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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 (>250 mAh/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 (V\textsubscript{O}\textsubscript{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\textsubscript{x}-NTs with varying spacer 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\textsubscript{x}-NTs consists of multiwalled scrolls of crystalline VO\textsubscript{2} layers with approximate composition VO\textsubscript{16} and primary amines in between the layers acting as spacer molecules.
- Formal Vanadium oxidation states V\textsuperscript{V}/V\textsuperscript{IV} = 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.

Discussion

The VO\textsubscript{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-intercalation in the multiwalled VO\textsubscript{x}-NTs occurs within the space between the individual vanadium oxide layers of the nanotubes while the underlying VO\textsubscript{2} frameworks constructing the walls are affected only to a minor degree by the intercalation.

Materials and Methods
- VO\textsubscript{x}-NTs hydrothermally synthesized V\textsubscript{2}O\textsubscript{3} + 2C\textsubscript{12}H\textsubscript{25}NH\textsubscript{3} \xrightarrow{160^\circ\text{C},7 \text{ days}} C\textsubscript{12}V\textsubscript{O}\textsubscript{x}-NT
- Ion exchanged with Mg

- C\textsubscript{12}V\textsubscript{O}x-NTs with approximate composition V\textsubscript{7}O\textsubscript{16} and interlayer spacing, c = 27.7 Å, when dodecyl amine \( \text{C}_{12}H_{25}\text{NH}_3 \) is used as spacer molecule.
- TEM micrographs (Fig. 3-4) of the VO\textsubscript{x}-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\textsuperscript{2+} resulting in a characteristic layer spacing.

Results
- In house PXD diffraction (Fig 2) of the VO\textsubscript{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 = 27.7 Å, when dodecyl amine \( \text{C}_{12}H_{25}\text{NH}_3 \) is used as spacer molecule.
- 40l reflections are found at higher angles. These can be fitted to the 2D tetragonal basal layer (Fig. 1) with \( a = b = 6.12 Å \).

Conclusions
- Mg\textsuperscript{2+} was successfully intercalated into C\textsubscript{12}V\textsubscript{O}x-NTs
- Expansion and subsequent distortion of V\textsubscript{O}\textsubscript{2}-layers
  - Increase in interlayer spacing
  - Second and smaller interlayer spacing forms
- Results indicate 150 mAh/g reversible capacity at C/10-rate

References

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