n\,H_2O$ xerogel includes one short vanadyl bond with a length of 1.55–1.58 Å and a nearly planar system formed by four V–O bonds with a length of ~1.90 Å.[11]

Elucidation of the structure of the $V_2O_5 \cdot n\,H_2O$ xerogel requires the study of the state of its hydrogen–oxygen groups.[12] Two H_3O^+ groups per 6 $V_2O_{5-\delta} \cdot 1.6\,H_2O$ molecules have been found. This correlates well with the data on ion exchange, which suggest that polyvanadates of the type $M_2V_{12}O_{31-\delta} \cdot n\,H_2O$ are formed under equilibrium conditions. The number of three-spin systems decreases linearly as the amount of M^+ ions in $V_2O_{5-\delta} \cdot n\,H_2O$ increases, thus indicating the exchange of cations of the corresponding metals for these systems. The specimens contain relatively isolated protons as OH groups. Their content in $V_2O_{5-\delta} \cdot 1.6\,H_2O$ correlates with the content of tetravalent vana-

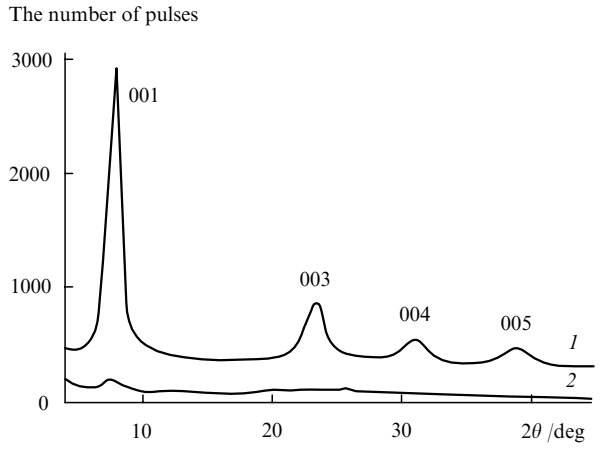


Figure 1. Diffractograms of the $V_2O_5 \cdot n\,H_2O$ xerogel film (*1*) and powder (*2*).

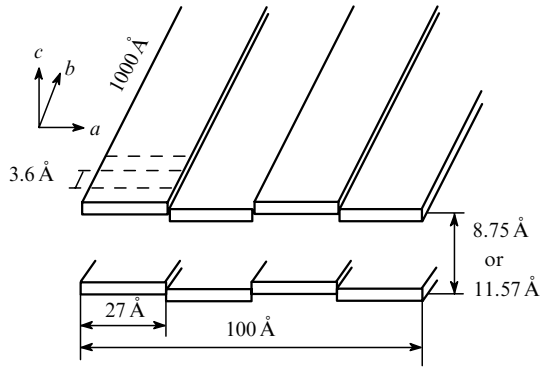


Figure 2. Schematic representation of the layered structure of the $V_2O_5 \cdot n\,H_2O$ xerogel.[5]

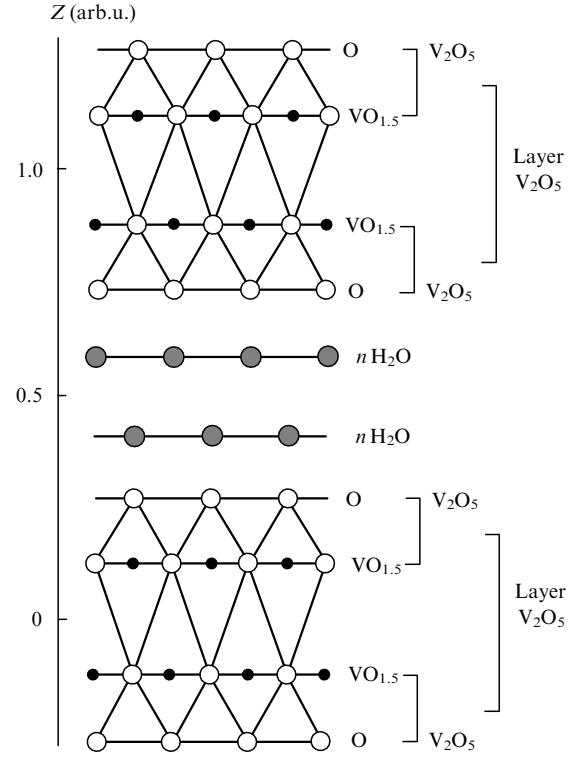


Figure 3. Structural model of the $V_2O_5 \cdot 1.7\,H_2O$ xerogel.[9]

dium. Comparison of the results obtained in ^{1}H NMR studies of polyvanadium acids with different compositions allows one to conclude that isolated protons are present in two non-equivalent states and that most of the protons are bound to tetravalent vanadium. Approximately one-half of the OH groups, appeared upon partial dehydration of three-spin systems with reduction of the water content in the xerogel from 1.6 to 1.4 moles, belongs to bridging groups $V^{5+}-OH$, which are exchange-active in contrast to the $V^{4+}-OH$ groups.

Based on the ^{1}H NMR data, the structure of the $V_2O_5 \cdot n\,H_2O$ xerogel can be represented as a result of the interaction of water molecules with coordinatively unsaturated vanadium atoms of the orthorhombic oxide. This process is accompanied by cleavage of V–O–V bonds followed by formation of two bridging OH groups. These bind water molecules to give highly mobile three-spin systems. According to the suggested model (Fig. 4), three types of protons can be distinguished in polyvanadium acid $H_2V_{12}O_{31} \cdot n\,H_2O$ ($V_2O_5 \cdot n\,H_2O$): the protons of water molecules coordinated with V=O groups belong to the first type (this is a zeolite-type water, which is absorbed reversibly and forms a network of hydrogen bonds); the protons involved in the three-spin systems (H_3O^+) belong to the second type; the protons of bridging hydroxo-groups (OH^-) chemically bound to vanadium atoms, which can be removed as the xerogel structure is destroyed, belong to the third type.

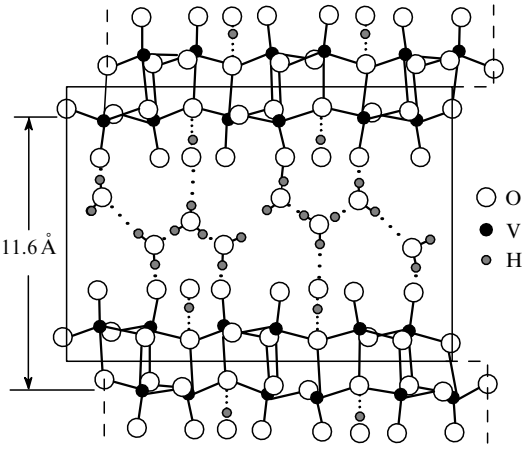


Figure 4. Structural model of the $H_2V_{12}O_{31} \cdot n\,H_2O$ xerogel.

Usually, $V_2O_5 \cdot n\,H_2O$ xerogel contains tetravalent vanadium ions which may be present in the vanadium–oxygen layers or in the hydrated $VO(H_2O)^{2+}$ ions between the layers.[13] The presence of V^{4+} ions can easily be detected by ESR[14] and chemical analysis. Their content in the samples depends on the nature of the reducing agent used in the synthesis of the gel and can reach 20 mass %.[5,15] The study of $V_2O_{5-\delta} \cdot n\,H_2O$ by X-ray photoelectron spectroscopy has revealed[16] that the positions of the V2p-band correspond to binding energies of 517.5 and 516.5 eV for penta- and tetravalent vanadium, respectively. The O1s binding energies are equal to 530.1 for O–V, 531.6 for the OH groups and ~533.2 eV for water molecules.

It should be mentioned that the structural characteristics of vanadium(V) oxide xerogel are similar to those of anhydrous intercalated phases of the $H_xV_2O_5$ and $M_xV_2O_5$ types (see Ref. 2). For instance, $H_xV_2O_5$ ($x \leqslant 0.5$) has a structure of V_2O_5 with unit cell parameters $a = 11.51$, $b = 3.56$, $c = 4.37$ Å; the IR spectrum of the former compound is analogous to that of V_2O_5 with the exception of the band at 928 cm^{-1}, which is attributed to the OH bond. This band is also present in the spectrum of polyvanadium acid. The unit cell of the β-phase of $M_xV_2O_5$ (the composition of which corresponds to the formula $M_xV_{12}O_{30}$) can adopt four intercalated monovalent ions.

III. Intercalation of cations

Vanadium(V) oxide xerogel exhibits ion-exchange properties.[12,17] The presence of exchangeable protons in the xerogel can be detected by adding an excess of any alkali metal salt to an aqueous suspension of $H_2V_{12}O_{31} \cdot n\,H_2O$. The following reaction occurs:

$$H_2V_{12}O_{31}\ (\text{solid}) + 2\,M^+ \rightleftharpoons M_2V_{12}O_{31}\ (\text{solid}) + 2\,H^+. \qquad (1)$$

The liberating protons are titrated with alkali and the ratio M : V is calculated taking into account the amount of the original xerogel. For the monovalent cations, the mean value of this ratio equals 0.17 ± 0.01, which is in good agreement with the formula of polyvanadium acid. Hydrated polyvanadates with different degrees of replacement of the protons by alkali or alkaline-earth metal ions can be obtained by the ion-exchange method. IR and ^{51}V NMR spectra of such samples are similar to the corresponding spectra of the original polyvanadium acid, thus indicating the unique chemical nature of these compounds. The mean $\log K_{H,M}$ values at 295 K ($K_{H,M}$ is the coefficient of the exchange of protons in poyvanadium acid by alkali metal cations or NH_4^+), which depend linearly on the radii of hydrated cations, are given in Table 1. Taking into consideration the ion-exchange coefficients, the cations can be arranged in the following series according to their ability to replace the protons: $La^{3+} > K^+ \geqslant Ba^{2+} > NH_4^+ > Ca^{2+} > Na^+ \geqslant Al^{3+} > Sr^{2+} > Mg^{2+} \geqslant Ni^{2+} \geqslant Zn^{2+} \geqslant Mn^{2+} > Cd^{2+} > H^+ > Li^+$ (see Ref. 18).

Table 1. Ion exchange coefficients of the protons of polyvanadium acid for metal cations or NH_4^+ ($T = 295$ K).[18]

Cation	$\log K_{H,M}$	Cation	$\log K_{H,M}$	Cation	$\log K_{H,M}$
Li^+	0.40 ± 0.05	Ca^{2+}	1.21 ± 0.03	Mn^{2+}	0.28 ± 0.02
Na^+	0.54 ± 0.04	Sr^{2+}	1.03 ± 0.04	Co^{2+}	0.48 ± 0.04
K^+	1.07 ± 0.03	Ba^{2+}	2.10 ± 0.12	Ni^{2+}	0.44 ± 0.02
NH_4^+	0.99 ± 0.06	Zn^{2+}	0.43 ± 0.03	Al^{3+}	1.60 ± 0.02
Mg^{2+}	0.45 ± 0.11	Cd^{2+}	0.27 ± 0.02	La^{3+}	3.50 ± 0.30

It was estimated by the potentiometric titration method,[19] that the exchange capacity of the $V_2O_5 \cdot n\,H_2O$ specimens with respect to the cations of monovalent metals ($M^+ : V_2O_5$) is close to 0.3. The rate of exchange $H^+ : M^+$ is mainly limited by the diffusion of cations at the xerogel–electrolyte solution interface. The values of the diffusion coefficient (D) determined for the alkali metal ions and protons agree well with the data on the selectivity of ion exchange for polyvanadium acid:

Ion	Na^+	K^+	Cs^+	H^+
$10^8 D$ cm^2 s^{-1}	5.0 ± 0.4	4.8 ± 0.4	2.1 ± 0.2	1.6 ± 0.2

Upon intercalation of sodium, potassium and cesium monovalent cations into the interlayer space of $V_2O_5 \cdot n\,H_2O$ xerogel, the interlayer distances become equal to 10.9, 11.0 and 11.1 Å, respectively.

It was found[20] that the x value in the formula of xerogel $M_x^{z+}(V_2O_5)^{(0.3-0.4)-} \cdot n\,H_2O$ is mainly determined by the exchange capacity and equals 0.33–0.36, 0.16 and 0.11 for mono-, di- and trivalent cations, respectively. Two types of cations were distinguished: the first type of cations are solvated with one water layer ($d = 10.9$–11.3 Å), while solvation of the second type of cations takes two water layers ($d = 13.4$–14.2 Å). For the first type of cations, the charge-to-radius ratio is $z/r < 1.67$ e Å^{-1}, all of them, except Ba^{2+}, are monovalent ions. For the second type of cations (di- and trivalent ions), $z/r > 1.67$ e Å^{-1}. Analogous correlation is observed for the parameter characterising the change in the enthalpy upon hydration of the ions: intercalation of the cations is accompanied by the formation of a monolayered hydration shell if $\Delta H > -1465$ kJ mol^{-1}, while a double hydration layer is formed if $\Delta H < -1465$ kJ mol^{-1}. The interrelation-

ship between the ionic radii of the intercalated cations and the degree of their hydration has been established. This depends on the number of water molecules associated with the ions during their movement through the solution and equals the amount of water which is determined at temperature below 160 °C. The cations M^{z+} can be arranged in the following order with respect to the degree of hydration: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ and $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$.

Interesting results were obtained[21] in the studies on the topochemistry and kinetics of the intercalation of polycation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Al_{13}) into $V_2O_5 \cdot n\,H_2O$ xerogel powders and films. Insertion of this polycation is accompanied by a gradual change in the interlayer distance up to a constant value of 17.5 Å. Obviously, the rate of intercalation is mainly influenced by such geometrical factors as the specific surface area of the xerogel and the length of the possible path of migration of intercalated cations. With the Al_{13} polycation, stable xerogels, based on vanadium(V) oxide, can be obtained by double ion exchange.[21] In the first stage of the ion-exchange process, $V_2O_5 \cdot n\,H_2O$ xerogel is involved in the exchange with any mono-, di- or trivalent cation including VO^{2+}. In the second stage, the replacement of M^{z+} in the compounds obtained $M_x^{z+}V_2O_5 \cdot n\,H_2O$ *via* $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ occurs. Finally, stable layered materials $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}-V_2O_5$ are formed. If the cations characterised by the ratio $z/r < 1.67$ e Å^{-1} are used in the first step, the xerogel $Al_{13}-V_2O_5$ with $d \approx 15$ Å and a specific surface area $s_0 = 10-30$ m^2 g^{-1} is obtained. If VO^{2+} or the ions characterised by $z/r > 1.67$ e Å^{-1} are involved in the ion-exchange process, compounds with $d \approx 18$ Å and a specific surface area >80 m^2 g^{-1} are formed. The second type of compounds can be considered as xerogels $Al_{13}-V_2O_5$ with pillared structure, because the specific volume of their micropores amounts to ~ 0.3 ml g^{-1}, while the distance between the vanadium–oxygen layers is close to 9.4 Å, which corresponds to the diameter of the Al_{13} cation.

Xerogels with a similar pillared structure are formed in the ion-exchange process of polyvanadium acid with clusters $M_6Cl_{18}(OH)_n(H_2O)_m^{(4-n)+}$ (M = Mo, Nb).[22] For this purpose, an aqueous suspension of $V_2O_5 \cdot n\,H_2O$ xerogel is mixed with 1.6 M ethanolic solution containing the cluster ion. The compound obtained has an interlayer distance of ~ 14.3 Å, its specific surface area is 15 m^2 g^{-1}.

$V_2O_5 \cdot 1.9\,H_2O$ obtained by hydrothermal treatment of the xerogel exhibits a high ion-exchange capacity, which is comparable with that of zeolites, and significant selectivity with respect to Cs^+ ion.[23] In the presence of highly concentrated aqueous solutions of salts MCl_z, where $M = Li^+$, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+} and Sr^{2+} ($M^{z+}:Cs^+ = 250$), the xerogel absorbs cesium ions selectively. The selectivity with respect to the cesium cation changes in the following sequence: $Li^+ > Mg^{2+} > K^+ > Na^+ > Ca^{2+} > Sr^{2+} > Ba^{2+}$. The cesium distribution coefficient changes in the same sequence from 226 for Ba to 981 for Li^+. This selectivity of the xerogel allows one to use it for the extraction of Cs^+ from radioactive solutions.

The ion-exchange properties of xerogel $V_2O_{4.86} \cdot 2.2\,H_2O$ obtained under hydrothermal conditions have been studied in detail.[24] This compound is characterised by a high content of V^{4+}; the interlayer distance is 14.2 Å. The main exchangeable groups in $V_2O_{4.86} \cdot 2.2\,H_2O$ are VO^{2+} ions, and the formula of this oxide can therefore be written as $(VO)_{0.10}V_2O_5 \cdot 2.3\,H_2O$. Compounds $Na_{0.37}V_2O_5 \cdot 1.1\,H_2O$, $K_{0.32}V_2O_5 \cdot 0.9\,H_2O$, $Rb_{0.31}V_2O_5 \cdot 0.8\,H_2O$ and $Cs_{0.28}V_2O_5 \cdot 0.8\,H_2O$ in which the interlayer distances are close to 11 Å were isolated upon treatment of the initial xerogel with 0.2 M solutions of M_2SO_4 (M = Na, K, Rb, Cs). In the case of the exchange reaction involving Li^+ cations, only 20% of the VO^{2+} ions are replaced and compound $Li_{0.12}(VO)_{0.08}V_2O_5 \cdot 2.4\,H_2O$ is formed. The order of selectivity Li < Na < K < Rb < Cs reported coincides with that for the xerogel obtained under usual conditions.[18] Commonly, the insertion of vanadyl ions between the layers of $V_2O_5 \cdot n\,H_2O$ xerogel leads to three phases of compound with the general formula $(VO)_{0.10}V_2O_5 \cdot n\,H_2O$: phase I ($n = 2.30$, $d = 14.21$ Å) is formed at room temperature, phase I-α ($n = 1.12$, $d = 11.64$ Å) is formed at 70 °C and phase I-β ($n = 0.45$, $d = 12.21$ Å) is formed at 122 °C.[25] In these compounds, two V_2O_5 planes and an interstitial plane of VO^{2+} and water molecules can be distinguished; the twin V_2O_5 planes in the layer are situated at a distance of 2.7 Å from each other. Phase transitions are accompanied by transformation of the four interlayer planes present in phase I into two planes in the formation of phase I-α and then into one plane in the formation of phase I-β.

An ion-exchange method was used for the synthesis of precursors of new structures resembling the structures of α-phases of oxide vanadium bronzes.[26] Intercalation compounds $Ba_{0.16}V_2O_5 \cdot 1.52\,H_2O$ ($d = 11.2$ Å), $Ni_{0.16}V_2O_5 \cdot 2.47\,H_2O$ ($d = 13.4$ Å), $Fe_{0.11}V_2O_5 \cdot 2.35\,H_2O$ ($d = 14.1$ Å), $Al_{0.11}V_2O_5 \cdot 2.78\,H_2O$ ($d = 14.2$ Å) were obtained by the interaction of $V_2O_5 \cdot n\,H_2O$ xerogel with aqueous solutions of the corresponding salts. Further thermal treatment at the temperature of crystallisation of the compounds, *viz*., at 520 (Ba and Ni), 535 (Fe) and 600 °C (Al) leads to the formation of α-phases of $M_xV_2O_5$. The parameters of the unit cells of these compounds do not depend on the nature of the metal M and are equal to $a = 11.43$, $b = 3.55$ and $c = 4.35$ Å.

$Al_{0.11}V_2O_{5.15}$ was obtained by an analogous method with thermal treatment at 520 °C for 2 h (see Ref. 27). The specimen contained 1%–2% V^{4+} and had the following unit cell parameters: $a = 11.51$, $b = 3.56$ and $c = 4.38$ Å. Upon the interaction of $V_2O_5 \cdot n\,H_2O$ xerogel with aqueous Ag^+ solutions, β-$Ag_{0.35}V_2O_5$, α-$AgVO_3$ and a new compound, *viz*., δ-$AgVO_3$, which crystallises in the monoclinic syngony with the unit cell parameters $a = 32.96$, $b = 2.60$, $c = 3.62$ Å and $\beta = 91.88°$, were obtained at different relative silver and vanadium concentrations in the reaction media (see Ref. 28).

Interactions of lanthanide trichlorides with polyvanadium acid in water result in the formation of xerogels of lanthanide polyvanadates.[29] After keeping the reaction mixtures for 24 h, the solid phase was filtered out, washed with water and acetone and dried in a vacuum. According to the results of elemental analysis, the following compounds were obtained: $Pr_{0.15}V_2O_5 \cdot 3.7\,H_2O$, $Nd_{0.11}V_2O_5 \cdot 3.5\,H_2O$, $Sm_{0.12}V_2O_5 \cdot 2.7\,H_2O$, $Eu_{0.12}V_2O_5 \cdot 2.1\,H_2O$, $Ho_{0.13}V_2O_5 \cdot 3.2\,H_2O$, $Er_{0.13}V_2O_5 \cdot 3.2\,H_2O$, which may be represented more correctly as the corresponding salts of polyvanadium acid $H_2V_{12}O_{31} \cdot n\,H_2O$ with incomplete substitution of the lanthanide cations for the protons. The X-ray diffraction studies on these compounds have shown that their structures are less ordered than the structure of $H_2V_{12}O_{31} \cdot n\,H_2O$. The 001 reflections appear as most intense ones for $Nd_{0.007}V_2O_5 \cdot 1.4\,H_2O$ ($d = 13.6$ Å), $Nd_{0.11}V_2O_5 \cdot 1.7\,H_2O$ ($d = 14.5$ Å) and for $Nd_{0.20}V_2O_5 \cdot 2.0\,H_2O$ ($d = 14.9$ Å), the average size of the xerogel particles is 242 Å. The IR spectra of these substances are similar to each other, but the band at 1010 cm^{-1} corresponding to the vibration of the V=O bond in the initial acid, is displaced to 1032 cm^{-1} for $Nd_{0.20}V_2O_5 \cdot 2.0\,H_2O$.

Compounds $M_{0.11}V_2O_5 \cdot n\,H_2O$ ($M = Cr^{3+}$, Fe^{3+}) were obtained by ion exchange for 20 min at room temperature.[30] $V_2O_5 \cdot 1.6\,H_2O$ ($d = 11.60$ Å) and a 0.1 M solution of $M(NO_3)_3$ were used as the starting compounds. The interlayer space of the resulting compounds ($d = 14.10$ for $M = Fe^{3+}$, 14.40 Å for $M = Cr^{3+}$) contains two layers of water molecules. It appears to be more correct to call these compounds polyvanadates $M_xV_{12}O_{31} \cdot n\,H_2O$ as in the case of the intercalation of lanthanides.[29] Dehydration of $Cr_{0.11}V_2O_5 \cdot 2.34\,H_2O$ proceeds in a stepwise manner in the intervals 20–200 °C and 200–350 °C and is finished by the crystallisation of amorphous products of thermolysis at 410 °C accompanied by an exothermic effect. At 520 °C, mixed oxides $M_{0.11}V_2O_{5.16}$ are formed, which give only 001 peaks in the diffractograms of their film samples. Ion exchange is employed for the preparation of xerogels of the polyvanadates $M_2(V_{12}O_{31})_3 \cdot n\,H_2O$ (M = Ln, Al, Ga, In, *n* changes in the range

$27 \leqslant n \leqslant 40$ depending on the air humidity)[11] and xerogels of cerium(III) and cerium(IV) polyvanadates with the compositions $Ce_2(V_{12}O_{31})_3 \cdot n\,H_2O$ ($11.0 \leqslant n \leqslant 15.0$) and $[Ce(OH)_2]_xH_{2-2x} \cdot V_{12}O_{31} \cdot n\,H_2O$ ($0.07 \leqslant x \leqslant 0.50$ and $11.0 \leqslant n \leqslant 27.0$).[31]

Metal ions present in the dispersion medium affect the properties of vanadium(V) oxide gel.[32] In the presence of Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Cr^{3+} and La^{3+} cations, the aggregative stabilities of the hydrosols depend on the amount of metal ions included in the layered structure. The influence of intercalated cations on the absorption of water by $V_2O_5 \cdot n\,H_2O$ has been studied.[33] Lithium cations affect weakly the water absorption. This is explained by their small charge and their ability to form highly hydrated compounds. Intercalated Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Cr^{3+} and La^{3+} cations exert a dual effect on the water absorption. The hydrophilicities of the cations favour higher absorption of water vapour from air at low relative humidity. At the same time, the energy of the system increases upon intercalation of such cations due to the increase in the interlayer electrostatic charge, which lowers the ability of the layers to move apart.

Intercalation of the NH_3 molecules into $V_2O_5 \cdot n\,H_2O$ xerogel has been studied.[34] It was found that the first absorbed NH_3 molecules interact with water of the hydrate to form the NH_4^+ ions [according to our data, with the formation of the compound $(NH_4)_2V_{12}O_{31} \cdot n\,H_2O$]. Later on, NH_3 molecules or the NH_4^+ ions, which cannot be detected by IR spectroscopy, were identified on the surface of the xerogel. After the introduction of water vapour in the gas phase containing NH_3, the topotactic formation of ammonium metavanadate takes place in the 001 plane of the xerogel. In this process, the NH_3 and H_2O molecules occupy the positions between the vanadium–oxygen layers, then dissolution of the hydrate structure occurs followed by crystallisation of NH_4VO_3.

Intercalation of cations into vanadium oxide xerogel can be carried out with the use of the corresponding organometallic compounds.[35] The reaction of $V_2O_5 \cdot 0.4\,H_2O$ aerogel with dibutylmagnesium, trimethylaluminium and dimethylzinc in heptane at room temperature gave the corresponding composites, which contained 4 moles of Mg^{2+}, 3.33 moles of Al^{3+} and 2.5 moles of Zn^{2+} per mole of V_2O_5.

A new type of mixed composites was synthesised based on vanadium(V) oxide xerogel and montmorillonite clay, namely, bentonite. The green-coloured product has the composition $Al_2O_3 \cdot 4\,(SiO_2)_2 \cdot x\,(V_2O_5) \cdot y\,H_2O$ ($x = 2.7–3.5$ and $y = 2.6–3.5$)[36] or bentonite $\cdot\, y\,V_2O_5 \cdot z\,H_2O$ ($y = 1.5–4.0$ and $z = 5–12$).[37] The composite is promising as a cathode material for chemical current sources: it possesses high conductivity inherent in the vanadium–oxygen xerogel layers and ion-exchange properties characteristic of the laminar clays. The compound has a layered type structure with $d = 12.8$ Å. This value is intermediate between the d values of 10.8 and 15.2 Å, which correspond to the initial substances, *viz.*, $V_2O_5 \cdot n\,H_2O$ xerogel and bentonite. According to thermogravimetric analysis,[36] dehydration of the composite occurs in discrete steps. In the first step, 2.5 moles of weakly bound water are removed at a temperature below 120 °C. The second step, close to 180 °C, corresponds to the removal of 0.6 moles of stronger bound water. Full dehydration with removal of the remaining 0.4 moles of H_2O occurs at 400 °C. The formation of V–O–Si bonds in the mixed composite was confirmed by a comparative analysis of the IR spectra of the compounds. A new intense absorption band at 835 cm^{-1} appears and vibrations of the V=O and Si–O bonds in the region 1010–1045 cm^{-1} become weaker. Intercalation of the redox-active hexaammineruthenium complex in the interlayer space of the composite bentonite–$V_2O_5 \cdot n\,H_2O$ xerogel leads to an increase in its electrochemical response by at least 4 orders of magnitude. It thus follows that the films of the intercalated composite can be used as a material for the preparation of modified electrodes. Moreover, this composite is stable in aqueous solutions, and therefore no special polymeric coatings are needed.

A layered structure of vanadium(V) oxide xerogel is retained upon replacement of vanadium by tetra- and hexavalent ions. The chemistry, thermodynamics and properties of the intercalation compounds $M_xV_{2-y}T_yO_{5\pm\delta} \cdot n\,H_2O$ (M is proton, an alkali or alkaline-earth metal ion; T = Ti, Mo, W, Cr) have been documented.[38–48] It was found that even small additives of the element T favour polymerisation of the sol to give stable gels. High intercalation capacity with respect to M^{z+} and thermal stability are characteristic of the intercalation compounds based on such complex vanadium oxides. Depending on the proportion of V to T, the compounds exhibit predominantly the properties of electronic or ionic conductors.

Vanadium-containing intercalation compounds include layered substances of the general formula $VTO_5 \cdot n\,H_2O$ ($VOTO_4 \cdot n\,H_2O$) and intercalation compounds based on them, $M_xVTO_5 \cdot n\,H_2O$ (T = P, As, Nb, S, Mo).[49] The latter compounds are obtained by redox intercalation of the cations M = Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+} in aqueous and non-aqueous media in the presence of a reducing agent.[50–53] The reduction of vanadium is mediated by intercalation of a reducing agent followed by reduction of the isolated V^{5+} centres rather than by electron transport through a lattice of $VTO_5 \cdot 2\,H_2O$. Intercalation of inorganic cations into $VPO_5 \cdot 2\,H_2O$ disturbs the short-range order, as follows from both the broadening and the decrease in intensity of the diffraction maxima, and lowers the crystallinity of the initial vanadium(V) phosphate. $VO(HPO_4) \cdot 0.5\,H_2O$ also has a layered structure. Studies on the intercalation of Zn^{2+}, Ni^{2+} and Pd^{2+} into this compound have shown that the activities of intercalation compounds as catalysts of hydrogenation depend on the method of intercalation.[54, 55]

IV. Intercalation of organic compounds and complex ions

The study of the intercalation of a homologous series of compounds $C_nH_{2n+1}N(CH_3)_3Br$ ($n = 1–18$) and $C_nH_{2n+1}NH_2$ into $V_2O_5 \cdot 1.6\,H_2O$ xerogel has revealed[5] the influence of steric factors on the structure of the complex formed. Depending on the length of the hydrocarbon chain, its orientation with respect to the vanadium–oxygen planes changes: the chain can be parallel ($n < 7$), inclined ($7 \leqslant n \leqslant 11$) or perpendicular ($n > 11$) to these planes. The interlayer distance changes correspondingly (Table 2). With the parallel arrangement of alkylammonium ions or alkylamines, the distance between vanadium–oxygen layers does not depend on the length of the alkyl chain and is equal to 12.9 and 12 Å for the compounds of the $RN(CH_3)_3Br$ and RNH_2 types, respectively. On average, the complex compound contains 0.3–0.4 moles of the intercalant per mole of V_2O_5. These complexes are stable up to 160 °C, at higher temperatures amorphous vanadium(V) oxide is formed, which transforms into orthorhombic V_2O_5 at 400–450 °C. Intercalation of trimethylammonium ions occurs by a cation-exchange mechanism, while in the case of amines, the mechanism is more complex and includes transfer of the electrons between the matrix and the compounds being intercalated.

Table 2. Interlayer distances (Å) for complexes $V_2O_5 \cdot n\,H_2O$–$C_nH_{2n+1}N(CH_3)_3Br$ (**I**) and $V_2O_5 \cdot n\,H_2O$–$C_nH_{2n+1}NH_2$ (**II**).[5]

n	I	II
12	31.1	27.9
13	–	29.4
14	33.5	30.6
15	–	32.1
16	36.5	33.7
18	38.0	36.3

Amine-interalated layered vanadium(V) oxides of the general formula $V_2O_5(H_2O)(C_nH_{2n+1}NH_2)_2$ (n = 4, 6, 8) have been synthesised.[56] The synthesis was carried out by vigorous stirring of a suspension of $V_2O_5 \cdot 0.6\,H_2O$ and an n-alkylamine (molar ratio 1 : 15) at room temperature for 48 h. The compositions of the compounds obtained may be expressed by the formulae $V_2O_5(H_2O)_{1.00}(C_4H_9NH_2)_{1.69}$, $V_2O_5(H_2O)_{1.09}(C_6H_{13}NH_2)_{1.82}$ and $V_2O_5(H_2O)_{1.26}(C_8H_{17}NH_2)_{1.80}$. The compounds possess laminar structures with interlayer distances of d_{001} = 13.8, 16.4 and 19.6 Å for butyl-, hexyl- and octylamine, respectively. The study of the ion-exchange properties of amine-intercalated compounds in aqueous 4 M solutions of CH_3COONa and CH_3COOK showed that alkylammonium ions form bilayers between the vanadium – oxygen layers. These ions are easily replaced by Na^+ or K^+ cations, which decreases the interlayer distance to 7.9 and 7.0 Å, respectively, independent of the length of a hydrocarbon substituent. A structural model for vanadium oxide intercalated with octylamine is shown in Fig. 5. On heating of this compound to 200 °C, its structure changes and d_{001} becomes equal to 22 Å. This d_{001} value as well as a layered structure are preserved up to 400 °C. Above 600 °C, a crystalline phase of V_2O_5 is formed.

IR, XPS and ESR studies of the interlayer absorption of ammonia, pyridine (py) and pyrazine into $V_2O_5 \cdot n\,H_2O$ xerogel have revealed the protonation of the nitrogen-containing bases (B) absorbed in the interlayer space.[57]

$$V^{5+}(H_2O) + B \longrightarrow [V(OH)]^{4+} + B{-}H^+. \qquad (2)$$

Despite partial reduction of pentavalent vanadium upon absorption, the mechanism of intercalation consists mainly of protonation of the base by hydroxonium ions, which compensate the negative charge of the vanadium-oxygen layers (0.2 e per vanadium ion) and/or by water molecules with the formation of OH groups. Treatment of $V_2O_5 \cdot nH_2O$ xerogel with ammonia or pyridine resulted in the disappearance of the hyperfine structure from the ESR spectra. In the IR spectra of the compounds obtained, the absorption band at 975 cm^{-1} appears, which relates to $\nu(V^{4+}{=}O)$ vibrations. These vibrations contribute much less than the stretching vibrations $V^{5+}{=}O$ with the maximum absorption at 1020 cm^{-1}. Treatment of $V_2O_5 \cdot 1.5\,H_2O$ xerogel with ammonia and pyridine affords compounds with the compositions $V_2O_5(NH_4^+)(OH^-) \cdot 0.5\,H_2O$ and $V_2O_5[(pyH^+) \cdot (OH^-)]_{0.3} \cdot 0.6\,H_2O$ with interlayer distances 10.53 and 13.00 Å, respectively.

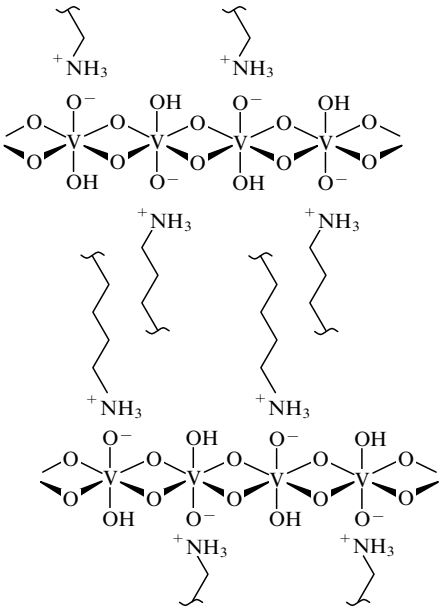


Figure 5. Structural model of the vanadium(V) oxide xerogel intercalated with octylamine.

The orientation of the pyH^+ ions is such that the C_2 axis of the heterocycle is perpendicular to the vanadium – oxygen layers.

Molecules of various solvents can easily replace water molecules in the $V_2O_5 \cdot 1.6\,H_2O$ xerogel;[5] the interlayer distance changes in this case (Table 3). Mono- or divalent cations solvated by the molecules of organic solvents are also intercalated into the xerogel.[5] The interlayer distance in the complexes obtained by intercalation of Li^+, Na^+, K^+, Rb^+, Cs^+ and Mn^{2+} into the xerogel is determined by the nature of the solvent and by the charge-to-effective radius ratio characterising the guest cation (Table 4).

Table 3. Maximum (d_1) and intermediate ($d_2 - d_4$) interlayer distances (Å) for composites $V_2O_5 \cdot n\,H_2O$ – organic solvent.[5]

Solvent	d_1	d_2	d_3	d_4
Sulfolane	22.7	17.6	–	13.9
Propylenecarbonate	22.2	21.6	17.5	13.0
Ethylenecarbonate	20.6	–	–	–
N-Methylacetamide	18.9	–	15.8	–
Dimethyl sulfoxide	17.6	–	16.5	–
Glycerol	16.6	–	–	–
Ethylene glycol	16.6	–	13.0	–
2-Aminoethanol	16.2	–	–	–
Formamide	14.4	–	–	–
Diethyl carbonate	14.2	–	–	–
N-Methylformamide	13.9	–	–	–
Tetrahydrofuran	13.8	–	–	–
Acetamide	12.7	–	–	–

Table 4. Interlayer distances (d/Å) for intercalation compounds $V_2O_5 \cdot n\,H_2O$ – organic solvent – M^{z+} (Ref. 5).

Solvent	d for intercalation compound with M^{z+}					
	Li^+	Na^+	K^+	Rb^+	Cs^+	Mn^{2+}
Dimethyl sulfoxide	18.4	18.7	14.1	11.0	11.0	18.3
N,*N*-Dimethylformamide	16.6	16.8	13.6	13.7	11.0	16.5
N-Methylacetamide	18.7	18.8	19.1	14.8	11.0	18.1
N-Methylformamide	16.1	16.6	16.4	14.6	11.0	16.2

Intercalation of molecules of n-alcohols into $V_2O_5 \cdot n\,H_2O$ has been considered [58] as the absorption of alkyl chains containing a different number of carbon atoms and having a polar OH group. It was found that methanol and ethanol molecules are oriented parallel to the vanadium – oxygen layers, while the molecules of alcohols with more than two carbon atoms have a perpendicular orientation. From the character of the alcohol absorption – desorption isotherms it was determined that $\sim$0.5 moles of an alcohol are irreversibly intercalated into 1 mole of $V_2O_5 \cdot n\,H_2O$. These alcohols can be displaced by the action of water vapour followed by evacuation. The interlayer distances in the complexes do not depend on the vapour pressure of the alcohol in the case of alcohols with the number of carbon atoms n = 2 – 4, while in the case of $n > 4$, a noticeable increase in d is observed, which is not proportional to the size of the alcohol molecule. It is obvious that the mechanism of intercalation of n-alcohol molecules differs from that of alkylammonium cations and alkylamines.

The study of the thermal decomposition of complexes $V_2O_5 \cdot n\,H_2O$ – n-alcohol has revealed [59] that a layered structure of the matrix is retained up to 100 °C. Upon oxidation of the intercalated alcohol at 200 – 300 °C, the vanadium – oxygen framework is destroyed. However, the decomposition products hamper crystallisation of vanadium oxide and the sample remains amorphous up to 550 °C according to X-ray diffraction analysis.

In the case of intercalation of such readily oxidisable organic molecules as aniline,[60,61] pyrrole[62] and thiophene,[5,63] layered composite materials are obtained which contain a conducting polymerised layer in the interlayer space of the xerogel and combine a unique laminar microstructure of the matrix and the properties of a conducting polymer. The formation of these compounds is based on the redox reaction in which a monomer udergoes oxidation and polymerises, while vanadium(V) is partially reduced to a tetravalent state. The complex compound $(C_6H_4NH)_{0.44} \cdot V_2O_5 \cdot 0.5\,H_2O$ is a dark-blue colour and retains the layered structure of the xerogel with $d = 13.94$ Å. The conductivity of the compound obtained is higher than that of the original $V_2O_5 \cdot n\,H_2O$ xerogel by 4 orders of magnitude and amounts to $\sim 0.5\ \Omega^{-1}\ cm^{-1}$ at room temperature. Intercalation of 2,2′-bithiophene affords a black xerogel with the composition $(C_8H_4S_2)_{0.44} \cdot V_2O_5 \cdot 0.54\,H_2O$ possessing metallic lustre, its conductivity amounts to $0.1\ \Omega^{-1}\ cm^{-1}$ at room temperature.

Layered intercalation compounds of $V_2O_5 \cdot n\,H_2O$ xerogel with the cations $(CH_3)_4N^+$, $(C_2H_5)_4N^+$ and $C_6H_5NH_3^+$ are synthesised in aqueous solutions of tetramethylammonium, tetraethylammonium and anilinium salts, respectively.[64] The diffractograms of these compounds are characterised by the very narrow lines of the 00l reflections. The interlayer distances in the compounds synthesised are equal to 12.9, 13.1 and 13.9 Å, respectively.

An aerogel composite vanadium(V) oxide–polypyrrole (PPyr) is obtained[65] as a co-polymerisation product of pyrrole and a vanadylalkoxide precursor. Hydrolysis of $VO(OC_3H_7)_3$ in a mixture pyrrole + water + acetone leads to the formation of a monolithic green–black gel, drying of which yields aerogel with a specific surfce area of $150-257\ m^2\ g^{-1}$ and a density of $0.1-0.2\ g\ cm^{-3}$. Electroconductivity of this composite decreases with the increase in the content of pyrrole. When V_2O_5 and the colloidal polypyrrole are used as the starting compounds, the latter compound is intercalated into the ribbons of vanadium(V) oxide. This microcomposite gel (the specific surface area is $80-140\ m^2\ g^{-1}$) has an electroconductivity equivalent to that of V_2O_5.

The microstructure and properties of the aerogel composite V_2O_5–PPyr depend on the method of its synthesis.[62,66] The composite prepared by dispersion of presynthesised polypyrrole particles into $V_2O_5 \cdot n\,H_2O$ (the matrix) has a nano-dimensional scaly nonhomogeneous structure. 'Post-gel' polymerisation, which includes sequential polymerisation of inorganic and organic phases, improves the microstructure of the hybrid material. The electroconductivity of the preformed specimens with the composition $(PPyr)_{0.35}V_2O_5 \cdot 1.8\,H_2O$ is equal to $(2-7) \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$. This value lies in the interval between the conductivities of aerogel $V_2O_5 \cdot n\,H_2O$ ($< 10^{-5}\ \Omega^{-1}\ cm^{-1}$) and polypyrrole ($5.6 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$). The results of a study of the hybrid material by cyclic voltammetry showed that its capacity with respect to reversibly intercalated lithium ion amounts to 1.4 moles of Li per mole of $(PPyr)_{0.35}V_2O_5$. The specific discharge capacity of the cathode based on this material is twofold less than that of the cathode prepared from aerogel $V_2O_5 \cdot n\,H_2O$ and is equal to 95 mA h g^{-1}. 'Joint synthesis', consisting of simultaneous spontaneous polymerisation of the organic and inorganic precursors, leads to the formation of the hybrid composite $(PPyr)_{0.8}V_2O_5 \cdot n\,H_2O$ with nano-dimensional scaly homogeneous microstructure. The intercalation capacity of this material with respect to lithium equals 3.0 moles per mole. Redox intercalation of polypyrrole into the laminar hybrid material bentonite–vanadium(V) oxide xerogel affords a semoconducting ternary composite,[67] which combines the properties of layered V_2O_5 and the conducting polymer.

Redox-mediated intercalation of aniline and its salts into the $V_2O_5 \cdot n\,H_2O$ xerogel can be accompanied by their polymerisation.[61,68] At the molar ratio of anilinium iodide to $V_2O_5 \cdot n\,H_2O$ equal to 4, compound $(C_6H_5NH_3)_{0.4}V_2O_5 \cdot 0.4\,H_2O$ was obtained, while in the case of oxidative polymerisation of aniline, the complex $[(1/n)(C_6H_4NH)_n]_{0.4} \cdot V_2O_5 \cdot 0.4\,H_2O$ (Fig. 6) is formed.[61] IR spectra of these substances differ noticeably in frequencies of the stretching vibrations of V—O bonds: the main bands appear at 1000, 750, 496 cm^{-1} and at 990, 852, 530 cm^{-1} for the former and the latter compound, respectively. Intercalative intralaminar growth of the polymer in the nanocomposites polyaniline (PAni)–$V_2O_5 \cdot n\,H_2O$ is promoted by molecular oxygen which is activated by vanadium ions. The process results easily in the formation of the monolayers of PAni with the interlayer distance of 5.6 Å.[68] Both during and after polymerisation, oxygen plays the role of the electron acceptor.

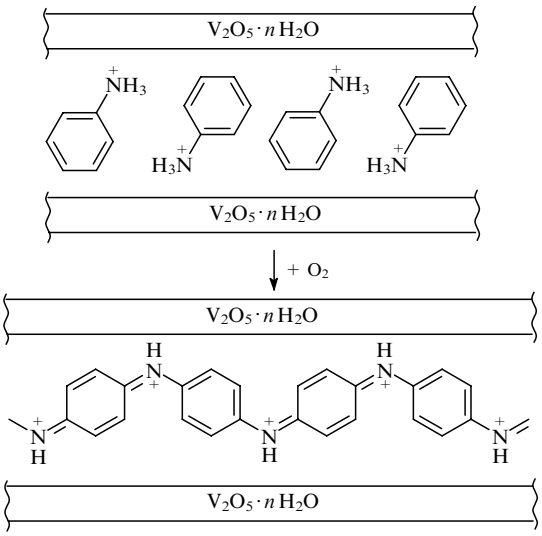


Figure 6. Schematic representation of the polymerisation of anilinium in the $V_2O_5 \cdot n\,H_2O$ xerogel.[61]

The study of the hybrid system PAni–$V_2O_5 \cdot n\,H_2O$ xerogel with different molar ratios of the components has revealed the formation of two phases, *viz.*, $(C_6H_4N)_{0.6}V_2O_5 \cdot n\,H_2O$ and $(C_6H_4N)_{1.2}V_2O_5 \cdot n\,H_2O$.[69] The interlayer distance in the former phase is 14 Å, which corresponds to the intercalation of one monolayer of PAni into the xerogel. In the latter phase, the interlayer distance is ~ 20 Å, which is consistent with intercalation of two monolayers of PAni. On ageing of the nanocomposites $(PAni)_xV_2O_5 \cdot n\,H_2O$ in air, partial reoxidation of reduced vanadium and further oxidative polymerisation of the oligomers of PAni inside the layers of the xerogel occurs, which leads to elongation of the polymeric chains. The latter conclusion is confirmed by the increase in molecular mass of PAni extracted from aged intercalation compounds as compared to freshly prepared ones. Thermal stability is higher for the aged samples of PAni than for the initial ones. All the samples of $(PAni)_x \cdot V_2O_5 \cdot n\,H_2O$ are paramagnetic. Magnetic susceptibility obeys the Curie–Weiss law; the van Fleck contribution does not depend on temperature. Electroconductivity of the freshly prepared hybrid material PAni–$V_2O_5 \cdot n\,H_2O$ depends on the degree of polymerisation of aniline inside the layers of xerogel and is always higher for the aged samples. At room temperature, the electroconductivity is equal to $10^{-6}-10^{-1}\ \Omega^{-1}\ cm^{-1}$, while the thermoelectric power has a negative value which changes from -30 to 200 μV deg^{-1} depending on the degree of polymerisation.

An analogous composite compound was obtained upon interaction of the emeraldin base with the V_2O_5 sol.[70] The interlayer distance in the dark-violet composite $(PAni)_{0.65} \cdot V_2O_5$ amounts to 13.8 Å, its electroconductivity is $3 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$; this compound is virtually insoluble in most organic solvents. ESR studies have revealed that the electron density is transferred from the lone electron pair on the nitrogen atom of the polymeric chain to V^{5+}.

Dark-green complexes with the compositions $(PAni \cdot HClO_4)_{0.52} \cdot V_2O_5$ and $(PAni \cdot HBF_4)_{0.55} \cdot V_2O_5$ containing doped polyaniline have been described.[70] Their interlayer distances (14.0 and 13.8 Å, respectively) are somewhat larger than for $(PAni)_{0.65} \cdot V_2O_5$. It is apparently caused by additional intercalation of the anion-dopant into the layered structure. Due to the presence of doped polymer in the compounds $(PAni \cdot HClO_4)_{0.52} \cdot \cdot V_2O_5$ ($\sigma = 8 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$) and $(PAni \cdot HBF_4)_{0.55} \cdot V_2O_5$ ($\sigma = 9 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$), their electroconductivities are higher than those of the non-doped $(PAni)_{0.65} \cdot V_2O_5$. The composites synthesised are redox-active in both aqueous acidic and organic aprotic electrolytes. For instance, virtually no destruction of $(PAni)_{0.65} \cdot V_2O_5$ occurred upon multiple cycling in 1 M HCl solution in the potential range of 0.2 – 1.0 V.

A new hybrid material based on a binary polymeric component including poly(2,5-dimercapto-1,3,4-thiadiazole) (PDMcT) and PAni was synthesised.[71] It was reported [72] that intercalation of the 2,5-dimercapto-1,3,4-thiadiazole (DMcT) dimer leads to its polycondensation with formation of the composite (PDMcT)/V_2O_5. Dithiol DMcT is a promising charge-accumulating material. Due to a reversible redox reaction, it polymerises upon oxidation (charge) and depolymerises upon reduction (discharge). It is known that DMcT and PDMcT are not conductors, but their participation in electrochemical processes allows one to increase the effeciency of exploitation of the conducting polymer, *e.g.*, PAni. A hybrid material (PDMcT)/V_2O_5 is obtained by mixing a methanolic solution of the monomer DMcT with $V_2O_5 \cdot n\,H_2O$ gel in the molar ratio 1 : 2. The reaction mixture is then kept under constant stirring at room temperature for 24 h. The resulting brown precipitate is filtered off, washed with methanol and dried at 50 °C in a vacuum.

Synthesis of a green-coloured composite (PDMcT + PAni)/V_2O_5 is carried out according to the same scheme with addition of aniline to the reaction mixture in the ratio V_2O_5 : Ani = 1 : 1. X-Ray and IR studies on the hybrid material built of a binary polymeric component and $V_2O_5 \cdot n\,H_2O$ xerogel confirmed cointercalation of DMcT and Ani with the formation of polymers, *viz.*, PDMcT and PAni, in the V_2O_5 matrix. In the IR spectrum, the band at 1015 cm^{-1}, corresponding to the vibrations of the V = O bond, is displaced to the low-frequency region up to 1000 and 1005 cm^{-1} for PAni/V_2O_5 and (PDM_cT + PAni)/V_2O_5, respectively. The interlayer distance in the xerogel increases from 11.79 to 13.83 Å for all the polymer-intercalated specimens. Studies on the electronic structure showed insignificant distortions of octahedral symmetry of VO_6, which are accompanied by partial reduction of the V^{5+} ions. The specific discharge capacity for the composites polymer/V_2O_5 is lower than that for the original $V_2O_5 \cdot n\,H_2O$ xerogel (205 mA h g^{-1}) and amounts to 200 and 187 mA h g^{-1} for PDMcT/V_2O_5 and (PDMcT + PAni)/V_2O_5, respectively. This effect can probably be associated with a decrease in the vanadium oxidation state. However, the discharge capacity increased by 10% for PDMcT/V_2O_5 and by 17% for (PDM_cT + PAni)/V_2O_5 after treatment of the specimens in the flow of oxygen at 100 °C for 3 h. Possibly, the enhancement of the electrochemical characteristics occurs due to partial reoxidation of vanadium ions and formation of longer polymeric chains in the interlayer space of the $V_2O_5 \cdot n\,H_2O$ xerogel. Intercalated PDMcT can be considered as an active additive to PAni, intensifying a reversible process of lithium intercalation – deintercalation.

Intercalation compounds of $V_2O_5 \cdot n\,H_2O$ xerogel with complexes $M(bipy)_3^{2+}$ (M = Ru, Ni and Co; bipy is bipyridine) are of interest as photochemical materials and can be used in photocatalysis for decomposition of water.[73] The formation of an intercalation compound with the complex is accompanied by an increase in the interlayer distance by ~8 Å, which corresponds to intercalation of a monolayer of $M(bipy)_3^{2+}$ (Table. 5). The content of $M(bipy)_3^{2+}$ in the $V_2O_5 \cdot n\,H_2O$ xerogel is somewhat less than the theoretical value (0.2 moles per mole of V_2O_5) and amounts to 0.16, 0.14 and 0.11 moles for M = Ru, Ni and Co, respectively.

Table 5. Compositions and interlayer distances for intercalation compounds $V_2O_5 \cdot n\,H_2O - M(bipy)_3^{2+}$ (Ref. 73).

$M(bipy)_3^{2+}$	M : V_2O_5	bipy : M	d_{001} /Å
$Ru(bipy)_3^{2+}$	0.072	3.1	16.3
	0.12	3.1	17.1
	0.16	3.0	17.3
	0.16	3.2	17.1
$Ni(bipy)_3^{2+}$	0.14	3.2	17.4
$Co(bipy)_3^{2+}$	0.11	2.9	16.3

Thermal studies on this composite showed that a layered structure of $V_2O_5 \cdot n\,H_2O$ xerogel is stabilised upon intercalation of cations.

Xerogel-based nanocomposites with the general formula $(PEO)_xV_2O_5 \cdot n\,H_2O$ were obtained by stirring aqueous solutions of poly(ethylene oxide) (PEO) with vanadium(V) oxide gel followed by slow evaporation of water.[74] The interlayer distance in the compounds obtained changes from 13.2 to 16.8 Å in the region $x = 0.5 - 1.0$, whereas, at $1 < x < 3$, it changes from 17.6 to 18.3 Å. It was established by means of X-ray diffraction that the composites contain a monolayer or a bilayer of PEO molecules when $x < 1$ and $x \geqslant 1$, respectively. The PEO chains are close to each other and fill completely the interlayer space of the xerogel by wavy mono- or bilayers.

Complex compounds of $(PEO)_xV_2O_5 \cdot n\,H_2O$ with alkali metal ions are actively studied with the aim of their use as solid electrolytes and as materials with electrochromic properties.[75] A red composite $(PEO)_x \cdot V_2O_5 \cdot n\,H_2O$ has an interlayer distance of 13.2 Å, the chains of PEO are situated linearly in the interlayer space. A single-phase specimen is obtained in the ratio PEO : ($V_2O_5 \cdot n\,H_2O$) < 0.8. The composite is well moulded to a thin film which is more flexible than that of $V_2O_5 \cdot n\,H_2O$. The film of this specimen absorbs water reversibly, its content changes from 1.6 to 1.8 moles per mole of V_2O_5. Besides, the film can be involved in redox intercalation according to the reaction

$$x\,LiI + PEO/V_2O_5 \cdot n\,H_2O \longrightarrow \longrightarrow Li_xPEO/V_2O_5 \cdot n\,H_2O + (x/2)\,I_2\,. \quad (3)$$

The composite is a dark-blue colour and the interlayer distance 13.0 Å; its electroconductivity is higher than that of the original xerogel.

The PEO/$V_2O_5 \cdot n\,H_2O$ films are light-sensitive, they acquire a blue colour upon irradiation with a mercury lamp. These changes in colour are caused by the light-induced reaction in which PEO is oxidised by a pentavalent vanadium. The film of the original $V_2O_5 \cdot n\,H_2O$ xerogel is not light-sensitive. IR studies have shown that no structural changes occur on its irradiation. It has been revealed by ESR that the process is only accompanied by the increase in the concentration of V^{4+} centres. Measurements of the magnetic susceptibility have shown a noticeable increase in the magnetic moment which amounted to 0.8 μ_B per formula unit at 300 K. Upon irradiation of the intercalation compound, its conductivity increases by ~2 orders of magnitude, while the solubility decreases. A film with the composition $(PEO)_{0.5} \cdot V_2O_5 \cdot n\,H_2O$ exhibits semiconducting properties, its conductivity at room temperature equals $10^{-2}\ \Omega^{-1}\ cm^{-1}$.

By intercalation of such water-soluble polymers as tetrakis(*N*-methyl-4-pyridyl)porphine,[76] poly(ethylene glycol),[77] poly(propylene glycol), poly(vinylpyrrolidone), methylcellulose [78] and poly(4-ethylphenol) [79] into the $V_2O_5 \cdot n\,H_2O$ xerogel, ordered nanocomposite materials were obtained, their mechanical, optical and electrical properties can be controlled.

Intercalation of *N*-morpholinoisothiocyanate alone or together with copper ions into vanadium(V) oxide xerogel affords new complex compounds $(C_5H_8N_2OS)_{0.35}H_2(V_{12}O_{31-\delta}) \cdot 8.8\,H_2O$ and $(C_5H_8N_2OS)_{0.35} \cdot Cu_{0.2}H_2(V_{12}O_{31-\delta}) \cdot 10.5\,H_2O$, the inter-

layer distances in which are equal to 11.55 ± 0.05 and 14.30 ± 0.05 Å, respectively.[80] Intercalation of $C_5H_8N_2OS$ molecules was found to increase thermal stability of the xerogel (from 345 to 370 °C). As the temperature decreases from +50 to −50 °C, the electroresistivity increases sharply for these compounds, and the copper-containig xerogels always possess lower resistivities.

Upon interaction of 3,4-dihydroxyphenylalanine with $V_2O_5 \cdot n\,H_2O$ gel, a new hybrid material with the composition $(C_8H_9NO_2)_xV_2O_5 \cdot n\,H_2O$ was synthesised, which is characterised by a dark-blue colour and metallic lustre.[81,82] The composite retains the laminar structure of the xerogel at $x < 0.02$, its interlayer distance is ~15 Å. A thin-film sample of this material possesses high stability in the electrochemical intercalation–deintercalation of Li^+ and is completely recovered even after 60 oxidation–reduction cycles. It was found that the intercalation of the alanine derivative into the $V_2O_5 \cdot n\,H_2O$ xerogel lowers the activation energy of conductivity from 0.35 to 0.20 eV.

Compounds of the $V_2O_5 \cdot x\,(ML_2X) \cdot n\,H_2O$ type (M = Fe, Co, L is cyclopentadienyl, X = Cl, Br, I) were obtained by interaction of 5×10^{-3} M aqueous solution of ML_2X with vanadium(V) oxide xerogel.[5] The interlayer distance in these compounds depends neither on the water content in the initial xerogel nor on the nature of the anion and amounts to ~13.22 Å. For the intercalation compounds with organometallic complexes, the main mechanism of formation consists of the exchange between the cations of the intercalant and the protons of hydrated polyvanadium acid. The formula of the iron-containing compounds was established as $V_2O_5 \cdot 0.4\,Fe(C_5H_5)_2 \cdot n\,H_2O$ ($n < 0.5$). Heating of the intercalation compounds in air up to 100 °C results in the loss of absorbed water. The structure of iron- and cobalt-containing complexes remains virtually unchanged up to 200 and 340 °C, respectively. Analysis of the widths of reflections in the diffractograms showed that the coherence length is noticeably increased for these compounds, in particular, for the cobalt-containing ones. Pentadienyl rings are oriented perpendicular to the layers of the basic structure and scaly-like stratifying occurs.

Complexes $V_2O_5 \cdot (H_2O)_{0.6} \cdot [FcH]_{0.27}$, $V_2O_5 \cdot (H_2O)_{0.6} \cdot [FcMe_2]_{0.22}$ and $V_2O_5 \cdot (H_2O)_{0.6} \cdot [FcCH_2NHMe_2^+]_{0.16}$ were obtained by intercalation of the $V_2O_5 \cdot n\,H_2O$ xerogel with ferrocene, 1,1′-dimethylferrocene or (ferrocenylalkyl)ammonium halides, respectively, using their ethanolic solutions.[83] These complex compounds are formed mainly due to a redox reaction between iron and the V^{5+} ions and partly due to an ion exchange. The interlayer distances for the xerogels intercalated with ferrocene or with its alkylamino derivatives are virtually the same (13.2–13.5 Å) (Table 6), which suggests parallel orientation of the alkylammonium cation with respect to the vanadium–oxygen layers (Fig. 7). X-Ray spectroscopic and ESR studies have revealed that the Fe^{3+} ions are localised near the V^{4+} ions. Analogous conclusions have been drawn[84] from the study on the intercalation of diferrocenyl compounds containing bridging alkyl groups [$Fc(CH_2)_nFc$; n = 1, 2] into the interlayer space of the $V_2O_5 \cdot n\,H_2O$ xerogel. In this case, intercalation is also caused by a redox reaction between iron and the V^{5+} ions. The guest molecules in $V_2O_5 \cdot (H_2O)_{0.8} \cdot (Fc^+CH_2CH_2Fc^+)_{0.23}$ are oriented nearly parallel to the vanadium–oxygen layers. Orientation of a cobaltocenium ion in the interlayer space of the complex compound $V_2O_5[Co(C_5D_5)_2]_{0.2} \cdot (H_2O)_{0.5}$ has been studied by ^2H NMR.[85] It was found that the C_5 axes are directed parallel to the vanadium–oxygen framework.

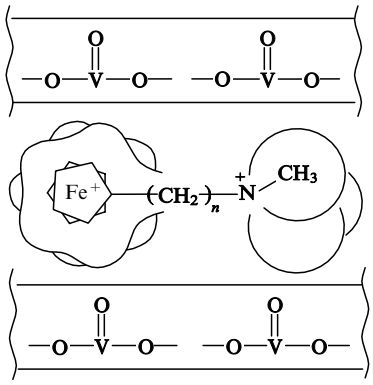


Figure 7. Schematic representation of the arrangement of (ferrocenylalkyl)ammonium compounds in the interlayer space of the $V_2O_5 \cdot n\,H_2O$ xerogel.[83]

The possibility of intercalation of vanadium(V) oxide xerogel with various macrocyclic compounds as, for instance,

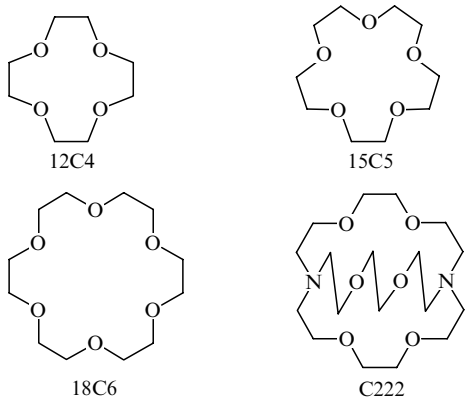
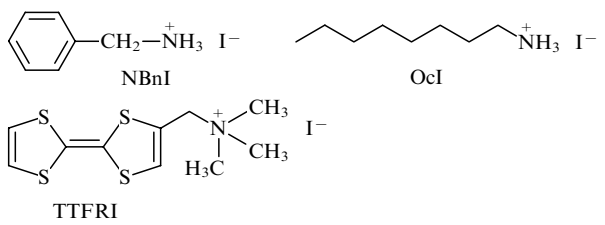


Table 6. Compositions and interlayer distances for intercalation compounds based on the $V_2O_5 \cdot n\,H_2O$ xerogel.[83–86]

Intercalation compound	d_{001} /Å	Intercalation compound	d_{001} /Å
$V_2O_5 \cdot (H_2O)_{1.6}$	11.6	$V_2O_5(18C6)_{0.19} \cdot 0.83\,H_2O$	17.1
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [FcH]_{0.27}$	13.4	$V_2O_5(C222)_{0.12} \cdot 0.39\,H_2O$	17.4
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [FcMe_2]_{0.22}$	13.4	$Li_{0.26}V_2O_5(12C4)_{0.35} \cdot 0.15H_2O$	16.3
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [FcCH_2NHMe_2^+]_{0.16}$	13.5	$Li_{0.26}V_2O_5(15C5)_{0.27} \cdot 0.03H_2O$	17.3
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [FcCH_2NMe_3^+]_{0.15}$	13.2	$K_{0.26}V_2O_5(18C6)_{0.07} \cdot 0.39H_2O$	16.2
$V_2O_5 \cdot (H_2O)_{0.8} \cdot [FcCH_2CH_2NH_3^+]_{0.21}$	13.4	$V_2O_5(Bn)_{0.17} \cdot 0.61\,H_2O$	13.5
$V_2O_5 \cdot (H_2O)_{0.8} \cdot [FcCH_2CH_2NMe_3^+]_{0.14}$	13.5	$V_2O_5(Bn)_{0.31} \cdot 0.35\,H_2O$	13.8
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [FcCH_2NHMe_2^+]_{0.18}$	13.0	$V_2O_5(Oc)_{0.11} \cdot 0.89\,H_2O$	12.4
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [FcCH_2CH_2NH_3^+]_{0.22}$	13.4	$V_2O_5(Oc)_{0.25} \cdot 0.29\,H_2O$	12.4
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [PhCH_2NHMe_2^+]_{0.29}$	14.2	$V_2O_5(Oc)_{0.33} \cdot 0.29\,H_2O$	20.5
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [PhCH_2NMe_3^+]_{0.24}$	14.1	$V_2O_5(Oc)_{0.46} \cdot 0.10\,H_2O$	24.0
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [n\text{-}C_8H_{17}NH_3^+]_{0.33}$	26.0	$V_2O_5(TTFR)_{0.06} \cdot 1.32\,H_2O$	12.5
$V_2O_5(12C4)_{0.44} \cdot 0.54\,H_2O$	20.4	$V_2O_5(TTFR)_{0.16} \cdot 1.15\,H_2O$	13.8
$V_2O_5(15C5)_{0.22} \cdot 0.65\,H_2O$	16.9		



where 12C4 is 12-crown-4, 15C5 is 15-crown-5, 18C6 is 18-crown-6, C222 is cryptand-2,2,2, NBnI is benzylammonium iodide, OcI is octylammonium iodide, and TTFRI is *N*,*N*,*N*-trimethylammoniomethyltetrathiafulvalene iodide, was discussed.[86–89]

The formation of a hybrid product based on crown ethers proceeds by a complexation mechanism. Cyclic guest molecules interact as the ligands with protons or metal ions (Li^+, Na^+) localised in the interlayer space of the xerogel with simultaneous partial replacement of water molecules. The compositions and the interlayer distances of the compounds obtained are given in Table 6. IR spectroscopic studies have revealed that the absorption band characterising $\delta(H-O-H)$ vibrations is shifted from its position for the initial matrix (1620 cm^{-1}) to 1635 and 1644 cm^{-1} for $18C6/V_2O_5$ and $12C4/V_2O_5$, respectively. This indicates strengthening of the energy of binding between the water molecules and vanadium–oxygen layers in the intercalation compounds. It is obvious that intercalation of macrocyclic compounds into the $V_2O_5 \cdot n\,H_2O$ xerogel decreases the mobility of the protons and the ionic component of conductivity. Application of hybrid materials based on crown ethers for ion-selective membranes and sensors was proposed.[89]

Intercalation compounds of the $V_2O_5 \cdot n\,H_2O$ xerogel with tetrathiafulvalene (TTF) and benzidine (Bzd) are of interest as promising novel materials. In essence, they can be assigned to 'molecular bronzes'. Intercalation proceeds by a charge transfer mechanism. Irreversible intercalation of TTF into the $V_2O_5 \cdot n\,H_2O$ xerogel in a water–ethanolic solution leads to the formation of a complex compound $(TTF)_x \cdot V_2O_5$ ($x < 1.8$)[90] in which the interlayer distance amounts to 13.7 Å. This compound is insoluble in water, contains a large amount of strongly bound water and up to ~25% of vanadium ions in a tetravalent state. Electronic conductivity of $(TTF)_x \cdot V_2O_5$ depends on the stoichiometric composition of these complexes. The conductivity for specimens with $x = 0.17$ and 1.5 is larger than that for V_2O_5 by factors 46 and 15, respectively.

Black flake-like precipitate of compounds $(Bzd)_x-V_2O_5$ with a maximum Bzd content ($x = 1$) is formed in an irreversible reaction of $V_2O_5 \cdot n\,H_2O$ xerogel dispersed in water with an ethanolic solution of Bzd over a few seconds.[90] In the structurally similar compound $(TTF)_x-V_2O_5$, saturation with respect to intercalant is not achieved even at $x = 2.9$. The diffractogram of compound $(Bzd)_x-V_2O_5$ was found to contain 00l reflections corresponding to an interlayer distance of 15.6 Å. The benzidine molecules in the xerogel are inclined with respect to the vanadium–oxygen layers. Electronic conductivity of the complex compound $(Bzd)_x-V_2O_5$ ($\sigma = 2.8 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$) differs only slightly from that of the original xerogel.

The conditions for the preparation of intercalation products of $V_2O_5 \cdot n\,H_2O$ gel with methyl-, heptyl- and benzylviologens have been described.[91,92] As a result of ion exchange, the organic components are situated between the layers of the xerogel and orientation of their molecules depends on the type of viologen. With respect to the vanadium–oxygen layers, the molecules intercalated into the interlayer space of the xerogel are parallel (as a monolayer) in the case of methyl- and benzylviologens and perpendicular in the case of heptylviologen.

With intercalation of octyl-, benzyl- and TTF-ammonium iodides,[86] which is accompanied by a partial reduction of V^{5+} to V^{4+}, the conductivity of the $V_2O_5 \cdot n\,H_2O$ xerogel increases by 1.5–2 orders of magnitude. The compositions and interlayer distances for the compounds obtained are given in Table 6. The electroconductivity of the octyl-containing hybrids $V_2O_5(Oc)_x \cdot n\,H_2O$ depends on the x value and on the orientation of organic molecules in the interlayer space. At $x \leqslant 0.2$, the alkyl chains are situated parallel, while, at $x > 0.5$, they are mainly perpendicular to the vanadium–oxygen layers. The electroconductivity of the specimens with transversal geometry of the intercalant is limited by the mobility of charge carriers, *i.e.*, the electrons. Their mobility is associated with overcoming a high potential barrier on moving across the vanadium–oxygen layers. As a consequence, an increase in the interlayer distance leads to decrease in conductivity of the octyl-containing complex.

Mechanical activation of vanadium(V) oxide xerogel accelerates significantly the initial intercalation step as was established[93] with an example of n-hexadecyltrimethylammonium bromide. The interlayer distance in the compound obtained under equilibrium conditions equals 14.45 Å. This value is very close to the value of quadruplicate diameter of the alkyl chains (14.52 Å) and is twice as large as the parameter b of the crystal lattice of n-hexadecyltrimethylammonium bromide. It thus follows that the latter compound is situated parallel to the layers of the laminar structure of the xerogel.

Photo- and electrophotoactive nanocomposite materials can be obtained using organic dyes as intercalated substances. The study on the kinetics of intercalation of methylene blue (MB^+) into $V_2O_5 \cdot n\,H_2O$ gel by absorption spectroscopy in the range 500–800 nm has shown that the driving force of the process is the reduction of methylene blue by the V^{4+} species (see Ref. 94). Interaction of MB^+ with the gel can be described by the following scheme:

$$MB^+\ (soln.) \longrightarrow [MBH] \longrightarrow MBH^{2+}\ (abs.) \longrightarrow MB_2^{2+}\ (abs.) \quad (4)$$

Reduction of methylene blue is followed by protonation, reoxidation by oxygen and dimerisation of the dye. The rate constant for the transformation of protonated methylene blue into the dimer is 100 mol $litre^{-1}\ s^{-1}$.

Compounds based on the layered oxides VTO_5 (T = P, As, S, and others) with a structure of vanadyl phosphate $VOPO_4$ (Ref. 95) are relative to the above-considered intercalation compounds. In the phases intercalated by pyridine, this coordinates to vanadium and is situated perpendicular to the VTO_5 layers. Reduction of vanadium(V) virtually does not occur and the layers of the original matrix are retained. Cations of relatively large sizes, *e.g.*, ferrocenylalkylammonium, can be intercalated into a layered structure of $VOPO_4 \cdot H_2O \cdot EtOH$.[84,96]

The results of the study on the intercalation of $VOPO_4 \cdot H_2O \cdot EtOH$ with ferrocene and its alkyl derivatives (1,1′-dimethyl-, ethyl-, n-butyl-) as well as by cobaltocenium cations, carried out in ethanol, have been reported.[97] The interlayer distances in the compounds obtained are increased with respect to the interlayer distance of the initial phosphate (d_{001} = 7.5 Å) and reach 8.8–10.3 Å. Intercalated molecules of ferrocene and its derivatives were found to be situated perpendicular to the VPO_5 layers.

Layered hydrates of mixed oxides $VAsO_5 \cdot 3\,H_2O$ and $VPO_5 \cdot 2\,H_2O$ interact with alkylammonium iodides in an aqueous medium or in organic solvents with formation of compounds with the general formula $(RNH_3)_x V^{IV}_x V^{V}_{1-x} TO_5 \cdot H_2O$ ($R = C_nH_{2n+1}$, $n = 3–8$; $x = 0.4–0.6$; T = As, P). It is of note that the parameter d_{001} depends linearly on the number of carbon atoms in the alkyl radical C_nH_{2n+1}. A layered structure of the initial hydrates of mixed oxides $VTO_5 \cdot n\,H_2O$ is retained in these intercalation compounds.

Mixtures of aliphatic alcohols ranging from ethanol to n-heptanol are intercalated into the lattice of non-hydrated vanadyl sulfate $VOSO_4$ with the formation of the inclusion compounds.[98] Intercalation compounds of $VOPO_4 \cdot n\,H_2O$ with glycerol have been obtained.[99] These substances are unstable; on keeping in air, glycerol reduces vanadium to a tetravalent state and the specimen changes its colour from yellow to green. Incorporation of the

glycerol molecules into the interlayer space of vanadium(V) phosphates leads to disordered compounds.

The process of intercalation of aniline derivatives into $VOPO_4 \cdot n\,H_2O$ has been studied.[100, 101] It was found that their intercalation into the interlayer space of vanadyl phosphate occurs only due to protonation of amino groups or oxidation of the iodide ion accompanied by reduction of V^{5+} to V^{4+}.

V. Nanotubular forms of intercalation compounds

A search for various nano-structured functional materials is accompanied by the development of studies into the synthesis and investigation of properties of non-carbon nanotubes (nanotubulenes, NTs).[102] Vanadium(V) oxide-based nanotubulenes have been synthesised not long ago.[103] For their preparation, a sol–gel method was found to be effective, which allows one to obtain the xerogel with explicitly pronounced quasi-one-dimensional structure of the layers. By combination of the sol–gel method with hydrothermal treatment in air at 180 °C for 5 h, a nanowire with the composition $V_2O_5 \cdot 0.3\,H_2O$ and with a length of several tens of micrometers and a width of several tens of nanometers was synthesised.[104, 105]

An extensive body of experimental data on the chemistry of intercalation compounds based on the $V_2O_5 \cdot n\,H_2O$ xerogel served as a basis for searching new methods for synthesis of nanotubular forms of vanadium(V) oxide. Obviously, the possibility of changing the distance between the vanadium–oxygen layers in the layered structure of the xerogel upon intercalation of molecules of various organic substances in the interlayer space was used in the design of vanadium–oxide NT: in this case, the organic guest molecules act as a template and determine the structure of multi-layered nanotubular composites.

It was suggested[106–108] that primary amines $C_nH_{2n+1}NH_2$ ($4 \leqslant n \leqslant 22$) or diamines $H_2N(CH_2)_nNH_2$ ($14 \leqslant n \leqslant 20$) be used as structure-forming templates. For instance, ethanolic solutions of vanadium(V) triisopropyl oxide $(Pr^iO)_3VO$ and an amine taken in the molar ratio 2 : 1, were stirred for 1 h followed by hydrolysis. After ageing of this system for 12–96 h, an orange composite was obtained, which transformed into a black monophasic product after hydrotermal treatment in an autoclave at 180 °C for 2–7 days. The product was isolated in the form of nanotubes with a length of up to 15 μm, an outer diameter of 15–150 nm and an inner diameter of 5–50 nm. The walls of the tubes consisted of 2–30 layers of crystalline vanadium oxide with the amine or diamine molecules intercalated in the space between the layers. The distance between the layers was proportional to the length of alkylamine and changed in the range from 17 to 38 Å. The general formula of these compounds can be written as $VO_xO_{y/2} \cdot (C_nH_{2n+4}N)_y$. In the case of diamines, the tubes had thicker walls and smaller inner diameters than in the case of amines. The structure of the vanadium–oxygen layers comprised tetrahedra of VO_4 and tetragonal pyramids of VO_5. The tubes of vanadium oxide remained stable after removal of the amines and were destroyed upon thermal treatment above 250 °C.

Unlike mesoporous metal oxides with laminar structures, the composites under consideration are characterised by a tubular morphology and well-structured walls. According to the published data,[104] the 'volutes' of vanadium–oxygen layers are very flexible, they can be stretched in a line and can be involved in numerous exchange reactions. It was reported[109] that the synthesis of NT with the use of vanadium(V) oxychloride and oxide as precursors occurs in two stages. In the first step, $VOCl_3$ or V_2O_5 was mixed with a primary amine $C_nH_{2n+1}NH_2$ ($11 \leqslant n \leqslant 20$) in an inert atmosphere, then hydrolysed in an acetate buffer (pH 7) or in water. The next step consisted of hydrothermal treatment at 180 °C for 7 days. According to data from elemental analysis, the compositions of the NT synthesised from $VOCl_3$ or V_2O_5 correspond to the general formulae $VO_{2.45\pm0.05} \cdot (C_nH_{2n+4}N)_{0.27\pm0.01}$ ($11 \leqslant n \leqslant 16$) and $VO_{2.43\pm0.03} \cdot (C_nH_{2n+4}N)_{0.27\pm0.01}$ ($11 \leqslant n \leqslant 20$), respectively. Morphological characteristics of the vanadium oxide NT obtained from different precursors and templates are given in Table 7. It should be mentioned that the ends of the NT obtained by this method are open and characterised by a multi-layer morphology formed by the 'volutes' of vanadium–oxygen layers.

Table 7. Morphologic characteristics of the vanadium-oxide nanotubulenes (the template is $C_nH_{2n+1}NH_2$).[109]

Precursor	n	Outer diameter NT /nm	Inner diameter NT /nm	Number of layers	Length NT /μm
$(Pr^iO)_3VO$	$4 \leqslant n \leqslant 22$	15–150	5–50	2–30	1–15
$VOCl_3$	11	50–100	15–35	10–20	1.5–5
	16	80–100	20–35	11–14	0.8–1.5
V_2O_5	11	70–140	20–35	9–13	2–12
	12	50–90	15–35	7–13	1–3
	16	70–100	20–45	6–11	1–2
	20	60–90	20–45	6–10	1–3

Changes in the pH of the V_2O_5 gel by addition of ammonia allows one to synthesise NT with definite structural characteristics.[110] In neutral or weakly acidic media, tubes with an interlayer distance proportional to the length of the amine are formed. Nanotubulenes obtained at pH 9–10 have unique wall structures; these are built of the VO_x layers alternating regularly with intercalated molecules of the amine or ammonia (the interlayer distances VO_x-VO_x are equal to 2.0 and 0.9 nm, respectively). Nanotubulenes formed with the use of ammonia are characterised by a significantly larger outer diameter (> 250 nm) and by a smaller length (2–5 μm) as compared with the NT synthesised at pH 4–8. The general formula of the new NT was suggested to be $[(NH_4)_yVO_x][(C_nH_{2n+1}NH_3)_zVO_x]$. An excess amount of the amine in the NT is easily replaced by sodium, potassium, magnesium, calcium, strontium, iron, cobalt, nickel or copper cations.[111] This method of modification of VO_x-nanotubulenes may become effective for improving properties of the initial composite. This procedure does not change the tubular morphology and only decreases the interlayer distance from 2.8 nm (for $C_{12}H_{25}NH_3VO_x$) to 0.9–1.2 nm depending on the cation.

A new manganese-containing intercalation compound with tubular morphology with the general composition $Mn_{0.1}VO_{2.5+\delta} \cdot n\,H_2O$ was synthesised[112] by ion exchange starting from the layered precursor $V_2O_{5+\delta}(C_{12}H_{25}NH_3)$. For the NT obtained, the section diameter and the length reached 100 nm and 1300 nm, respectively. These NT contained such defects as partial destruction of the layers and their zigzag-like shape. The structure of the layers is tetragonal with unit cell parameters a = 6.157(3) and c = 10.52(3) Å. This compound was assayed as a cathode material in the electrochemical intercalation of lithium. It was found that 0.5 moles of lithium per mole of V_2O_5 are reversibly intercalated into these NT at a potential of ~2 V. The specific discharge capacity of the battery amounted to 140 A h kg^{-1}.

It was proposed[113] to use derivatives of *trans*-(1*R*,2*R*)- and *trans*-(1*S*,2*S*)-1,2-diaminocyclohexane as templates in the synthesis of helical chiral VO_x-nanotubulene structures. In the case of the *R*,*R*-enantiomer, a left-handed helix was always formed, while in the case of *S*,*S*-enantiomer it was right-handed.

Carbon NT can be used as templates for obtaining nanostructured vanadium oxide.[114, 115] The synthetic procedure includes covering of a carbon NT with V_2O_5 gel and subsequent removal of carbon by calcination at 700 °C. The carbon NT are pretreated with boiling HNO_3 for 24 h for creation of acidic centres on the surface. The diameters and the lengths of the NT synthesised according to this procedure amounted to 20–55 nm and 2–3 μm, respectively. Electron diffraction studies of the specimens have revealed their orthorhombic structures with unit cell parameters a = 11.44, b = 3.54 and c = 4.35 Å.

Unfortunately, most investigations into the VO_x-nanotubulenes are concerned mainly with synthetic procedures and studies on the morphology of specimens. Only a few publications (see, *e.g.*, Ref. 116) contain data on the physicochemical properties and evaluate the prospects for the application of vanadium-oxide NT as oxidation catalysts,[115] a cathode material for reversible lithium batteries [117–120] and a semiconducting material for the preparation of field-controlled transistors.[121]

VI. Applications of intercalation compounds

Most studies on the application of vanadium(V) oxide xerogels have focused on their use in the design of chemical power sources.[122] Compared to the crystalline vanadium oxides, the xerogels form very mobile layered structures in which various cations and molecules of organic substances can easily be intercalated and deintercalated. The advantages of xerogels include the ion-electronic type of conductivity and the possibility of displacing water molecules by hydrophilic organic solvents. Studies on the cathodic behaviour of superfine powders, films and nanocomposites of the intercalation compounds in the electric power sources with lithium anode merit special attention.[123–125] In a 1 M solution of $LiClO_4$ in propylenecarbonate (PC), the exchange of water molecules with molecules of the organic solvent occurs without application of a voltage; this is accompanied by an increase in the interlayer distance up to 21.5 Å. However, the solvent is further displaced by lithium and $Li_{0.4}V_2O_5$ is formed. In the discharge step, the formation of compounds $Li_{1.1}V_2O_5$ and $Li_{1.6}V_2O_5$ was detected. The layered structure of the xerogel is destroyed in the final step of intercalation of Li^+. The steady-state potential for the film with the composition $V_2O_5 \cdot 2.2\,H_2O$ in a 1 M solution of $LiClO_4$ in PC amounts to 3.20–3.85 V relative to metallic lithium.[126] The parameter d_{001} of the xerogel $Li_xV_2O_5 \cdot n\,H_2O$ changed from 11.6 to 16.7 Å on keeping the specimen in a solution of $LiClO_4$, decreased to 10.4 Å ($x = 0.2$) upon cathodic lithiation and then remained constant up to $x = 0.7$ in $Li_xV_2O_5 \cdot n\,H_2O$.

According to the reported data,[127] intercalation of PC results in compounds $V_2O_5 \cdot 0.1\,H_2O \cdot 0.3\,PC$ with the parameter $d_{001} = 22.0$ Å, which decreases to 11.0 Å for the ratio Li : V = 0.01 in the xerogel. Intercalation of Li^+ is accompanied by simultaneous insertion of PC, which weakens the interaction between the protons of the interstitial water and oxygen of the xerogel. Kinetic studies on a compound with the composition $Li_{0.3+x}V_2O_5 \cdot\ 0.2\,H_2O \cdot PC$ have revealed [128] that the chemical diffusion coefficient of lithium ions (D_{Li}) decreases from 10^{-8} to 10^{-9} cm^2 s^{-1} as the x value increases from 0 to 0.2. The above-mentioned values of D_{Li} are higher than the value of 10^{-11} cm^2 s^{-1}, characteristic of the crystalline V_2O_5 in the region $0 < x < 1$. As the content of lithium ions increases ($0.2 < x < 1.3$), their mobility decreases and the D_{Li} value becomes equal to 5×10^{-11} cm^2 s^{-1} at $x = 1.3$. Using a chemical or electrochemical method, up to 4 moles of lithium per mole of V_2O_5 can be intercalated. With this material, the specific cell capacity of 1600 W h kg^{-1} can be reached, which is significantly higher than for any other material based on vanadium oxide.[129]

It was mentioned [130, 131] that the degree of intercalation of lithium ions into the films of $V_2O_5 \cdot n\,H_2O$ xerogel depends on the morphology of films, which can be modified by adding carbon (in the form of a powder) in the course of the synthesis of the gel. The degree of lithium intercalation is also affected by the electronic conductivity of the xerogel, which can be increased by adding silver (in the form of a powder) or copper to the gel.[132, 133] Thin films with a molar ratio M : V = 0.005–5 (M = Ag, Cu) have been obtained from this type of composite. An increase in the electronic conductivity of the xerogel by 2–3 orders of magnitude was thus achieved. The amount of lithium intercalated into the composite reaches 4 moles per mole of V_2O_5; lithium is intercalated reversibly at a very high rate. For M = Cu, the capacity of the cathodes does not drop even after 450 charge–discharge cycles.[133]

Nanocomposites with the compositions $(PPyr)_xV_2O_5$ ($x = 0.4–0.9$), $(PAni)_{0.4}V_2O_5$ and $(PTh)_xV_2O_5$ ($x = 0.3–0.8$, PTh is polythiophene) were tested as cathode materials in lithium power sources.[63, 134] The best characteristics as regards reversibility of the intercalated cations were obtained for the polyaniline-containing composite.[135–138] Its capacity with respect to Li^+ is 40% higher than that for the original material, *viz.*, $V_2O_5 \cdot n\,H_2O$. Intercalation of a PAni derivative, namely, poly[*N*-(3-sulfopropyl)aniline] (PSPAni) resulted in a new composite $(PSPAni)_{0.3} \cdot V_2O_5 \cdot n\,H_2O$ exhibiting a specific discharge capacity of cathode equal to 307 A h kg^{-1} and reduction kinetics faster than for the initial xerogel.[139, 140] The electrochemical characteristics of the composites $(C_6H_4N)_xV_2O_5$ ($x = 0.35–0.40$), annealed in oxygen at 150 °C and treated with hydrogen peroxide to oxidise the reduced vanadium have been reported.[135] The intercalation of Li^+ remains reversible in the composite even after profound reduction corresponding to intercalation of 3 moles of lithium; the lithium diffusion is deeper than in the case of $V_2O_5 \cdot n\,H_2O$. At a current density of 10 μA cm^{-2}, the potential changes over the range from 3.8 to 1.8 V and the specific discharge capacity becomes equal to 370 A h kg^{-1}. On the 15th day after the synthesis, the composite material $(C_6H_4N)_{0.6}V_2O_5 \cdot 0.3\,H_2O$ not subjected to oxidative treatment had an electroconductivity of 0.09 Ω^{-1} cm^{-1} and $d_{001} = 14.14$ Å.[136] The specific discharge capacity of this compound, equal to 161 A h kg^{-1}, increased to 302 A h kg^{-1} after its annealing in an oxygen atmosphere at 80 °C for 5 h. This value of capacity corresponds to intercalation of 2.7 moles of lithium per mole of the composite material.[136, 141] As the temperature of annealing of the specimen increases, the electrochemical activity of PAni in the composite material decreases.

The use of the nanocomposites PPyr–vanadium(V) oxide xerogel as a cathode material for power sources with a lithium anode has been discussed.[63, 66, 142] Supercritical dessication of the xerogels (under cryogenic conditions) allows one to obtain materials with a large specific surface area (150–257 m^2 g^{-1}) and a density of 0.1–0.2 g cm^{-3} (see Ref. 142). Intercalation of lithium into these composites depends strongly on the concentration of the oxidant [for instance, $Fe(NO_3)_3$] used in their synthesis.[66] For the compound $(PPyr)_{0.8}V_2O_5$ obtained without an oxidant, the specific capacity equals 240 A h kg^{-1} upon intercalation of 3 moles of lithium per mole of composite. In the synthesis performed under conditions where Pyr : V = 1 and Fe : V = 0.05, the composite obtained had the specific discharge capacity 180 A h kg^{-1} upon intercalation of 2.8 moles of lithium. With an increase in the PPyr content to 8.5 moles per mole of $V_2O_5 \cdot n\,H_2O$ and the Fe : V ratio to 2, the specific capacity of the xerogel decreased to 25 A h kg^{-1} and the amount of intercalated lithium decreased to 1.8 moles.

Hydrated intercalation compounds with the composition $M_xV_2O_{5-\delta} \cdot n\,H_2O$, where M is an alkali metal ion, were used in the design of new compact power sources, namely, reserve batteries of bipolar construction with aqueous electrolytes.[122] Such sources are needed for aerological investigations of the surface atmospheric layers. The process of intercalation of Mg^{2+}, Zn^{2+} and Al^{3+} cations into the vanadium(V) oxide xerogel in both the propylenecarbonate-based and aqueous elecrolyte can be used in the design of high-energy batteries. Such power sources will be less dangerous and cheaper than the lithium batteries.

Intercalation compounds based on vanadium(V) oxide xerogel are of interest as solid electrolytes [75] conducting M^{z+} cations and as electrochromic materials:[143] they change their colour in the intercalation–deintercalation of protons or lithium ions. Relatively simple technology for obtaining films of these substances allows one to produce electrochromic displays of large area. For instance, the film of polyvanadium acid deposited on the conducting layer of indium and tin oxides changes colour from yellow to green at the voltage ±1.5 V.[144] The time constant of such an

electrochromic device amounts to 2–20 s depending on the power of the current source; the duration of memory is 20 h, the number of cycles may reach 8×10^4. The film varies in colour from yellowish-green to grayish-violet according to the amount of intercalated lithium.

$V_2O_5 \cdot n H_2O$ xerogels are of interest as precursors for the synthesis of superfine powders and films of oxide vanadium bronzes [125, 145–148] and vanadates [27, 149] used as cathode materials in power sources. The bronze $Na_{0.33}V_2O_5$ with monoclinic syngony was obtained [150, 151] by annealing the $Na_{0.33}V_2O_5 \cdot 1.6 H_2O$ xerogel at 550 °C. Electrochemical intercalation of Li^+ and Na^+ ions into the β-phase of $Na_{0.33}V_2O_5$ obtained by the sol–gel method is achieved using solutions of the corresponding salts in PC. This leads to a significantly higher content of these ions as compared with the specimens synthesised by a solid-phase method.[146] In addition, the compound obtained by the sol–gel method possesses the higher (by two orders of magnitude) lithium diffusion coefficient. According to the data from cyclic voltammetry, the β-phase prepared by the sol–gel method has higher electrochemical activity. The oxide vanadium bronze with the composition $Fe_{0.12}V_2O_5$ prepared also by the sol–gel method was recommended as a cathode material in accumulators with a lithium anode. The discharge curve for this source has three plateaux corresponding to total capacity of 3.5 moles of lithium per mole of $Fe_{0.12}V_2O_5$. The specific discharge capacity of the bronze after the 40th cycle amounted to 200 A h kg^{-1} upon cycling in the range 3.8–2.0 V.

Usually, the oxide compounds obtained upon complete dehydration of vanadium xerogels have a large surface and easily undergo intercalation with Li^+ ions. For instance, 0.8 moles of lithium are intercalated into the oxide $Al_{0.11}V_2O_{5.15}$ at a current density of 20 μA cm^{-2} with the potential varying in the interval from 3.4 to 3.1 V. The chemical diffusion coefficient for Li^+ in $Li_xAl_{0.11}V_2O_{5.15}$ equals 10^{-10}–10^{-11} cm^2 s^{-1}. It increases in the interval $0.05 < x < 0.2$ and reaches a maximum at $x = 0.25$, then decreases in the range $0.25 < x < 0.50$ and remains virtually unchanged at $x > 0.50$. The current–voltage curve suggests the possibility of cycling the compound; this is characterised by the three peaks at about 3.35, 3.15 and 2.25 V. Similar studies have been performed on the mixed oxide $Fe_{0.11}V_2O_{5.16}$ (see Ref. 149). Electrochemical intercalation with lithium yielded the compound $Li_xFe_{0.11}V_2O_{5.16}$ ($0 < x < 2.4$). As in the case of $Li_xAl_{0.11}V_2O_{5.15}$, the chemical diffusion coefficient for Li^+ ions depends strongly on x. The Fe^{3+} cations localised in the V_2O_5 octahedra act as stabilisers of the host lattice. As a result, the appearance of phases of the $Li_xV_2O_5$ type upon intercalation of lithium slows down.

Polyvanadate xerogels deposited onto inert plates were used [152] as precursors for obtaining films of oxide vanadium bronzes with the composition $M_xV_2O_5$ (M = Na, Ag, Ba). After annealing at 550 °C of thin layers of compounds $M_xV_2O_5 \cdot n H_2O$ prepared from $V_2O_5 \cdot n H_2O$ by ion exchange in the 0.1 M aqueous solution of MCl, compounds $Na_{0.33}V_2O_5$ and $Ag_{0.33}V_2O_5$ with the β-phase structure of oxide vanadium bronze are formed. The electroconductivity of β-phase films is strongly anisotropic and depends on the nature of the cation M^+. For $Na_{0.33}V_2O_5$, $\sigma_{\parallel} = 8$ and $\sigma_{\perp} = 4 \times 10^{-2}$ Ω^{-1} cm^{-1} at room temperature, while for $Ag_{0.33}V_2O_5$ the corresponding values are 3 and 1.5×10^{-2} Ω^{-1} cm^{-1}, respectively. The characteristic times of electron mobility are approximately the same for both these compounds and are equal to 10^{-11} s. The mobilities of Na^+ and Ag^+ ions are characterised by the times $\tau = 5 \times 10^{-12}$ and $\tau = 2 \times 10^{-11}$ s, and by the activation energies 0.12 and 0.08 eV, respectively. A higher mobility of electrons ($\tau = 10^{-10}$ s) is observed in the case of $Ba_{0.16}V_2O_5$.

The results of X-ray and thermal studies on the oxide vanadium bronzes with the compositions $Ba_{0.17}V_2O_5$, $Ni_{0.17}V_2O_5$, $Al_{0.11}V_2O_5$ and $Fe_{0.11}V_2O_5$ prepared by the sol–gel method were reported.[26] It was noted that, unlike the solid-phase procedure, the sol–gel method allows one to synthesise thin layers of bronzes $M_xV_2O_5$ of the α type with rhombic structures. The orientation of these layers depends on the nature of the intercalated cation. The layers situated parallel to the support surface can be parallel (Fe^{3+} and Al^{3+}), perpendicular (Ba^{2+}) or either parallel or perpendicular (Ni^{2+}) to the planes of the V_2O_5 layers. With the cesium cation, bronze of a hexagonal syngony with the composition $Cs_{0.35}V_2O_5$ and the unit cell parameters $a = 13.34(1)$ and $c = 3.610(1)$ Å is formed under the same conditions.[153]

From the mixed (as regards the intercalated cation) xerogels, films of oxide vanadium bronzes of the β type, with compositions $Li_{0.11}Na_{0.23}V_2O_5$, and $Li_{0.23}Na_{0.14}V_2O_5$ were obtained by an analogous method.[154] Electroconductivities of these bronzes are also strongly anisotropic. At room temperature, $\sigma_{\parallel} = 5.98 \times 10^{-2}$ and $\sigma_{\perp} = 5.48 \times 10^{-5}$ Ω^{-1} cm^{-1} for the first bronze and $\sigma_{\parallel} = 0.138$, $\sigma_{\perp} = 1.08 \times 10^{-4}$ Ω^{-1} cm^{-1} for the second one. The activation energy of the conductivity of the films is close to 0.08 eV at ~100 K and increases to 0.11 eV as the content of sodium ion decreases.

VII. Conclusion

In recent years, intercalation compounds based on the xerogels of complex and simple vanadium oxides have been the most extensively studied. Different views on the nature of hydrated vanadium(V) oxide existed for a long time but are currently united due to the progress in the studies on the structures of films and the mechanisms of intercalation of cations and organic molecules. In this respect, the results obtained in determining the content and types of the hydrogen–oxygen groups by ^1H NMR are of considerable importance.

The preparation of ordered nano-, meso-, micro- and macrostructures of intercalation compounds is typical of modern experimental research. Synthetic procedures, chemical composition and morphology of the xerogel are usually reported, but the data concerning physicochemical and physical properties are scarce and concern mainly the cathodic behaviour of these substances in chemical power sources. Studies on the electronic structure and the reactivities of the nanocomposites consisting of vanadium–oxygen layers and intercalated organic components are lacking. A new direction for applications of the intercalation compounds is becoming evident, which consists of their use as nanoreactors in the synthesis of polymers [61] or nanotubular carbon structures.[155]

New publications dealing with intercalation compounds based on V_2O_5 xerogels have appeared after completion of this review. Studies on the refinement of a bilayer structure of vanadium(V) oxide xerogel are of interest.[156] Investigations into the preparation of bulk [157] and film [158] materials with mesoporous structures have begun. A superlight macroporous crystalline intercalation compound of $V_2O_5 \cdot n H_2O$ was synthesised that contains intercalated hexadecylamine molecules ($d = 33.4$ Å) with alkyl chains perpendicular to the planes of the vanadium–oxygen layers.[159] All this evidences progress in the studies on the class of compounds under consideration.

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