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Operando PXD of Vanadium-Based Nanomaterials as Cathodes for Mg-ion Batteries

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Fig 1: Schematic illustration of the working principle of a secondary Mg-ion battery with Mg metal (grey) as anode and a vanadium compound (blue) as cathode.

We have synthesized series of vanadium oxides with varying chemical composition and varying nanotopologies, e.g., multiwalled vanadium oxide nanotubes (VO x NTs). The mechanism for Mg-intercalation and deintercalation was studied by operando synchrotron powder X-ray diffraction measured during battery operation using the AMPIX battery cell (Fig 2).

- The VO x NTs were synthesized via a hydrothermal route.

The resultant VO x NTs consists of multiwalled scrolls of crystalline VO x layers with approximate composition V x O x, and primary amines in between the layers acting as spacer molecules.

- The structure allows for reversible intercalation and deintercalation of guest ions.

- TEM micrographs (Fig 4) of the VO x NTs as prepared was collected on a FEI "Talos" F200X (S)TEM-microscope verifying the multiwalled tube structure.

- In house PXD diffraction (Fig 5) of the VO x NTs as prepared was obtained on a Rigaku MiniFlex diffractometer.

00 reflections are found at low angles. These are associated with the interlayer spacing, c = 27.7 Å. All 00 reflections are found at higher angles. These can be fitted to the 2D tetragonal basal layer (Fig 3) with a = b = 6.12 Å.

Fig 5: Schematic illustration of the multiwalled VO x NT structure. Five fold (square pyramidal) coordinated V are depicted in blue and four fold (tetrahedral) coordinated V are depicted in green. The protonated primary amines, acting as spacer molecules are further organized in a hexagonal arrangement.

The obtained black VO x NT powder was mixed with conductive carbon black and a binder material in the ratio 60 : 20 : 20 w/w. The obtained VO x NT powder was mixed with conductive carbon black and a binder material in the ratio 60 : 20 : 20 w/w. The obtained VO x NT powder was mixed with conductive carbon black and a binder material in the ratio 60 : 20 : 20 w/w. The obtained VO x NT powder was mixed with conductive carbon black and a binder material in the ratio 60 : 20 : 20 w/w.

Fig 2: Schematic drawing of the AMPIX battery cell for operando PXD measurements battery electrode materials. Adapted from ref. 4.

During discharge of the battery the (001) diffraction signal moved to lower angles, corresponding to a larger interlayer spacing, and decreased in intensity. Simultaneously a new peak formed at a higher angles corresponding to shorter interlayer spacing.

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

Conclusions
- Mg x+ was successfully intercalated into VO x NTs
- Expansion and subsequent distortion of V O x layers
  - Increase in interlayer spacing
  - Second and smaller interlayer spacing forms
- Results indicate 150 mA g -1 reversible capacity at C/10-rate

References

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Fig 4: TEM micrograph of as prepared C x VO x NTs

Fig 5: PXD pattern of as prepared C x VO x NTs obtained with a C x ray source

Fig 6: Discharge potential at C/10-rate as a function of Mg inserted into the host VO x NT material. Discharge time equal to 10h.

Fig 7: A) Operando PXD patterns as function cell discharge state, B) Principal (001) layer spacing for selected discharge states, showing a new forming interlayer, C) interlayer spacing and normalized intensities as function of discharge state.

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Fig 3: Operando PXD patterns as function of discharge state showing the (001) layer spacing and normalized intensities as function of discharge state.