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Vanadium Oxide Nanotubes as Cathode Material for Mg-ion Batteries

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Introduction
Vanadium oxide compounds as cathode material for secondary Li-ion batteries gained interest in the 1970’s due to high specific capacity (>250mAh/g), but showed substantial capacity fading.1 Developments in the control of nanostructured morphologies have led to more advanced materials, and recently vanadium oxide nanotubes (VO$_2$-NT) were shown to perform well as a cathode material for Mg-ion-batteries.2 In this study we have synthesized a series of VO$_x$-NTs with varying spatial molecules. The mechanism for Mg-intercalation and deintercalation was studied by TEM-EDX and operando synchrotron powder X-ray diffraction measured during battery operation.

• The VO$_x$-NTs consists of multiwalled scrolls of crystalline VO$_2$ layers with approximate composition VO$_{1.5}$s and primary amines in between the layers acting as spacer molecules.3
• Formal Vanadium oxidation states V$^3$/V$^5$ = 2/5
• Primary amines can be exchanged with metal cations with a subsequent change in layer spacing.4
• The structure allows for reversible intercalation and deintercalation of guest ions.

Results
• In house PXD diffraction (Fig 2) of the VO$_x$-NTs as prepared was obtained on a Rigaku Miniflex diffractometer.
• 00l reflections are found at low angles. These are associated with the interlayer spacing, c ~ 27.7Å, when dodecyl amine C$_{12}$H$_{25}$NH$_2$ is used as spacer molecule.
• 400 reflections are found at higher angles. These can be fitted to the 2D tetragonal basal layer (Fig. 1) with
  a = b = 6.12Å.

• TEM micrographs (Fig. 3-4) of the VO$_x$-NTs collected on a FEI “Talos” F200X (S)TEM-microscope verify the multiwalled tube structure.
• Smaller spacing observed in Mg$_2$VO$_x$-NTs and Mg detected by EDX in the tubes.
• Mg-intercalation in the multiwalled VO$_2$-NTs occurs within the space between the individual vanadium oxide layers of the nanotubes while the underlying VO$_2$ frameworks constructing the walls are affected only to a minor degree by the intercalation.

Discussion
The VO$_x$-NTs are able to accommodate large change in layer spacing (~50%) upon exchange of the intercalated ions and retain their structural integrity. This ability makes it a interesting cathode material for Mg-ion batteries.

In the operated battery the (001) diffraction signal moved to lower angles during discharge, corresponding to a larger interlayer spacing. Simultaneously a new peak formed at a higher angles corresponding to shorter interlayer spacing.

• Mg$_2$ was successfully intercalated into C$_{12}$-VO$_2$-NTs
• Expansion and subsequent distortion of VO$_{1.5}$-layers
  - Increase in interlayer spacing
  - Second and smaller interlayer spacing forms
• Results indicate 150 mAh/g reversible capacity at C/10-rate

Materials and Methods
• C$_{12}$-VO$_x$-NTs hydrothermally synthesized
  V$_2$O$_5$ + 2C$_{12}$H$_{25}$NH$_2$ $\xrightarrow{160^\circ C, 7\ days}$ C$_{12}$-VO$_2$-NT
• Ion exchanged with Mg
  C$_{12}$-VO$_x$-NT $\xrightarrow{Mg^{2+}}$ Mg-VO$_x$-NT
• The obtained black C$_{12}$-VO$_x$-NT or Mg-VO$_x$-NT powders were mixed with conductive carbon black and a binder material in the ratio 60 : 20 : 20 wt%
  active material : carbon : binder and uniaxial pressed (1.8T) to a pellet.
• Mg metal, with a ~1mm Ø hole to allow passage of the X-ray beam, was used as anode material
• 1M MgClO$_4$ in acetonitrile was used as electrolyte and Whatman filter paper as separator.

Fig 1: Schematic illustration of the multiwalled C$_{12}$-VO$_2$-NT structure. Five fold (square pyramidal) coordinated V are depicted in blue and four fold (tetrahedral) coordinated V are depicted in green. In red the protonated primary amines, acting as spacer molecules can be exchanged with metal cations such as Mg$^{2+}$ resulting in a characteristic layer spacing.

Fig 2: PXD pattern of as prepared C$_{12}$-VO$_x$-NTs and ion exchanged Mg$_2$VO$_x$-NTs obtained with a Cu K$_\alpha$ source.

Fig 3: TEM micrograph of a) as prepared C$_{12}$-VO$_x$-NTs and b) ion exchanged Mg$_2$VO$_x$-NTs.

Fig 4: TEM micrograph of a) as prepared C$_{12}$-VO$_x$-NTs below EDX mapping of N (green), O (red), and V (blue). b) ion exchanged Mg$_2$VO$_x$-NTs below EDX mapping of Mg (magenta), O (red), and V (yellow).

Figure 5: a) discharge potential at C/10-rate as a function of Mg inserted into the host C$_{12}$-VO$_2$-NT material. Discharge time equal to 10h. b) principal (001) layer spacing for selected discharge states, showing a new forming interlayer, c) PXD data of the cathode material collected at I711 beamline at MAX-lab using 0.994Å λ wavelength.

Fig 5: a) discharge potential at C/10-rate as a function of Mg inserted into the host C$_{12}$-VO$_2$-NT material.

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