Structural Evolution During Li- and Mg- Intercalation in Vanadium Oxide Nanotube Electrodes for Battery Applications

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ABSTRACT

Multi-walled vanadium oxide nanotubes are an intriguing class of materials due to their complex and functional structure. They have especially gained attention as an electrode material for rechargeable ion batteries exhibiting Li-ion storage capacities up to 250 mAh/g. The pristine nanotube materials and their electrochemical properties have previously been investigated extensively; however little knowledge exists on the structural transformations induced by ion-storage in vanadium oxide nanotube electrodes. In this work, the changes in the atomic- and nano-scale structure during lithium and magnesium ion storage in two types of vanadium oxide nanotubes are investigated by *operando* powder X-ray diffraction and total X-ray scattering. A linear expansion and contraction of the VO_x layers with vanadium reduction and oxidation is observed, while the inter-layer spacing is found to be drastically dependent on the nature of the templating molecules or ions residing in the inter-layer space of the pristine tubes. The study demonstrates how certain conditions will lead to destruction of the multi-layer-structure of the tubes, while leaving the individual VO_x layers intact. Pair distribution function analysis reveals that vanadium reduction induces a change in the vanadium coordination geometry in the VO_x layers from square pyramidal to octahedral.

INTRODUCTION

Rechargeable lithium (Li) ion batteries are dominating the market of portable electronics and are increasingly used in large scale applications, e.g. electric vehicles, systems for load-leveling on the electrical grid and storage of renewable energy.^{1–3} Thus, improving the Li-ion battery technology further to meet the demands of these applications is of great interest. Concurrently, development of future generations of battery technologies is attracting increased attention. Mg-ion batteries may pose a future alternative to the Li-ion technology due to the significantly higher abundance of magnesium, and the prospective of reaching energy densities well above what is attainable using Li-ion batteries.^{4–7} However, the Mg-ion battery technology is still far from constituting a commercially viable alternative to the Li based technology; primarily due to the absence of well-functioning cathode materials and to some extent due to the lack of stable standard electrolyte systems.^{8–10}

Figure 1. Schematic illustration of multi-walled vanadium oxide nanotubes. Square pyramidal $[\text{VO}_5]$ units are depicted in blue and tetrahedral $[\text{VO}_4]$ units are depicted in green. Templating dodecylamines are depicted in red. This configuration is denoted $\text{C}_{12}\text{-VO}_x\text{-NT}$. The amines can

be exchanged with metal cations such as Mg^{2+} resulting in a change in the characteristic layer spacing. This material is denoted $\text{Mg-VO}_x\text{-NT}$. The drawing is made with inspiration from ref. 13-14.

Open-ended multi-walled vanadium oxide nanotubes (denoted $\text{VO}_x\text{-NT}$) may be a promising electrode material for Mg-ion storage. This type of material was initially synthesized by Spahr *et al.* in 1998 through solvothermal synthesis.¹¹ The structure of $\text{VO}_x\text{-NT}$ (Figure 1) can be described as scrolls or concentric circles of vanadate layers, here denoted VO_x , separated by primary protonated amines. Besides balancing the charge of the vanadate layers, the amines also act as template molecules during the solvothermal synthesis. The structure of the VO_x layers resembles the triclinic $\text{BaV}_7\text{O}_{16} \cdot n\text{H}_2\text{O}$ bronze structure,¹² and can be described as bi-layers of square pyramidal $[\text{VO}_5]$ bound together by tetrahedral $[\text{VO}_4]$ units. According to this structural model there are two amines per V_7O_{16} -unit.¹³⁻¹⁶ The inter-layer spacing between the VO_x layers is dependent on the carbon chain length of the templating primary amine used in the synthesis, i.e. 2.77 nm for dodecylamine.^{17,18} The templating amines can be exchanged by some alkali, alkali earth and transition metal cations. The exchange of the amines with metal cations is accompanied by a decrease in the inter-layer spacing to a new characteristic spacing, which depends on the cation, e.g. for exchange with Mg^{2+} the inter-layer spacing reduces to 1.27 nm.^{18,19}

The potential of using $\text{VO}_x\text{-NT}$ as cathode materials in Li-ion batteries has been explored in multiple studies. With amines in the structure, the $\text{C}_n\text{-VO}_x\text{-NT}$ (n denotes the number of carbon atoms in the amine) materials typically reach discharge capacities in the range 120-180 mAh/g. Interestingly, it has been shown that annealing $\text{VO}_x\text{-NTs}$ under inert conditions at $>200^\circ\text{C}$ can

increase the initial capacity (~215 mAh/g) and improve the rate capability.^{20,21} Unfortunately, the cyclic stability of the C_n -VO_x-NTs is generally rather poor with typical capacity losses of 45-85% during the initial 10 cycles. A general trend of increasing Li-ion storage capacity (up to ~250 mAh/g) and improved cyclic stability (up to 90% retention after 100 cycles) with ion-exchange of the amines by metal-ions (e.g. Na⁺, K⁺ and Ca²⁺) has been established.²² Interestingly, the type of cation inserted by ion-exchange appears to affect the capacity, e.g. layered δ -Mg-V₂O₅ displays ~75% higher Li-ion intercalation capacity than δ -Ca-V₂O₅.²³ Only a few studies have so far been published on VO_x-NTs used as an Mg-ion electrode. These studies found the material to have capacities between 75-230 mAh/g using Mg(AlBu₂Cl₂)₂ in THF or Mg(ClO₄)₂ in de-aerated acetonitrile as electrolytes.²⁴⁻²⁶

Despite the considerable number of studies exploring VO_x-NT materials as battery electrodes, very little is known about how the atomic structure of these materials changes upon electrochemical ion-intercalation and –extraction. Nordlinder *et al.* found that Li-storage in Ca-VO_x-NTs causes an apparently irreversible contraction of the inter-layer spacing during the first cycle.²⁷ In contrast, Jiao *et al.* observed an increase in the layer spacing during Mg-intercalation in C₁₈-VO_x-NTs.^{24,25} The significance of this remarkable difference between the two material as well as the changes occurring within the VO_x-layers are still unexplored. Understanding the structural evolution during battery operation, i.e. under dynamic conditions, is of vital importance as it determines the potential, capacity, reversibility and stability of the material. This prompted us to conduct a thorough investigation of the structural changes induced in both the long range and local structure during Li- and Mg-ion storage in both amine-filled and ion-exchanged VO_x-NTs.

Currently no standard electrolyte system performing well in every aspect for Mg-ion secondary cells exists. Simple magnesium salts in organic aprotic solvents, such as $\text{Mg}(\text{ClO}_4)_2$, tend to form passivating layers on the Mg-metal anode resulting in rapid capacity fades.^{28–30} However, high capacities can be achieved for the first ion intercalation, which makes $\text{Mg}(\text{ClO}_4)_2$ suitable for investigating the deep-discharge ion-intercalation mechanism. In contrast, $\text{Mg}(\text{TFSI})_2$ -based electrolytes provide a higher degree of reversible Mg stripping and deposition on the anode without formation of passivating layers, thus allowing for repeated charge-discharge cycles.¹⁰ Therefore, the $\text{Mg}(\text{TFSI})_2$ electrolytes are suitable for studying multi-cycle effects. Consequently, two Mg-electrolyte systems, i.e. 1 M $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile and 1 M $\text{Mg}(\text{TFSI})_2$ in diglyme, were used in this study.

Herein, Rietveld refinement based analysis of synchrotron radiation powder X-ray diffraction (SR-PXRD) data is combined with pair distribution function (PDF) analysis of total X-ray scattering (TS) data to investigate the evolution of the atomic structure during Li- and Mg-ion storage in two types of vanadium oxide nanotubes: amine-containing $\text{C}_{12}\text{-VO}_x\text{-NTs}$ and ion-exchanged $\text{Mg-VO}_x\text{-NTs}$. The *operando* scattering studies are coupled with a thorough characterization of the as-synthesized nanotube materials and of the electrochemical performance.

METHODS

Synthesis of $\text{VO}_x\text{-NTs}$. The $\text{C}_{12}\text{-VO}_x\text{-NTs}$ were synthesized from 6.369 g (34.4 mmol) dodecylamine (98%, Sigma-Aldrich) and 6.250 g (34.4 mmol) of $\alpha\text{-V}_2\text{O}_5$ ($\geq 99.8\%$, Sigma-Aldrich) mixed in 19 mL ethanol and mechanically stirred for 2 hours. Deionized water (31 mL) was added and the suspension was aged for 72 hours. The hydrolyzed vanadium oxide mixture

was solvothermally treated at 180°C for seven days in a Teflon-lined steel autoclave. The obtained slurry was washed with deionized water and dried at 60°C under vacuum overnight to obtain the C₁₂-VO_x-NTs as a black powder with a dark green hue. The synthesis ran in good yield generally providing >8 g of C₁₂-VO_x-NTs. The percentage yield is not given as the exact stoichiometry of the material is unknown.

The Mg-VO_x-NTs were obtained by ion exchange of 1g of the as prepared C₁₂-VO_x-NTs stirred for 24 hours in 1000 mL of a 1 M MgCl₂ (≥98%, Sigma) ethanol/H₂O solution, as described by Reinoso *et al.*¹⁹

Electrochemical cell preparation. For electrochemical analysis, the VO_x-NT materials were mixed with Super P conductive carbon (CENERGY, C45) and polyvinylidene fluoride binder (HSV900 PVDF, MTI Corporation) in mass ratio 8:1:1 in *N*-Methylpyrrolidine (NMP) (97%, Sigma-Aldrich) and coated onto carbon coated Al-foil (18μm thick, MTI Corporation) with 400 μm thickness at 8 mm/s using a Tape Casting Coater (MTI Corp.). The coating was dried at 60°C for >18 hours and subsequently at 90°C for 1 hour. Discs of 10 mm diameter were cut using a Precision Disc cutter (MTI Corp.) and dried at 60°C under vacuum for at least four hours. The average loading of active material was 3 mg/cm².

For tests in Li-ion cells, electrolyte of 1 M LiPF₆ in ethylene carbonate:dimethyl carbonate 1:1 v/v was used as-received (99.9%, Solvionic). For tests in Mg-ion cells two types of Mg-ion electrolytes were used: a magnesium bis(trifluoromethylsulfonyl)imide (TFSI) salt in diglyme and a magnesium perchlorate salt in acetonitrile. The TFSI electrolyte was prepared from Mg(TFSI)₂ (99.5%, Solvionic) dried at 180°C under vacuum for 18 hours prior to addition of anhydrous diglyme (99.5%, Sigma-Aldrich) to obtain a 1 M solution. The solution was further dried with molecular sieves and the water content was measured by Karl Fisher titration to 14

ppm. The perchlorate electrolyte was prepared from $\text{Mg}(\text{ClO}_4)_2$ ($\geq 99.0\%$, Sigma-Aldrich) and dried at 200°C under vacuum for 18 hours prior to addition of anhydrous acetonitrile (99.8% , Sigma-Aldrich) to obtain a 1 M solution.

Galvanostatic charge-discharge tests were carried out using two-electrode Swagelok cells, with 10 mm diameter cathodes, 12 mm diameter Whatman GL/B separators, seven drops of electrolyte, and mechanically polished hand-rolled Li foil (99.9% , Aldrich) cut to 10 mm diameter discs for Li-ion cells, and 0.25 mm thick Mg foil (99.9% , GoodFellow) punched to 10 mm diameter discs for Mg-ion cells.

X-ray scattering studies. *Ex situ* powder X-ray diffraction (PXRD) patterns of the as prepared VO_x -NTs were collected on a Rigaku MiniFlex 600 or a PANalytical X'Pert Pro. On the former, data were collected in reflection geometry using a D/teX Ultra detector with a step size and speed of 0.02° and $10^\circ/\text{min}$, respectively. On the PANalytical X'Pert Pro data were collected in transmission mode using capillary spinner, a PIXcel1D detector and a step size and speed of 0.013° and $8^\circ/\text{min}$ respectively. Both instruments employ a Cu K_α X-ray source.

Powdered samples for *ex situ* X-ray TS measurements for pair distribution function (PDF) analysis were mounted in polyimide tubes (1.0 mm inner diameter, Cole-Parmer). For *operando* synchrotron radiation powder X-ray diffraction (SR-PXRD) and TS experiments, the VO_x -NTs materials were mixed with carbon black (Cabot Corporation) and Graphite SFG6 (IMERYS) and polyvinylidene fluoride binder (HSV900 PVDF, MTI Corporation) in mass ratio 6:1:1:2 in acetone. The dry cathode mixtures were ground in a mortar and uniaxially pressed into pellets of ~ 10 mg and a diameter of 6 mm. The pellets were mounted in AMPIX-type battery cells³¹ specially designed for X-ray scattering experiments. The cathode pellets were mounted together with 14 mm discs of Wathman GL/B separators wetted with the above mentioned electrolytes

and 12 mm diameter discs of the Li- or Mg-metal anode. For the Mg-ion cells, a 1.5 mm diameter hole was drilled in the center of the Mg-anode to allow passage of the X-ray beam.

The *operando* SR-PXRD data for the Li-ion cells and Mg-ion cells with perchlorate electrolyte were performed at the P02.1 beamline³² at PETRA III at DESY, Hamburg, Germany with an X-ray wavelength of 0.2073 Å. The *operando* SR-PXRD data for the Mg-ion cells with Mg(TFSI)₂ electrolyte were performed at the Swiss-Norwegian beamline BM01 at ESRF, Grenoble, France with an X-ray wavelength of 0.7353 Å. The *ex situ* and *operando* TS experiments were performed at the 11ID-B beamline at APS at Argonne Nat. Lab., Chicago, USA with an X-ray wavelength of 0.2112 Å. At PETRA III and APS scattering patterns were collected with a Perkin Elmer (XRD1621) area detector, and calibrated using a CeO₂ standard placed at the cathode pellet position in the AMPIX cell. At ESRF scattering patterns were collected with a PILATUS 2M area detector and calibrated using a LaB₆ standard. Scattering patterns were collected using X-ray exposure times of 30-240 seconds for each scan and for the *operando* experiments at fixed time intervals of 6-30 minutes between each scan.

Diffraction spots originating from the anode metal were masked before azimuthal integration of the raw scattering data using Fit2D software.³³ All patterns from a single sample were scaled to compensate for beam intensity fluctuations using the intensity of the primary beam shoulder average over a 2θ range at small angles carefully avoiding regions of the 00 l reflections. The PDF was calculated from the TS-data using the PDFgetX3 software³⁴ with an upper Q-range cutoff ($Q_{\text{max-instrument}}$) of 21 Å⁻¹ and r_{poly} value set to 0.9 Å.

Rietveld refinement of SR-PXRD data was performed using the software FullProf.³⁵ Herein, the structural model proposed for C₁₂-VO_x-NTs by Wörle *et al.*¹⁴ was used as starting model. The data backgrounds were described by linear interpolation between selected points, while

pseudo-Voigt profile functions were used to fit the diffraction peaks.³⁶ In general, the scale factor and the profile parameters (U , V and W) were refined for each pattern, while the zero-point offset was refined for the first pattern in one *operando* experiment. The lattice parameters, a and b , related to the VO_x plane, were obtained by refining the model to the $(hk0)$ -family Bragg peaks whilst fixing the c lattice parameter to an unphysical small value of $0.5\text{\AA}$, thereby forcing other (hkl) reflections outside the chosen Q -space range. For some datasets a tetragonal model was used, i.e. $a = b$. The inter-layer spacings were found from the $(00l)$ Bragg peak positions by fitting a Gaussian function with a BSpline baseline defined by three anchor points at each side of the peak to the most intense of the detected $(00l)$ peaks. The structural models by Wörle *et al.*¹⁷ were fitted in real space to the PDF data using the PDFgui software.³⁷ A CeO_2 standard was fitted to obtain the instrumental broadening parameter, Q_{broad} (0.0303). For the fitting of the PDF data a small box approach was used with the number of fitted parameters limited to scale, the in-plane unit cell parameter, a , of a tetragonal cell and in-plane isotropic atomic displacement parameters (ADPs) for V and O. The ADPs in the c -direction was enlarged to an unphysical value ($>0.5\text{\AA}^2$) to remove the inter-layer correlations from the model. The small box approach is preferred for data of lower quality especially for the *operando* data. In contrast a large box approach deploying a supercell which also describes the multiwalled tubular structure and curvature of the layers entails a large number of fitting parameters and hence demands high quality data.

Transmission electron microscopy. Bright field TEM micrographs, STEM High Annular Dark Field images and energy-dispersive X-ray spectroscopy (EDX) elemental mapping were conducted on a Talos F200X (S)TEM from FEI equipped with a Super X-EDS system as well as on a JOEL 2010F TEM equipped with an Oxford INCA EDX detector. Elemental maps were

visualized and analyzed using the open source python library HyperSpy.³⁸ Samples were prepared by dispersing the dry powder in absolute ethanol and sonicating it for a few minutes before drop casting samples onto lacey carbon copper TEM grids.

Elemental analysis. Elemental analysis of Li, Mg and V was conducted using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on electrochemical cycled electrode materials. The electrodes were washed several times with DMC after cell disassembly (to remove leftover electrolyte salt) and dried at 60°C under vacuum. Subsequently, ~1 mg of electrode mixture was scraped off the Al-foil and dissolved in 6 mL nitric acid (65%, EMSURE). The ICP-AES measurement was performed on a PerkinElmer Optima 2100DV spectrometer. Furthermore, CHNS combustion analysis was performed on a Vario MACRO cube from Elementar.

RESULTS AND DISCUSSION

***Ex situ* characterization of the as-synthesized raw VO_x-NT materials.** Formation of C₁₂-VO_x-NTs by solvothermal synthesis and transformation into Mg-VO_x-NTs by ion-exchange is confirmed by results from both TEM (Figure 2) and PXRD (Figure 3) investigations. The TEM micrograph for the as-prepared C₁₂-VO_x-NTs shows the open-ended structure of multilayered scrolls with an outer diameter of ~50 nm, a length of a few μm and VO_x inter-layer spacing of ~2.7 and ~1 nm for the C₁₂-VO_x-NTs and Mg-VO_x-NTs, respectively. The outer tube diameter does not change significantly with ion-exchange. In contrast, the diameter of the inner hollow region increases drastically. This is may be explained by the decrease in VO_x inter-layer spacing, which causes the total wall thickness of the tubes to decrease. Apparently this process occurs by sliding the VO_x layers in the direction of the tube curvature on the inside of the scroll, which will

“tighten” the wall of the scroll without changing the outer diameter. This observation suggests that the tubes are indeed composed of scroll-like VO_x-layers as oppose to concentric VO_x-tubes.

Figure 2. TEM micrographs of as-prepared (A) C₁₂-VO_x-NTs and (B) Mg-VO_x-NTs. For both samples, the smaller micrographs show HAADF STEM (top right) and EDX mapping of V (blue), O (red), N (green) and for the Mg-VO_x-NTs Mg (magenta) based on their respective K α emission lines.

EDX elemental mapping clearly shows that V, O and N counts are correlated with the area of both types of nanotubes. The K α count ratios, obtained from background corrected Gauss fitting of the K α lines in the EDX spectra (see Figure S1, supplementary information), for N_{K α} :V_{K α} is 0.24 and 0.13 for C₁₂-VO_x- and Mg-VO_x-NTs, respectively. Hence, some amine is exchanged by Mg in the latter, which is also confirmed by the observation of Mg-counts in the area of the VO_x-NTs giving a Mg_{K α} :V_{K α} count ratio of 0.07. In comparison, no Mg-counts beyond the background level are observed for C₁₂-VO_x-NTs (Mg_{K α} :V_{K α} $\sim 5 \cdot 10^{-4}$). In the TEM micrographs of the Mg-VO_x-NTs, a few NTs with the original layer spacing (2.76 nm) were observed (see

Figure S1). Thus, the ion-exchange has not occurred to a full extent and the sample contains a mix of $C_{12}\text{-VO}_x\text{-}$ and $\text{Mg-VO}_x\text{-NTs}$. Combustion analysis (see Figure S2 in supplementary information) also agrees reasonably with expected C, H, and N weight fractions for $C_{12}\text{-VO}_x\text{-NTs}$ and with a $\sim 70\%$ ion exchange of the dodecylamine with Mg^{2+} -ions in the $\text{Mg-VO}_x\text{-NTs}$.¹⁹

Figure 3. PXRD data of as-prepared $C_{12}\text{-VO}_x\text{-NTs}$ and $\text{Mg-VO}_x\text{-NTs}$ (Cu $K\alpha$ radiation). The $(00l)$ reflections provide information about the VO_x inter-layer spacing, while the $(hk0)$ reflections yield the in-plane a - and b -lattice parameters related to the VO_x layers.

The PXRD data for the $\text{VO}_x\text{-NTs}$ (Figure 3) resembles data previously reported for similar materials (ICSD card number 151099).¹⁴ The $\text{VO}_x\text{-NTs}$ have a characteristic inter-layer spacing between the VO_x layers (see Figure 1), which can be extracted from the positions of the $00l$ reflections at small diffraction angles ($2\theta \sim 2\text{-}15^\circ$ using Cu $K\alpha$ radiation).^{13,19} The as-prepared $C_{12}\text{-VO}_x\text{-NTs}$ have a layer spacing of $27.58(4)$ Å in agreement with reports of 2.77 nm.¹³ The $(00l)$ reflection shifts to higher angles for the ion exchanged $\text{Mg-VO}_x\text{-NTs}$, corresponding to a decrease in the inter-layer spacing to $1.131(1)$ nm, which is somewhat less than the reported 1.27 nm.¹⁹ The $(hk0)$ family reflections at higher angles originating from the VO_x in-plane a - and b -

axis are left unchanged in the ion-exchanged Mg-VO_x-NTs in accordance with previous reports.^{16,19}

The curvature and accompanying anisotropic strain of the VO_x layer structure leads to significant broadening and shift of the (*hk*0) Bragg reflections. Thus, a detailed analysis of the VO_x layer structure by traditional Rietveld refinement is inherently complicated. Therefore, TS data were collected and the PDFs were obtained (Figure 4A). The PDF of both C₁₂-VO_x-NTs and Mg-VO_x-NTs agrees well with the previously reported PDF of C₁₈-VO_x-NTs,¹⁶ and no major difference are observed between the PDFs of the two samples. Thus, differences in inter-layer spacing (which depends on the size of the inter-layer molecule/ion) does not affect the PDFs significantly likely due to disordered stacking of the VO_x layers, which dampens the longer range layer-to-layer correlations in the PDF. Instead, the PDF is dominated by information about the VO_x in-plane structure, which appears to remain relatively unchanged by the ion-exchange. However, the peaks in the PDF for Mg-VO_x-NTs are generally somewhat broadened as compared those of C₁₂-VO_x-NTs, which indicates that ion-exchange may cause a slight decrease in the structural order of the layers. This is also evidenced by the general dampening of the PDF observed for the Mg-VO_x-NTs. The local VO_x structure corresponds well with the main V-O and V-V atomic correlations based on the idealized V₇O₁₆ form (Figure 4B) of the layer structure described by Wörle *et al.*¹⁴ The main correlations of the V₇O₁₆ structure are shown along the PDF as vertical black lines for comparison (see details in supplementary information Table S1). The correlations between 1.5 and 2.5 Å correspond to the shortest V-O distances, i.e. in the [VO₄] tetrahedra, in the [VO₅] square pyramide and from V in [VO₅] in one bi-layer to the O-base of the nearest [VO₅] in the next bilayer. The majority of correlations from 2.5 to 7 Å originate from V-V distances, e.g. between edge-sharing [VO₅] units within a bi-layer (~3 Å),

between corner sharing $[\text{VO}_4]$ - $[\text{VO}_5]$ (~ 3.4 Å) and between $[\text{VO}_5]$ units in the two bi-layers (~ 3.4 Å). The higher r -region (>6.5 Å) can be simulated ($R_w \sim 54\%$) by the idealized V_7O_{16} structure if large atomic displacement factors (>0.5 Å²) are introduced in the c -direction to account for the lack of distinct inter-layer correlations. However, this approach is unsuccessful in describing the local structure of the VO_x layers, as they contain well-defined V-O and V-V correlations along the c -axis.

Figure 4. (A) PDF of as-prepared C_{12} - VO_x -NTs and Mg - VO_x -NTs. The inset shows the same data for r extending up to 60 Å. The dominating V-O and V-V distances in an idealized V_7O_{16} repeating unit based on the structure described by Wörle *et al.*¹⁴ are shown (black lines) for comparison (V-O counts are divided by 3 to account for the lower scattering power of O). (B) Structure of the V_7O_{16} layer viewed along the b - (top) and c -axis (bottom). The dominating V-O and V-V distances are marked.

Chemical intercalation of Mg into the C_{12} - VO_x -NTs and Mg - VO_x -NTs using n -butyl-magnesium was attempted in an effort to study the structure of the tubes after Mg-intercalation. Unfortunately, the process destroyed both the tube and the layer structure, as evident from the loss of the significant $(00l)$ and $(hk0)$ family reflections in the PXRD patterns. Furthermore, from

the PDF for this sample it was evident that the structure of the smallest repeating unit, V_7O_{16} , is drastically changed upon this treatment (See supplemental info Figure S3).

In the prepared electrode coatings and pellets, the inter-layer spacing of the $C_{12}-VO_x$ -NTs is increased to 3.21 nm (see supplemental info Figure S4A and B). A similar change was reported for electrodes prepared by Nordlinder *et al.*³⁹ At first it was assumed that intercalation of electrolyte molecules might cause this change. Therefore, a series of PXRD experiments were conducted on the as-prepared composite electrode pellets dispersed in electrolyte. Interestingly, presence of the electrolyte was not found to significantly influence the inter-layer spacing (see supplemental info Figure S4C). However, the inter-layer spacing was found to vary slightly between each electrode pellet. Thus, the slight difference in electrode preparation from sample to sample is believed to cause this structural change, in particular variation of the pressure used to prepare the pellets is assumed to be the main factor. Nonetheless, further investigations are needed to establish a definite link between correlation and causality. A consequence of these observations is that this system must be investigated by *in situ* or *operando* methods as comparing data from multiple electrodes will be complicated by the variation.

Electrochemical analysis of Li- and Mg-ion intercalation in VO_x -NTs. Initial specific discharge capacities of 195 ± 5 and 146 ± 36 mAh/g for Li- and Mg-ion cells (based on an average from three cells), respectively, are achieved for $C_{12}-VO_x$ -NTs (see Figure 5A and C). If assuming that the amount of inserted ions can be calculated directly from Coulomb counting $7.16Li$ and $5.33Mg$ per V_7O_{16} are intercalated, respectively. Unfortunately, the material displays a large capacity loss with repeated cycling. As expected, the $Mg(TFSI)_2$ (diglyme) electrolyte significantly decreases the rate of the capacity fade for Mg-ion storage but also provides a lower initial capacity compared to that in the cell with $Mg(ClO_4)_2$ (ACN) electrolyte. Interestingly, the

rate of capacity fade is faster in the Li-ion cell compared to the Mg-ion ($\text{Mg}(\text{TFSI})_2$) cell implying that the irreversibility is caused by processes occurring mainly at deep-discharge in the $\text{C}_{12}\text{-VO}_x\text{-NTs}$ rather than issues related to the Mg-ion chemistry. As a Li-ion electrode, $\text{Mg-VO}_x\text{-NTs}$ shows an initial discharge capacity similar to that of $\text{C}_{12}\text{-VO}_x\text{-NTs}$, while lower capacities are achieved for Mg-ion intercalation (Figure 5B and D). Compared to the $\text{C}_{12}\text{-VO}_x\text{-NTs}$, the capacity retention for the $\text{Mg-VO}_x\text{-NTs}$ appears to be significantly improved for Li-ion storage. A drastic capacity fade is still observed for Mg-ion storage when employing the $\text{Mg}(\text{ClO}_4)_2$ electrolyte, which underlines the instability of this component. Employing instead the $\text{Mg}(\text{TFSI})_2$ electrolyte, the cyclic stability of $\text{Mg-VO}_x\text{-NTs}$ appears slightly better than for $\text{C}_{12}\text{-VO}_x\text{-NTs}$. However, the improvement is far less than for Li-ion storage likely due to issues with intercalation/extraction of the more polarizing Mg-ion, e.g. for a nanostructures bilayer V_2O_5 electrode it has been shown that hydration of the Mg-ions are necessary to ensure reversible cycling.⁴⁰ The electrochemical properties are summarized in Table 1.

To confirm that the drawn current can be attributed to Li- or Mg-intercalation and -extraction as opposed to e.g. SEI formation or electrolyte decomposition, Li, Mg and V contents in the cycled electrodes were determined by ICP-AES analysis. In Figure 6, the Li/V and Mg/V ratios are represented as y in $\text{M}_y\text{V}_7\text{O}_{16}$ ($\text{M} = \text{Li}, \text{Mg}$) and compared to amounts of Li and Mg assumed inserted from coulomb counting in the electrochemical data. For the majority of cycled electrodes, the Li- and Mg-content detected by ICP-AES is either similar to or slightly exceeds the contents calculated from coulomb counting. This confirms that the current drawn generally can be associated with ion intercalation and extraction. The larger contents observed by ICP-AES are likely due to leftover electrolyte salt. This is underlined by the fact that the level of

excess remains relatively constant between the discharged and charged state (e.g. compare Li-contents for C_{12} -VO_x-NTs samples discharged and charged in LiPF₆).

Figure 5. (A-D) Representative discharge / charge curves for 1st, 2nd, 5th and 10th cycle of (A) C_{12} -VO_x-NTs and (B) Mg-VO_x-NTs against Li with 1M LiPF₆ in EC:DMC electrolyte in a three-

electrode cell, (C) C₁₂-VO_x-NTs and (D) Mg-VO_x-NTs vs. Mg in 1M Mg(ClO₄)₂ in ACN and 1M Mg(TFSI)₂ in diglyme electrolytes, and average discharge capacity of the first 10 discharges of (E) C₁₂-VO_x-NTs and (F) Mg-VO_x-NTs using the three electrolytes. The plots in (E) and (F) are based on an average from three cells. Inset shows coulombic efficiency as function of cycle number.

Table 1. Electrochemical performance of vanadium oxide nanotube, VO_x-NT electrodes. Type of counter electrode, electrolyte, VO_x-NT material, current density, capacity and capacity loss are listed. All values are based on an average of three cells.

Anode	Electrolyte salt (solvent)*	VO _x -NT material	Current density [mA/g] (C-rate)	Capacity [mAh/g]	Cap. loss (# cycles)
Li	LiPF ₆ (EC:DMC)	C ₁₂ -VO _x -NTs	10 (~C/10)	195±6	65% (10)
Li	LiPF ₆ (EC:DMC)	Mg-VO _x -NTs	10 (~C/10)	192±12	<10%
Mg	Mg(TFSI) ₂ (diglyme)	C ₁₂ -VO _x -NTs	5 (~C/20)	72±5	50%
Mg	Mg(ClO ₄) ₂ (ACN)	C ₁₂ -VO _x -NTs	5 (~C/20)	146±35	85%
Mg	Mg(TFSI) ₂ (diglyme)	Mg-VO _x -NTs	5 (~C/20)	33±12	26%
Mg	Mg(ClO ₄) ₂ (ACN)	Mg-VO _x -NTs	5 (~C/20)	58±8	97%

*) EC: Ethylene carbonate, DMC: Dimethyl carbonate, TFSI: bis(trifluoromethylsulfonyl)imide, ACN: acetonitrile

The ICP-AES confirms that Li-insertion is rather effective yielding compositions of Li_yV₇O₁₆ with $y > 7$ and ~5 for C₁₂-VO_x-NT and Mg-VO_x-NT, respectively. It is also evident that not all Li is extracted from the NTs upon charge. Thus, Li-ions appear to accumulate in the NT materials upon cycling, i.e. in the charged state there is >1 inactive Li per V₇O₁₆ after only five cycles. For Mg-ion storage using the Mg(TSFI)₂ electrolyte, ICP-AES confirms intercalation of Mg, however in relatively small amounts yielding a composition after the 1st discharge of Mg_{1.3}V₇O₁₆ and Mg_{1.0}V₇O₁₆ for C₁₂-VO_x-NT and Mg-VO_x-NT, respectively. Thus, only ~0.3Mg is intercalated in Mg-VO_x-NT when accounting for the amount of Mg from ion-exchange (70%). Significantly higher Mg-contents are detected when using the Mg(ClO₄)₂ electrolyte. However,

in this case the values calculated from the electrochemical data after the 1st discharge exceed those observed by ICP-AES (in some cases by ~50%). Thus, for this electrolyte system, a portion of the current cannot be attributed to Mg-intercalation and -extraction. This confirms the unstable nature of the $\text{Mg}(\text{ClO}_4)_2$ (ACN) electrolyte and underlines the importance of performing additional chemical analysis when determining Mg-ion capacity, i.e. coulomb counting alone does not suffice. It appears that in the $\text{C}_{12}\text{-VO}_x\text{-NT}$ electrodes Mg-ions tend to accumulate upon cycling, i.e. for both electrolyte systems, Mg is detected in relatively large amounts by ICP-AES in the charged electrodes. This effect might be due to ion-exchange of the amines with the Mg-ions.

Figure 6. Amounts of Li (red) and Mg (blue) in the electrodes at various discharge/charge states based on ICP-AES weight fractions compared to amounts calculated from coulomb counting in the electrochemistry data. The amount of Li and Mg for $\text{Mg-VO}_x\text{-NTs}$ determined from electrochemistry is based on 70% ion-exchange, i.e. y in the as-prepared $\text{Mg}_y\text{V}_7\text{O}_{16}$ is 0.7. All

electrodes were thoroughly washed (in the solvent also used for the electrolyte) prior to the analysis to remove as much of the Li- and Mg-salts from the electrolyte as possible.

***Operando* scattering studies of ion intercalation in VO_x-NT materials.** *Operando* SR-PXRD (see data in Figures S5-10, supplementary information) and -TS were performed during discharge and charge on selected combinations of VO_x-NT materials and electrolytes to obtain insight into the structural changes during ion intercalation in the VO_x-NTs.

During Li- and Mg-intercalation into both C₁₂-VO_x-NTs and Mg-VO_x-NT using Mg(ClO₄)₂ electrolyte, the in-plane unit cell parameters for the VO_x layers, i.e. *a* and *b*, increase as expected (Figure 7 and 8) due to the increase in ionic radius of vanadium induced by the reduction. The evolution of the VO_x inter-layer spacing, i.e. the *c*-axis, is less simple and varies significantly between the two materials and the two ions. In general, ion-intercalation into C₁₂-VO_x-NTs is accompanied by an increase in the inter-layer spacing and a significant loss of the long range stacking order suggesting either delamination of the tubes, or large variations in the inter-layer spacing across the tube. In contrast, ion-intercalation into Mg-VO_x-NT causes a decrease in the inter-layer spacing. This is most likely a result of the intercalated ions minimizing repulsion between the VO_x layers, which is an effect observed in several electrode materials such as LiCoO₂ and Li₃V₂(PO₄)₃.⁴¹⁻⁴³ Decreasing interlayer spacing have also been observed upon Mg-intercalation in bilayer V₂O₅ cathodes.⁴⁰ The effect is likely stronger in Mg-VO_x-NT than in C₁₂-VO_x-NTs due to the smaller distance between the VO_x layers. Furthermore, the long range stacking order is retained during ion intercalation into Mg-VO_x-NT.

Figure 7. Results of operando SR-PXD experiments for discharge and charge of C_{12} -VO_x-NTs (A-C) and Mg-VO_x-NTs (D-F) electrodes vs. Li using a 1 M LiPF₆ (EC:DMC) electrolyte. (A and D) in plane cell parameters a and b , (B and E) the layer distance c (black squares) and relative intensity of the (001)-peak (normalized to the total scattered intensity) (red) and (C and F) potential profiles for the galvanostatic discharge and charge. Current density was set to 10 mA/g (~C/20 equivalent for Li₇V₇O₁₆).

Intercalation of the initial ~3Li per V₇O₁₆ (~8 h) into C_{12} -VO_x-NTs causes the VO_x inter-layer spacing to increase by 4.3% or 0.13 nm (Figure 7). Simultaneously, the integrated normalized intensity of the 00 l reflection decreases by >60%. No further significant change to the layer spacing and the (00 l) intensity is observed as discharge and subsequently charge progresses, implying that the fraction of the material, which is still well-ordered in the c -direction is either inactive or has reached an upper limit of expansion. However, the potential profile and more

importantly the continued linear increase/decrease in the in-plane a - and b -axis indicate continued electrochemical activity for the remainder of the discharge and subsequent charge. Thus, despite the loss of stacking order, the material is still electrochemically active, i.e. the VO_x layers seem to retain their capability to store ions electrochemically. However, if delamination occurs the increased surface area may increase the rate of unwanted side-reactions and contribute to the rapid capacity fade observed for $\text{C}_{12}\text{-VO}_x\text{-NTs}$.

Figure 8. Results of *operando* SR-PXRD experiments for discharge and charge of $\text{C}_{12}\text{-VO}_x\text{-NTs}$ (A-C) and $\text{Mg-VO}_x\text{-NTs}$ (D-F) electrodes vs. Mg using a 1 M $\text{Mg}(\text{ClO}_4)_2$ (acetonitrile) electrolyte. (A and D) VO_x in-plane cell parameters a and b , (B and E) the layer distance c and relative intensity of the (001)-peak (normalized to the total scattered intensity) and (C and F) potential profiles for the galvanostatic discharge. Current density was set to 5 mA/g ($\sim \text{C}/20$ equivalent).

The decrease in the VO_x inter-layer spacing due to Li-intercalation in Mg- VO_x -NTs occurs in three stages, i.e. 0-2 hours ($y_{\text{Li}} = 0$ to 0.5), 2-12 hours ($y_{\text{Li}} = 0.5$ to 3.0) and 12-20 hours ($y_{\text{Li}} = 3.0$ to 5.0). In the latter regime, the inter-layer spacing is relatively constant. The initial Li-intercalation may cause the largest reduction of the repulsion and as more ions are inserted the effect eases. During Mg-ion intercalation the decrease in the layer spacing is linear over the entire discharge.

Using the $\text{Mg}(\text{TFSI})_2$ (diglyme) electrolyte *operando* PXRD data were collected during three consecutive discharge-charge cycles for Mg- VO_x -NTs (See Supplementary Information Figure S11). This provides some insight into the reversibility of the structural changes. In the first discharge the material behaves in approximately the same manner as observed when employing the $\text{Mg}(\text{ClO}_4)_2$ electrolyte. During repeated cycling the VO_x in-plane cell parameters, a and b , increase and decrease linearly with similar rates during reduction and oxidation of vanadium as expected. Thus, the behavior of the in-plane axis appears to be reversible relative to the change in oxidation state of vanadium. The discharge capacity is larger than the charge capacity in all three discharge-charge cycles for Mg- VO_x -NTs and the a - and b -axis gradually expands for every discharge, which indicates that part of the on-going capacity loss is caused by irreversible Mg-intercalation and Mg build-up. The behavior of the VO_x inter-layer distance is only partly reversible in this respect. Only little expansion of the inter-layer spacing is observed during each charge (Mg-ion extraction). In contrast, the contraction during the second and third discharge appears to occur at similar rates as during the first discharge.

To gain a better understanding of the local VO_x structure in the layers, *operando* TS experiments were conducted during Mg-intercalation in C_{12} - VO_x -NT and Mg- VO_x -NT to obtain the *operando* PDF data (Figure 9. Full *operando* dataset at low and high r are shown in Figures

S12 and S13). It is evident that no major restructuring of the VO_x layers occurs during ion-intercalation as only minor changes are observed in the PDFs over the course of discharge. Detailed PDF analysis is somewhat complicated by the electrode additives, i.e. conductive carbon and PVDF binder, which gives rise to C-C correlations in the low r -region (marked by dashed lines in Figure 9). To emphasize the changes in the PDFs during discharge, the difference PDFs, $\Delta G(r) = G(r) - G(r)_{t=0}$, are plotted as well. Herein, positive intensities are indicative of new correlations, while negative intensity means that some correlations are lost.

Figure 9. Selected PDFs based on *operando* total scattering X-ray data collected during discharge of (A) C₁₂-VO_x-NT and (B) Mg-VO_x-NT vs. Mg using an 1 M Mg(ClO₄)₂ (acetonitrile) electrolyte to achieve deep discharge. The current density was 5 mA/g (~C/40 equivalent). The top plots show the difference PDF, $\Delta G(r) = G(r) - G(r)_{t=0}$ (using the same line colors as for the PDFs). Note that the scale used for $\Delta G(r)$ is three times that used for $G(r)$. The red and black tick marks correspond to the main V-O and V-V correlations in V₇O₁₆, respectively, while the dashed lines show the main C-C correlations from the carbon additives in the electrode.

For both C₁₂-VO_x-NT and Mg-VO_x-NT changes in the PDFs appear mainly in three regions: ~2.0, ~3.2 and ~6.2 Å. The former change is related to alterations in the shortest V-O correlations. It appears that with Mg-insertion, the number of correlations ranging from 1.95- to 2.04 Å increases. For the as-prepared material this r-region was assigned to the long V-O correlation in the base of the [VO₅] square pyramids- Moreover, the length of the correlation increases slightly (approx. 0.05 Å). Simultaneously, intensity from the other V-O correlations seems to shift towards ~2.0 Å seen by small negative intensities in the difference PDFs. This can be explained by the change in coordination geometries associated with the changes in vanadium oxidation state. In V₇O₁₆, there are two V(V) and five V(IV) under the assumption that there are two mono-protonated amines per V₇O₁₆-unit (ensuring a charge per unit of -2). In tetrahedral coordination, [VO₄], vanadium is always in oxidation state +5, and a reduction will result in a dramatic structural change.⁴⁴ As the V₇O₁₆-layer structure is retained during discharge, reduction of [VO₄] is unlikely. The V-O bond in the tetrahedra may still change slightly as these can generally vary from 1.6 to 1.8 Å. In a square pyramid, [VO₅], vanadium can be in oxidation state +4 or +5. Reversible cycling between V in oxidation states +4 and +5 during Mg-ion storage have been confirmed in previous studies of V₂O₅ cathodes.⁴⁰ Thus, based on the oxidation states in the V₇O₁₆-unit, five out of six [VO₅]-pyramids contains V(IV). Reduction to V(III) is likely to change the coordination to octahedral, i.e. [VO₆].⁴⁴ This can easily occur without a major structural reconstruction by shifting vanadium in [VO₅] towards the other bi-layers, i.e. towards the square-base of the pyramid (Figure 10). Hereby, the V-O correlation between bi-layers (originally at 2.22-2.29 Å) shortens and become similar to those in the base of the pyramid (1.95-2.04 Å). This will effectively transform the square pyramids to distorted octahedra. The shift in V-position also increases the bond distance towards the oxygen, which used to form the top of

the pyramid. As V(III) tends to prefer ideal octahedral coordination, it is highly likely that all six V-O correlations will be ~ 2 Å. The described transformations also explain the intensity increasing with Mg-intercalation at ~ 3.2 Å, which have two contributions. Firstly, the intra bi-layer V-V correlation (originally at 2.95-3.00 Å) between edge-sharing $[\text{VO}_5]$ or $[\text{VO}_6]$ units increase as vanadium reduction progresses. Secondly, shifting the V-positions will shorten the inter bi-layer V-V correlation (originally at 3.32-3.45 Å). The fact that this change arises from two contributions is clearly observed in the difference PDF for $\text{C}_{12}\text{-VO}_x\text{-NT}$, where two peaks gradually merge at ~ 3.2 Å. The final major change at ~ 6.1 Å is induced by the increase in the in-plane a, b -unit cell parameters due to vanadium reduction. Thus, the correlation at 6.14 Å (see Figure 4) shifts towards higher r . This is clearly observed in the difference PDF and supports the findings from the *operando* PXRD experiments.

Figure 10. Illustration of the structural change in the V_7O_{16} -layers of the VO-NTs during ion-intercalation (i.e. reduction of vanadium). Notice how the coordination of V changes from square pyramidal, $[\text{VO}_5]$ in the original structure (top) to octahedral, $[\text{VO}_6]$ in the reduced V_7O_{16} layer by shifting the V-positions slightly.

A smaller extent of vanadium reduction is achieved for Mg-VO_x-NT (only 0.73Mg is inserted) compared to C₁₂-VO_x-NT. Hence, less drastic changes are observed and it is harder to judge signals from noise in the difference PDF. However, it seems like some correlations appear for Mg-VO_x-NT, which are not observed for C₁₂-VO_x-NT. These must be attributed to Mg-Mg or Mg-V correlations. The intensity appearing in the range 4.6-5.2 Å may be Mg-V correlations arising from the electrochemically intercalated Mg-ions being positioned between the VO_x layers (the inter-layer spacing is ~1.05 nm). This is plausible as the ions introduced by ion-exchange likely are rather randomly positioned close to the negatively charged VO_x layers to balance the charge. Hence, correlations are observed over a range of distances. A correlation also appears at ~3.9 Å, which may be Mg-Mg correlations between the ion-exchanged and intercalated Mg-ions.

The V₇O₁₆ model was fitted to a series of *r*-regions each covering 5 Å with center points from 8.5 to 33.5 Å in steps of 1 Å. The in-plane unit cell parameter, *a* (assuming a tetragonal cell, i.e. *a* = *b*), generally decreases with increasing center point (*r*) for the refinement, which is indicative of the curved nature of the VO_x-layers (see Figure S14 in the supplementary information). For both C₁₂-VO_x-NT and Mg-VO_x-NT the radius of the curvature is smaller in the discharged (reduced) materials. This is especially pronounced for Mg-VO_x-NT.

Interestingly, the PDF analysis provides an estimate of the maximum ion-storage capacity. The fact that the V₇O₁₆ layers remain intact during reduction as evidenced by both SR-PXRD and TS, means that the [VO₄]-geometry is not broken and vanadium must remain in oxidation state +5. Thus, only vanadium in square pyramids, hereof one V(I) and five V(IV), can be reduced. If these are all reduced to V(III), seven electrons can be stored. Thus, the maximum capacity of 7Li per V₇O₁₆ is reached in the electrochemical test (the capacity corresponds to 7.16Li per V₇O₁₆) for C₁₂-VO_x-NT, while the theoretical maximum of 3.5Mg is exceeded as 5.33Mg are stored

based on Coulomb counting for the cells employing the $\text{Mg}(\text{ClO}_4)_2$ -based electrolyte. However, our ICP analysis clearly showed that a part of this capacity stems from side reactions rather than ion-intercalation. Furthermore, the Mg-ion inserted by ion-exchange in $\text{Mg-VO}_x\text{-NTs}$ (1 Mg^{2+} per V_7O_{16} for an ideal ion exchange) is as expected not extractable and is an electrochemically inactive ion. Instead, this cation is stabilizing the overall multi-walled structure.

CONCLUSIONS

Two types of multi-walled vanadium oxide nanotubes, $\text{C}_{12}\text{-VO}_x\text{-NT}$ and $\text{Mg-VO}_x\text{-NT}$ were investigated as electrodes in Li- and Mg-ion batteries. The materials show high initial ion-storage capacities as electrodes in both Li- and Mg-ion batteries. Poor capacity retentions were generally observed for $\text{C}_{12}\text{-VO}_x\text{-NT}$, while for $\text{Mg-VO}_x\text{-NT}$ an apparently stable capacity of >190 mAh/g was achieved for Li-ion storage. Capacity retention the Mg-ion storage was improved by utilizing an electrolyte based on $\text{Mg}(\text{TFSI})_2$ instead of $\text{Mg}(\text{ClO}_4)_2$. However, lower initial capacities were achieved with the $\text{Mg}(\text{TFSI})_2$ electrolyte. ICP analysis revealed that employing an $\text{Mg}(\text{ClO}_4)_2$ electrolyte leads to significant side-reactions, which highlights the importance of not evaluating the degree of Mg-ion intercalation from electrochemical observations alone. The structural changes on the atomic scale during battery charge and discharge were investigated by *operando* SR-PXRD and PDF analysis. During Li- and Mg-intercalation the inter-layer spacing between the VO_x layers in $\text{C}_{12}\text{-VO}_x\text{-NTs}$ increases. Simultaneously, the VO_x stacking order significantly decreases with up to 60% loss of the diffracted intensity from the (00 l) reflections. These changes appear to be irreversible and may, together with the observed ion build-up, be the origin of the rapid capacity loss. In $\text{Mg-VO}_x\text{-NT}$, ion-intercalation causes a decrease in the inter-layer spacing due to minimization of the repulsion between the negatively charged vanadate

layers. For this material the stacking order of the VO_x layers is retained, which may explain the higher capacity retention. From Rietveld refinement it is evident that ion intercalation and -extraction in both C₁₂-VO_x-NTs and Mg-VO_x-NT, causes the VO_x layers to expand and contract reversibly with vanadium reduction and oxidation. PDFs (obtained from TS data) revealed that the local V₇O₁₆-structure of the VO_x layers remains intact during discharge and that the concurrent reduction of vanadium induces a change in vanadium coordination from five-fold square pyramidal to six-fold octahedral. The good capacity retention of the ion-exchanged VO_x-NTs combined with the ease of fabrication and high structural flexibility evidenced in this study underlines that these types of layered nanostructured materials holds a promise for battery applications and their structural variation should be explored further.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.xxxxxx.

EDX spectra and additional TEM micrograph of the as-prepared materials, list of the main VO_x-NT atomic correlations for the PDF analysis, results of the combustion analysis, PDF data of chemically lithiated sample, PXRD of as prepared electrode pellets and *operando* PXRD and PDF data.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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ABBREVIATIONS

ACN, acetonitrile; DMC, dimethyl carbonate; EC, ethylene carbonate; ICP-AES, inductively coupled plasma atomic emission spectroscopy; NMP, *N*-methylpyrrolidine; PC, propylene carbonate; PDF, pair distribution function; PVDF, polyvinylidene fluoride; PXRD, powder X-ray diffraction; Total X-ray scattering, TS; SR, synchrotron radiation; TEM, transmission electron microscopy; THF, tetrahydrofuran; TFSI, bis(trifluoromethylsulfonyl)imide; VO_x-NTs, vanadium oxide nanotubes.

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