Controlled Uptake and Release of Metal Cations by Vanadium Oxide Nanotubes

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Dedicated to Prof. *Albert Eschenmoser* on the occasion of his 75th birthday

Vanadium oxide nanotubes (C_n-VO_x-NTs) contain α-monoamines ($C_nH_{2n+1}NH_2$ with $4 \leq n \leq 22$) as templates intercalated between crystalline VO_x layers comprising multilayer tube walls. The present study reveals that a large proportion of the amines can easily be exchanged by metal cations. The tubular morphology is not affected by this reaction, but the distance between the VO_x layers, *i.e.*, 2.8 nm in C_{12}-VO_xNTs, decreases in the reaction product to 0.9 – 1.2 nm, depending on the metal salt actually applied. Alkali (Na^+, K^+), alkaline-earth (Mg^{2+}, Ca^{2+}, Sr^{2+}), and transition-metal salts (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) have successfully been intercalated. This reaction is partly reversible since intercalated sodium cations can be resubstituted by dodecylamine. This exchange produces again C_{12}-VO_x-NTs with the original inter-layer spacing. However, this release is successful only when sodium is complexed by a crown ether. Under these reaction conditions, even a cyclic uptake and release of Na^+ and amine, respectively, accompanied by a corresponding shrinkage and widening of the inter-layer distance, is observed while the tubular structure is widely preserved. Furthermore, a distinct selectivity of the metal-cation exchange has been observed.

1. Introduction. – Among nano-structured materials, the nanotubes are unique because of their strongly anisotropic geometry, which is associated with interesting physical and chemical properties. Four different contact regions, *i.e.*, the tube ends, inner and outer surfaces as well as the potential uptake capacities of the tube interior and of the inter-walls spaces offer many possibilities for structural modification and functionalization. Hitherto, carbon nanotubes are the best-known representatives of such morphology. Discovered soon after the fullerenes by *Iijima* in 1991 [1], this novel form of carbon has received great attention in materials research and nanotechnology because of possible applications such as, *e.g.*, storage devices, field emitters, components for nanoelectronics, as well as STM and AFM tips [2]. These fascinating perspectives catalyzed the successful search for other tubular materials in various systems [3].

The recently discovered vanadium oxide nanotubes (VO_x-NTs) [4 – 7] are of particular interest since vanadium oxides are widely applied in catalysis and in electrochemistry. The easy access to large amounts of these tubes by a *chimie douce* route predestines them as promising candidates for wide-spread investigations on the relation of anisotropy, reactivity, and physical properties.

The tube walls consist of vanadium oxide layers between which the organic molecules are embedded. In contrast to the carbon nanotubes, consisting of closed, concentric C layers, only a few VO_x-NTs are of this type, whereas most of the tube walls comprise scrolls of layers or disordered layer arrangements. Although this composite structure is rather complex, it appears to be highly flexible as indicated by the interesting electrochemical properties [8], as well as by the versatile exchange behavior of the VO_x-NTs. The irreversible exchange of embedded monoamines against diamines occurs readily and under preservation of the tubular morphology [9]. Moreover, a modification of the tube walls can be achieved by treatment with various metal cations [10][11]. In this study, we investigated the topochemical reactions of hexadecylammonium vanadium oxide nanotubes, C_{12}-VO_x-NTs with various metal salts, and we present the results of the structural characterization of the products.

2. Results and Discussion. – *Starting Material.* We have first tested the uptake of sodium cations by VO_x-NTs with different templates. Although the intercalation in C_4-VO_x-NTs (template: $BuNH_2$) by exchange against the template took part, as indicated by the shrinkage of the inter-layer distance (see below), the tubular form was heavily damaged. On the other hand, VO_x-NTs with docosylamine as the template do not react at all, *i.e.*, the intercalated amine molecules are not removed by the treatment with a sodium salt. In contrast, the exchange behavior of C_{12}-VO_x-NTs is excellent with respect to the readiness of the intercalation and the preservation of the tube morphology, which renders them a model system for all further such experiments.

Transmission electron microscopy (TEM) images of this material are shown in *Fig. 1*. Typical C_{12}-VO_x-NTs are 2 – 5 μm long with an outer diameter of *ca.* 100 nm. The tube walls consist of a layered structure with a layer distance of 2.8 nm according to X-ray powder diffraction (XRD) results. The VO_x layers appear as dark contrasts in the TEM images (*Fig. 1,b*). The organic template is embedded between these VO_x layers (brighter contrast in *Fig. 1,b*), and, accordingly, the inter-layer distance is proportional to the length of the alkyl chain length of the amine.

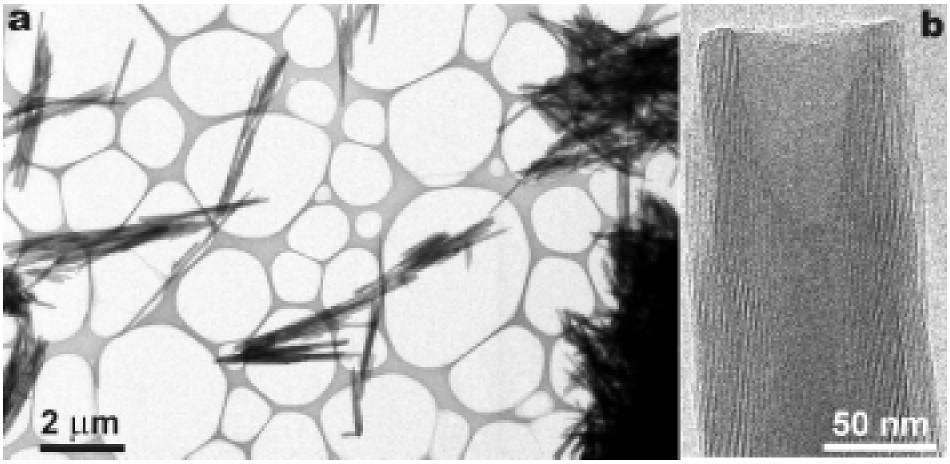

Fig. 1. *Typical TEM images of C_{12}-VO_x-NTs. a*) Tubes deposited on a *perforated* carbon foil. *b*) Tip of an open C_{12}-VO_x-NT. The layered structure inside the tube walls appears as alternating narrow dark lines and broad bright lines.

Preparative Results and Morphology. The intercalation of various metal cations, *i.e.*, alkaline, alkaline-earth, and transition metals, into C_{12}-VO_x-NTs by exchange against the template is possible (*Table 1*). In most cases, this reaction does not affect the tubular morphology seriously (*cf. Fig. 3*), although the removal of the embedded amine molecules by treatment with metal salts is combined with a drastic reduction of the VO_x layer distance: in the case of Na^+ from *ca.* 2.8 nm to 1.1 nm (*Fig. 2*). Thus, XRD is a fast and powerful method for probing the success of the reaction. As the reflections of the 00*l* type arise from the regular distances between the VO_x layers, the shift of their position towards larger scattering angles indicates the removal of the organic template. Depending on the metal salt actually applied, the resulting *d* values range from 0.96 to 1.27 nm (*Table 1*).

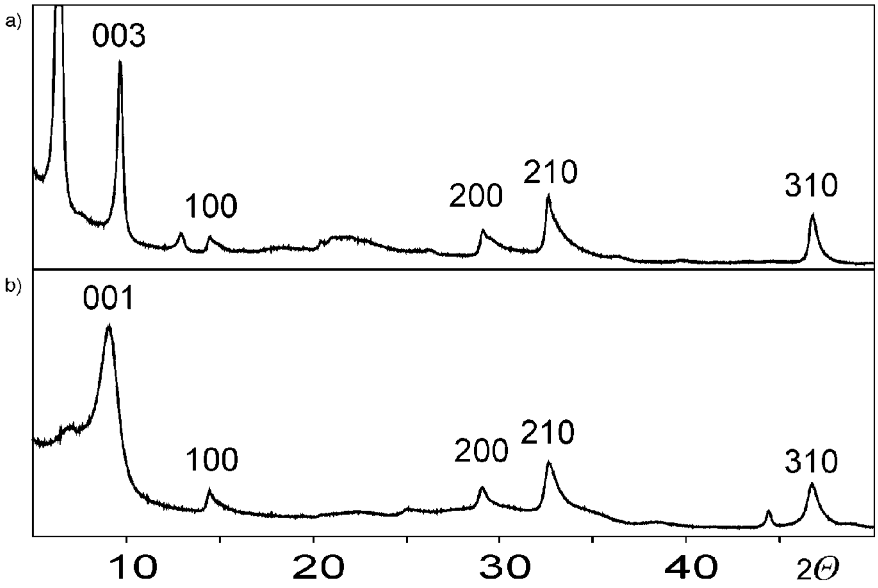

Fig. 2. *XRD Diagrams of* a) *the starting material C_{12}-VO_x-NTs and* b) *the product of the reaction with NaCl, designated as Na-VO_x-NTs.* Note that the position of the reflections 00*l* is shifted towards higher angles in *b*, indicating a decrease of the inter-layer distance, while the reflections *hl*0 are located on the same sites in both diagrams.

For the incorporation of Na^+ cations, several salts have been tested (*Table 1*). In all cases, the decreased inter-layer distance indicates the successful removal of the template. However, the measured *d* value varies between 0.96 and 1.12 nm. Since the anion appears to have a considerable influence, as indicated by these varying *d* values, we have always used the chloride salts in order to unify this influence in all exchange reactions performed with a wide range of different metal salts. Interestingly, an intercalation of alkaline metals other than Na^+ and K^+ is not possible. The treatment of C_{12}-VO_x-NTs with diluted RbCl and CsCl leads to a destruction of the tubes, and a lamellar product is formed. On the other hand, the tubular structure is not affected by LiCl solution, and the inter-layer distance measured by XRD is unaltered. In addition, elemental analysis proves that no exchange occurs. Most likely, the hydrate

Table 1. *XRD and EDX Results of the Treatment of C_{12}-VO_x-NTs* (inter-layer distance 2.8 nm) *with Metal Salts*

Salt	Inter-layer distance [nm] (XRD results)	EDX (Atomic percentage $(M/(M+V))\times 100$
NaCl	1.10	
NaOH	0.96	[a])
NaI	1.12	
KCl	0.97	21–25
$MgCl_2$	1.27	2
$CaCl_2$	1.10	13
$SrCl_2$	1.11	11 [a])
$FeCl_2$	1.08	
$CoCl_2$	1.09	10
$NiCl_2$	1.13	
$CuCl_2$	1.13	
$SmCl_3$	1.20	10 [a])
$TbCl_3$	1.15	[b])
NaCl + KCl	0.96	
NaCl + $CaCl_2$	1.11	

[a]) Tubes damaged. [b]) Morphology not determined.

core of Li^+ is too large to enter the layer structure. This assumption is supported by the fact that electrochemical Li^+ intercalation is observed in non-aqueous electrolytes [8].

Interestingly, a similar dependence of the exchange behavior on the cation size has been found for alkaline-earth metals. Mg^{2+} and Ca^{2+} cations are exchanged under preservation of the tubular morphology (*cf. Fig. 3,d*). Treatment with diluted $SrCl_2$ affects the tubular structure, and the morphology was partly damaged. Nevertheless, the usual decrease of the inter-layer distance (to 1.11 nm) is observed, indicating a successful exchange (*Table 1*). Solutions of $BaCl_2$, like those of RbCl and CsCl, destroyed the tubes completely.

Several early-transition-metal cations such as Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} can easily be exchanged with a quite good preservation of the tube shape. In contrast, an exchange reaction with $ZnCl_2$ solution has not been achieved yet. Furthermore, a decrease of the inter-layer distances has been obtained by treatment of C_{12}-VO_x-NTs with $SmCl_3$ and $TbCl_3$ (*Table 1*). Additional experiments show that Pb^{2+} is not exchanged, and that a complete destruction of the tubes to an amorphous material is induced by reaction with diluted $AgNO_3$.

Structural Characterization and Analytical Results. As already discussed above, the tubular morphology of the starting C_{12}-VO_x-NTs is widely preserved during the treatment with metal-salt solutions (*Fig. 3*). The most prominent structural change in these reactions is the considerable decrease of the distance between the VO_x layers, as detected by electron diffraction and X-ray diffraction (*cf. Fig. 2*). In contrast to that, the structure within the VO_x layers remains unaltered as indicated by the position of the reflections $hk0$ being located on almost the same sites in reciprocal space for C_{12}-VO_x-NTs and for the reaction product. Furthermore, the intensity of corresponding reflections $hk0$ is very similar in both patterns (*Fig. 2*). As discussed in [6], these reflections can be indexed on the basis of a two-dimensional square lattice with $a \approx$

0.62 nm. A square pattern of contrasts with this distance can frequently be observed in higher magnified TEM images (*cf. Fig. 5,b*). Remarkably, this part of the structure in the exchange products is more stable under the electron beam than it is the case for C_n-VO_x-NTs, which may be explained by increased interactions between the layers at shorter distances.

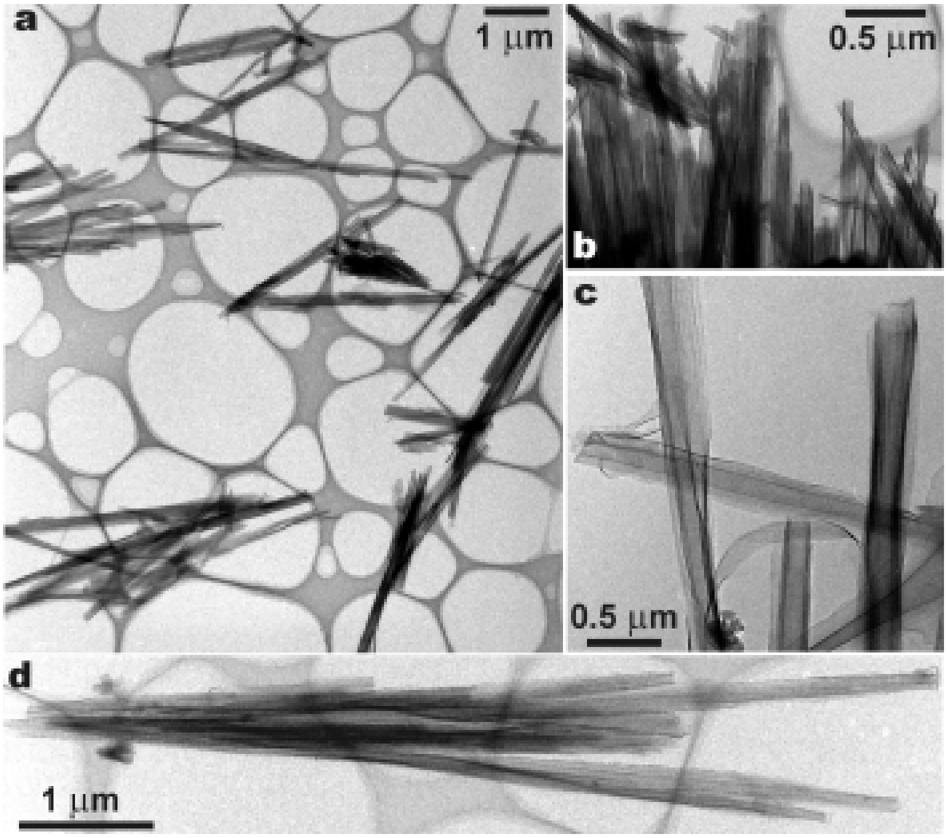

Fig. 3. *TEM Images of the reaction products obtained by treatment of C_{12}-VO_x-NTs with different salts. a*) NaCl: survey of well-structured tubes; *b*) KCl; *c*) NaCl: damaged tubes; *d*) $CaCl_2$.

In spite of the unaltered atomic structure of the VO_x layers in the reaction products, the arrangement of these layers differs significantly from that in amine-containing VO_x-NTs. A first indication for this was uncovered by the observation of the tubes in longitudinal projection, which often shows the presence of distortions in the tube walls (*Fig. 3,c*). A further insight into the origin of such defects is given by TEM images of the cross-sectional tube structure (*Fig. 4*). The VO_x layers are grouped into packs of three and more layers. These packs are frequently combined in thicker arrays and are less bent than the composite amine/VO_x layers in the C_n-VO_x-NTs. Straight arrays of such packs with loops at their ends frequently appear. Moreover, nearly square arrays with large inner diameters (> 200 nm) are sometimes present. These observations suggest that the (partial) removal of the amines leads to a stiffening of the layers and to an increased attractive force between the VO_x layers. In conjunction with a decreased tendency of the layers towards bending, this leads to the modified tubular morphology of the exchange product.

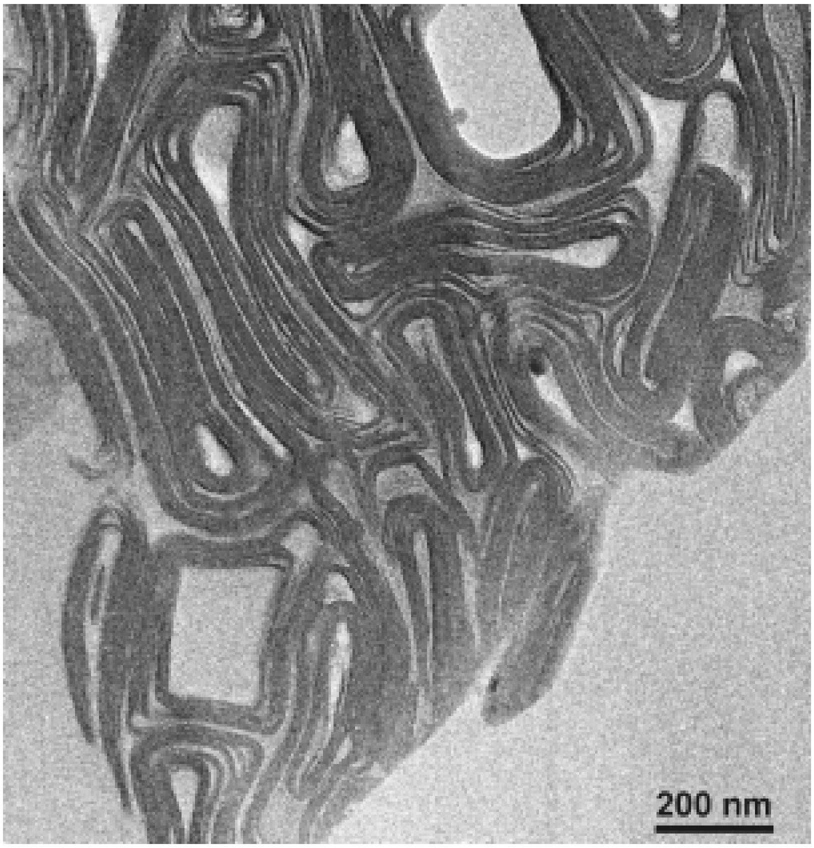

Fig. 4. *Cross-sectional TEM image of Na-VO_x-NTs* (product of NaCl treatment)

The incorporation of cations in the tubes was verified in most cases by element analysis (*Table 2*). C,H,N Analyses additionally revealed the amount of organic template remaining in the structure (*Table 2*). In the case of as synthesized C_{12}-VO_x-NT sample, there are 0.27 mol amine/mol V in the tubes, while 0.19 mol Na and 0.06 mol amine per 1 mol V are present in the Na^+ exchange product. These values correspond to an amine exchange of 70%. It is yet not clear whether the remaining amount of template is essential for the preservation of the tube shape or not. An incomplete removal of the amine is sometimes directly detected in TEM images: two different distances between the VO_x layers can be seen in *Fig. 5,c*. They correspond to the large inter-layer distance of the amine-containing sample and to the smaller distance of the exchange product. This observation clearly reveals that, in this tube, only a part of the amine has actually been removed.

Table 2. *Resulting Compositions of Several Exchange Products Obtained by Treatment of C_{12}-VO_x-NTs with Metal-Chloride Solution and of the Competition Products Obtained by Exposure of C_{12}-VO_x-NTs to Solutions of two Different Metal Chlorides*

Starting tubes and exchange products	Formula according to metal, and C, H, and N analysis	Mol guests/ mol V	Mol charges/ mol V
C_{12}-VO_x-NTs	$V_{1.00}O_{2.42}[C_{12}H_{28}N]_{0.27}$	0.27	0.27
Na-VO_x-NTs	$V_{1.00}O_{2.85}[C_{12}H_{28.00}N]_{0.06}Na_{0.19}(H_2O)_{0.40}$	0.25	0.25
K-VO_x-NTs	$V_{1.00}O_{2.40}[C_{12}H_{28.00}N]_{0.03}K_{0.21}$	0.24	0.24
Mg-VO_x-NTs	$V_{1.00}O_{2.19}[C_{12}H_{28.00}N]_{0.11}Mg_{0.08}(H_2O)_{0.57}$	0.19	0.27
Ca-VO_x-NTs	$V_{1.00}O_{2.30}[C_{12}H_{28.00}N_{1.00}]_{0.03}Ca_{0.12}(H_2O)_{0.54}(N)_{0.03}$	0.15	0.27
Sr-VO_x-NTs	$V_{1.00}O_{2.45}[C_{12}H_{28.00}N_{1.00}]_{0.02}Sr_{0.14}(H_2O)_{0.50}(N)_{0.01}$	0.16	0.30
(Na,K)-VO_x-NTs	$V_{1.00}O_{2.44}[C_{12.00}H_{28.00}N]_{0.02}K_{0.23}Na_{0.02}[C_2H_{6.00}O]_{0.03}(H_2O)_{0.10}$	0.27	0.27
(Na,Ca)-VO_x-NTs	$V_{1.00}O_{2.31}[C_{12}H_{28.00}N_{1.00}]_{0.02}Ca_{0.10}Na_{0.06}(H_2O)_{0.46}(N)_{0.01}$	0.18	0.28

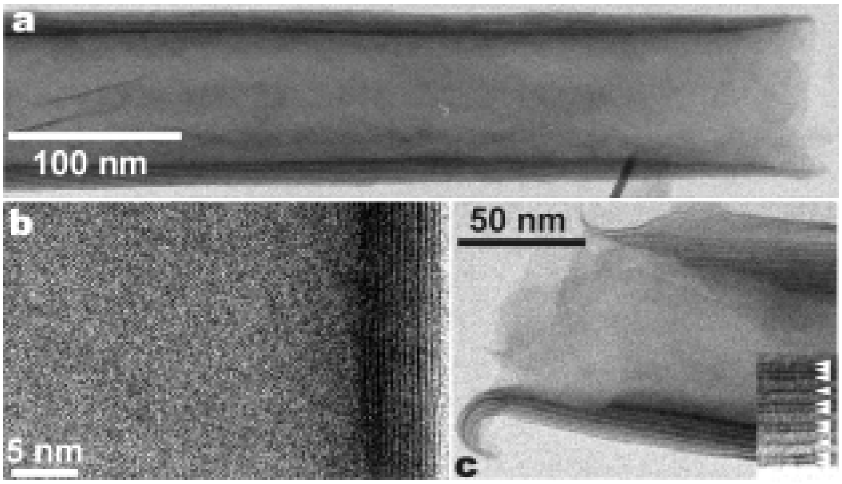

Fig. 5. *TEM Images of Na-VO_x-NTs* (product of NaCl treatment). *a*) Well-developed tube. *b*) Enlarged section of *a*), showing the structure within the VO_x layers. A distorted pattern of contrasts with a distance of 0.62 nm can be seen. *c*) Tube with two different inter-layer distances (*ca.* 2.0 nm and *ca.* 1.0 nm) inside the tube walls. The insert shows an enlargement.

The exchanges with K^+, Mg^{2+}, Ca^{2+}, and Sr^{2+} yielded very similar results (*Table 2*). The remaining amount of amine in the exchange product is even reduced to 0.03 mol/mol V except in the case of Mg^{2+}, where still 0.11 mol amine per 1 mol V is found. Nevertheless, in all exchange experiments the number of guest charges (*i.e.*, amines and cations) is always *ca.* 0.27 mol per 1 mol V.

The amount of incorporated cations has also been investigated by energy dispersive X-ray (EDX) analysis in the transmission electron microscope (*Table 1*). Although these results are not very precise, valuable additional information is thereby gained. EDX Analyses of separated tubes have unambiguously proved that the metal is indeed embedded somewhere inside the tubes. Owing to experimental limitations, it has not been possible to determine the exact location of the cations. Thus, the question whether they are on well-defined sites between the VO_x layers and/or in the tube cores still remains unanswered.

Reversible Uptake and Release. Starting with a sample containing 0.19 mol Na and 0.06 mol amine per 1 mol V, the reactivity of Na-VO_x-NTs towards various metal salts has been investigated. A part of the Na^+ cations can indeed be substituted by various other metal cations (*Table 3*). Remarkably, the number of negative charges in these tubes appears to be constant during the exchange reactions, since this number is always *ca.* 0.27 mol per 1 mol V. In particular, this finding is confirmed by exchange reactions in which Na^+ cations have been partly substituted by doubly charged cations: here, the relative number of guests is smaller, but the number of vals (unit charges) remains practically constant (*ca.* 0.27 mol (amine + Na^+ + $2M^{2+}$) per 1 mol V). The constant number of *ca.* 0.27 positive charges per V-atom indicates that the number of binding sites for guests appears to be constant and ionic. During exchange processes, there seems to be no significant change in the oxidation state of vanadium. In fact, even the changes of the inter-layer distances do not need any changes in the electronic states since only the structure between the VO_x layers is affected. Thus, the number of negatively charged oxo groups in the VO_x layers is constant and, consequently, this is also the case for the number of bound cationic species. Nevertheless, a simple 1:1 substitution of an amine molecule, which is protonated according to XPS measurements [6], by a metal cation is only an approximate description for these reactions. Probably, H^+ ions participate as well and accommodate – at least partly – the negative charge of the VO_x layers.

Table 3. *Composition of Various Exchange Products.* Secondary exchange with other metal cations starting from Na-VO_x-NTs; K-VO_x-NTs re-exchanged with dodecylamine and crown ethers (r/K-VO_x-NTs); repeated exchange of Na and amine starting with Na-VO_x-NTs

Exchange products	Formula according to elemental, and C, H, and N analysis	Mol guests/ mol V	Mol charges/ mol V
(Li,Na)-VO_x-NTs	$V_{1.00}O_{2.57}[C_{12}H_{28.00}N]_{0.01}Li_{0.02}Na_{0.22}(H_2O)_{0.59}$	0.25	0.25
(K,Na)-VO_x-NTs	$V_{1.00}O_{2.39}[C_{12}H_{28.00}N_{1.00}]_{0.02}K_{0.21}Na_{0.02}(H_2O)_{0.14}(N)_{0.01}$	0.25	0.25
(Mg,Na)-VO_x-NTs	$V_{1.00}O_{2.39}[C_{12}H_{28.00}N_{1.00}]_{0.01}Mg_{0.04}Na_{0.16}(H_2O)_{0.52}(N)_{0.01}$	0.21	0.25
(Ca,Na)-VO_x-NTs	$V_{1.00}O_{2.40}[C_{12}H_{28.00}N_{1.00}]_{0.02}Ca_{0.11}Na_{0.04}(H_2O)_{0.44}(N)_{0.02}$	0.17	0.28
(Sr,Na)-VO_x-NTs	$V_{1.00}O_{2.69}[C_{12}H_{28.00}N_{1.00}]_{0.01}Sr_{0.13}Na_{0.02}(H_2O)_{0.48}(N)_{0.01}$	0.16	0.29
r/K-VO_x-NTs	$V_{1.00}O_{2.17}[C_{12.00}H_{28.00}N]_{0.08}K_{0.18}(C_{12}H_{24}O_6)_{0.01}(H_2O)_{0.26}$	0.26	0.26
r/Na-VO_x-NTs	$V_{1.00}O_{1.90}[C_{12.00}H_{28.00}N]_{0.13}Na_{0.14}(C_{10}H_{20}O_5)_{0.01}(H_2O)_{0.39}$	0.27	0.27
Na/r/Na-VO_x-NTs	$V_{1.00}O_{2.93}[C_{12}H_{28.00}N_{1.00}]_{0.02}Na_{0.25}(H_2O)_{0.17}(N)_{0.01}$	0.27	0.27
r/Na/r/Na-VO_x-NTs	$V_{1.00}O_{2.27}[C_{12}H_{28.00}N]_{0.06}Na_{0.22}(H_2O)_{0.34}$	0.28	0.28

To replace the Na^+ cations in Na-VO_x-NTs and to incorporate amines again, the addition of crown ethers has been necessary. By treating Na-VO_x-NTs with a solution of dodecylamine and 15-crown-5, it is indeed possible to remove the Na^+ to a large extent and to replace it with an amine again (*Table 3*). The successful incorporation of the amine is indicated by the resulting inter-layer distance, which has increased to the same value (2.8 nm) as in the starting material C_{12}-VO_x-NTs. However, the elemental analysis shows that only half of the Na^+ has been replaced by amines again. 0.13 mol amine and 0.14 mol sodium, respectively, are detected per 1 mol vanadium (*Table 3*). It is remarkable that this rather small amount of amine is already sufficient to reach the original inter-layer distance. An important characteristic of this reaction is that the inter-layer distances are either 1.1 or 2.8 nm, and that they do not change continuously between these values. Apparently, the tubes switch between these two specific distances during an exchange experiment depending on a certain amine/metal ratio.

In general, it seems that incorporation of metal cations leads to a larger stabilization of the tubular structure than incorporation of ammonium cations. This conjecture does explain why metals are more difficult to remove than amines. Furthermore, this is supported by the observation that it is even possible to re-exchange the amines again by Na^+ cations.

$$C_n\text{-}VO_x\text{-}NT + Na^+ \rightarrow Na\text{-}VO_x\text{-}NT + C_nNH_3^+ \tag{1}$$

$$Na\text{-}VO_x\text{-}NT + C_nNH_3^+ + 15\text{-crown-5} \rightarrow C_n\text{-}VO_x\text{-}NT + Na^+/15\text{-crown-5} \tag{2}$$

$$C_n\text{-}VO_x\text{-}NT + Na^+ \rightarrow Na\text{-}VO_x\text{-}NT + C_nNH_3^+ \tag{3}$$

Element analyses reveal the presence of 0.25 mol Na and only 0.02 mol amine (*Table 3*), respectively, per 1 mol V-atoms. Therefore, in this third exchange reaction (*Reaction 3*), the amount of intercalated Na is even higher compared to the first step. This reversible uptake and release of Na^+ and amine can be repeated several times without destroying the tubular morphology (*Table 3*).

This method of using crown ethers to replace cations with amines worked as well with K-VO_x-NTs: by treating K-VO_x-NTs with 18-crown-6 and dodecylamine, it was possible to reduce the amount of K^+ in the tubes and to enlarge the amine content again (*cf. Reaction 2* and *Table 3*). However, in analogy to the Na-VO_x-NTs, the amine content is far below that of the synthesized C_{12}-VO_x-NTs.

Competition Experiments. An important result in the above-mentioned re-exchange experiments is that obtained with KCl solution. K^+ Cations seem to be favored for an incorporation into the tubes, because almost the whole amount of Na^+ has been substituted (*Table 3*). This observation was confirmed by an experiment which elucidated the competition between Na^+ and K^+ directly. The synthesized C_{12}-VO_x-NTs have been treated with an equimolar solution of NaCl and KCl whereupon the layer distance decreased from 2.83 to 0.96 nm, which corresponds to the typical inter-layer distance after K^+ exchange (*Table 1*). The elemental analysis reveals a molar ratio K/Na 10:1, which confirms the strong preference of C_{12}-VO_x-NTs for K^+. In an analogous competition experiment between Na^+ and Ca^{2+} cations, a similar but smaller preference for Ca^{2+} compared to Na^+ cations (Ca/Na 3:1) was found.

3. Conclusions. – The results presented exemplify that the uptake and release of different metal cations by vanadium oxide nanotubes can be controlled to a large extent. This possibility of removing the amine template and intercalating metal cation opens new methods for functionalizing the highly anisotropic tubular structure of VO_x-NTs. For many applications, *e.g.*, solar cells, supercapacitors, and batteries, such doping or intercalation possibilities represent an essential basic feature. Moreover, the successfully performed cycles of intercalation and de-intercalation are encouraging with respect to electrochemical applications. The pronounced selectivity of the VO_x-NTs in competitive exchange reactions, *i.e.*, the preferred incorporation of K^+ cations, contributes to the interesting properties of this distinguished novel material as well.

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Experimental Part

Preparation of the Nanotubes. A soln of vanadium (V) triisopropoxide and a primary amine ($C_nH_{2n+1}NH_2$ with $n = 4, 12, 20$) in a molar ratio of 2 : 1 in abs. EtOH (3 ml/g V precursor) was stirred under inert atmosphere for 1 h and then hydrolyzed with H_2O (5 ml/g V precursor). After aging (12 – 96 h), the hydrothermal treatment of the resulting composite in an autoclave at 180° (*ca.* 7 d) generated a black precipitate. After washing and drying, the product was phase-pure, consisting of tubes only [6]. Most chemicals were purchased from *Fluka* (vanadium(V) triisopropoxide from *ABCR*) and applied without further purification. Icosylamine was prepared from bromoeicosane applying the *Gabriel* synthesis procedures [12] [13].

Exchange Reactions. VO_x-NTs and a metal salt (molar ratio: 1 : 4, *Table 1*) were stirred for 2 h in EtOH/H_2O 4 : 1 (*v*/*v*) (1 ml/mg VO_x-NTs). The resulting black powder was washed with EtOH and hexane, and then dried in air (standard exchange procedure). In competition experiments, salts of two metals were taken in a molar ratio of 2 : 1 each with respect to the VO_x-NTs and treated as described in the standard exchange procedure. In re-exchange experiments, Na-VO_x-NTs and the metal salt were taken in a molar ratio of 1 : 4, and the reaction procedure was analogous to that given above. If crown ethers were used for secondary exchanges, they were applied in the same molar amount as the salt. In the exchange cycles, Na-VO_x-NTs, the amine, and the crown ether (molar ratio 1 : 4 : 4) were mixed and processed as described in the standard exchange procedure.

Characterization of Structure and Composition. The X-ray powder diffraction (XRD) diagrams of all samples were measured in transmission mode (0.3 mm glass capillaries, CuK_α radiation) on a *STOE STADI-P2* diffractometer equipped with a position-sensitive detector with a resolution of *ca.* 0.01° in 2Θ. Changes of the inter-layer distances indicated a successful intercalation. To verify the XRD result, each sample that showed such changes was investigated by transmission-electron microscopy (TEM). TEM and energy-dispersive X-ray spectroscopy (EDX) investigations were performed on a *CM30ST* microscope (*Philips*; LaB_6 cathode, operated at 300 kV) equipped with a *Noran Voyager* system. For the investigation of the longitudinal shape and structure, the nanotube material was deposited onto a perforated C foil supported on a Cu grid. To observe the structure in direction of the tube axis, a cross-sectional preparation technique was applied as described in [6]. Selected samples were investigated by elemental analysis. C, H, and N analysis was carried out by means of combustion test methods on a *LECO CHN-900*. The element analysis was carried out by means of inductively coupled plasma/optical emission spectroscopy (ICP-OES) on a *Thermo Jarrell Ash IRIS*.

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