



# Hydrothermal vanadium manganese oxides: Anode and cathode materials for lithium-ion batteries



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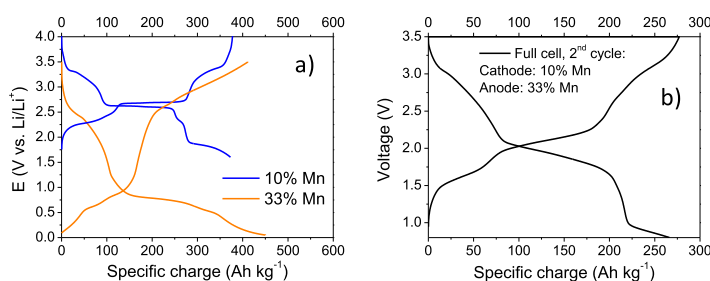
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## HIGHLIGHTS

- Cathodic and anodic vanadium manganese oxides for lithium-ion batteries from a single hydrothermal reaction.
- High capacity (380 A h kg<sup>-1</sup>) cathode based on hydrated vanadium oxide containing 10 at% Mn.
- Mn doping improves vanadium oxide slab ordering.
- Full cell with pre-lithiated Li<sub>5</sub>MnV<sub>2</sub>O<sub>6</sub> anode and Mn<sub>0.2</sub>V<sub>2</sub>O<sub>5</sub>·0.9H<sub>2</sub>O cathode with over 500 Wh kg<sup>-1</sup>.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Vanadium manganese oxides with Mn content up to 33 at% were synthesized by a low temperature hydrothermal route allowing for the preparation of both anodic and cathodic materials for Li-ion batteries. Low amounts of manganese (below 13 at%) lead to the formation of elongated particles of layered hydrated vanadium oxides with manganese and water intercalated between the V<sub>2</sub>O<sub>5</sub> slabs, while for higher Mn content of 33 at%, monoclinic MnV<sub>2</sub>O<sub>6</sub> is formed. Former materials are suitable for high energy cathodes while the latter one is an anodic compound. The material containing 10 at% Mn has the composition Mn<sub>0.2</sub>V<sub>2</sub>O<sub>5</sub>·0.9H<sub>2</sub>O and shows the best cathodic activity with 20% capacity improvement over V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O. Lithiated MnV<sub>2</sub>O<sub>6</sub> with Li<sub>5</sub>MnV<sub>2</sub>O<sub>6</sub> composition prepared electrochemically was evaluated for the first time as anode in a full-cell against Mn<sub>0.2</sub>V<sub>2</sub>O<sub>5</sub>·0.9H<sub>2</sub>O cathode. An initial capacity ca. 300 A h kg<sup>-1</sup> was measured with this battery corresponding to more than 500 Wh kg<sup>-1</sup>. These results confirm the prospect of using Li<sub>5</sub>MnV<sub>2</sub>O<sub>6</sub> anodes in lithium-ion batteries as well as high-capacity layered hydrated vanadium oxides cathodes such as V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O and Mn<sub>0.2</sub>V<sub>2</sub>O<sub>5</sub>·0.9H<sub>2</sub>O.

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## 1. Introduction

Vanadium and manganese are cheap and widely available elements for the synthesis of materials for electrochemical energy storage. These light elements possess high and accessible oxidation states, which make them desirable candidates for preparing intercalation materials for lithium-ion batteries. Vanadium pentoxide,

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with its layered structure, is one of the most studied vanadates for cathodic applications [1–6]. It tolerates the intercalation of high amounts of lithium but irreversible phase transformations lead to poor structural stability under cycling when more than 2 Li equivalents are intercalated. Doping techniques by metals (Ag, Al, Cr, Cu, Fe, Mo and Sn, for example) were proposed to improve properties such as the electronic conductivity, lithium percolation and to stabilize  $V_2O_5$  under cycling [7–17] but results remain unsatisfying.

Cathodes based on other vanadium oxides such as  $Li_xV_3O_8$  [18–21] and  $H_2V_3O_8$  [22–25] were also proposed. As for  $V_2O_5$ , the relatively low potential for lithium intercalation in such materials resulting in low battery voltage is compensated by the ability to intercalate high amounts of lithium (typically more than 3 Li equivalents), enabling batteries with high specific energy. Particularly, hydrated vanadium oxide with the chemical formula  $H_2V_3O_8$  possesses interesting characteristics as cathode material (intercalation of more than 4 Li equivalents for more than 1 kW h kg<sup>-1</sup>) [25–27]. Because of the large amount of intercalated lithium and its high reactivity towards the electrolyte, this material is inherently electrochemically instable and needs to be improved. We have recently proposed a method to decorate the surface of  $Li_xH_2V_3O_8$  fibers with an aluminum oxyhydroxide coating improving stability under cycling with  $LiPF_6$  electrolyte [28].

Xerogels and aerogels of hydrated  $V_2O_5$  were also proposed a few decades ago as high capacity materials [29–33]. The less ordered structure resulting from water incorporation in the interlayer along the *c* axis in the crystal structure allows for better electrochemical stability at the expense of a lower capacity in the same potential window when compared to anhydrous  $V_2O_5$ .

Few other studies related to vanadium manganese oxides can be found [34–38]. Watanabe et al. [38] reported a process for the preparation of  $M^{2+}\cdot V_2O_5\cdot nH_2O$  xerogels ( $M = Ca, Mn, Co, Ni$  and  $Cu$ ) allowing for an increase of the interlayer distance. Later, other authors evaluated the properties of  $Mn_xV_2O_{5+\delta}\cdot nH_2O$  as cathodes for lithium-ion batteries [35,39]. Namely, Lu et al. [35] reported that a  $Mn_xV_2O_5\cdot nH_2O$  material with Mn/V ratio of 0.068 could intercalate close to 200 mA h g<sup>-1</sup> between 4 and 2 V vs  $Li/Li^+$  for 18 cycles. Potiron et al. [39] stated that by dehydrating  $Mn_xV_2O_{5+\delta}\cdot nH_2O$  at different temperatures,  $\alpha$ - $V_2O_5$ , Mn-doped  $V_2O_5$  phases as well as other compounds such as  $MnV_2O_6$  can be formed.

Despite the fact that the vast majority of manganates and vanadates have properties suitable for cathodic application in lithium-ion batteries, other compounds are also envisageable as anode materials. Monoclinic  $MnV_2O_6$  can intercalate very high amounts of lithium in a broad potential range [40–43] suiting an anodic application. The morphology of this material is strongly dependent on the synthesis method with a direct influence on the electrochemical properties for lithium intercalation. A capacity on the 1st discharge in the range of 500 A h kg<sup>-1</sup> to ca. 1000 A h kg<sup>-1</sup> considering the potential window varying from 0.0 V to 3.5 V vs  $Li/Li^+$  or 0.05 V–3 V vs  $Li/Li^+$  has been reported. The very high charge registered in the 1st discharge partially originates from the electrolyte decomposition and growth of a solid electrolyte interface (SEI) as well as a phase transformation. A considerable capacity fade in the 2nd cycle (ca. to 50%) is due to structural and electrode/electrolyte interface stabilization. Zhang et al. recently showed that good cyclability after the 2nd cycle can be attained while keeping an anodic capacity of ca. 500 A h kg<sup>-1</sup> at a current rate of 100 A kg<sup>-1</sup> despite a higher potential compared to standard graphite anodes [43].

We here report a low temperature hydrothermal reaction allowing for the synthesis of vanadium manganese oxides for anodic and cathodic application in Li-ion batteries. The materials were characterized by transmission electron microscopy (TEM)

coupled with energy-dispersive X-ray spectroscopy (EDX) and electron diffraction, scanning electron microscopy (SEM/EDX), thermogravimetric analysis (TGA), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electrochemically. Different compounds were obtained by adjusting only the Mn/V ratio for the hydrothermal synthesis starting from  $V_2O_5$  and  $MnO_2$  precursors. We here first report a full Li-ion cell in which both cathode and anode materials are made of vanadium manganese oxides.

## 2. Experimental section

### 2.1. Hydrothermal synthesis of vanadium manganese oxides

The vanadium manganese oxides were synthesized by a hydrothermal reaction. Each reaction was performed in 20 mL of ultrapure water (MilliQ® Millipore 18.2 mΩ cm) containing 0.1 M of ethylene glycol (VWR Prolabo 98%),  $V_2O_5$  (Alfa Aesar 99.2%) and  $MnO_2$  (Alfa Aesar 99.9% metal basis) powders as precursors. The total vanadium and manganese atomic concentrations were kept at 0.011 mol for all compositions. Close to 1 g of final materials containing 5 at%, 10 at%, 20 at% and 33 at% Mn were prepared by this method. The desired amounts of  $V_2O_5$  and  $MnO_2$  were first added to the ethylene glycol aqueous solution and kept overnight in a round-bottom flask under stirring in a reflux at 80 °C. The resulting gel was transferred into a Teflon vessel of a stainless steel autoclave. The autoclave was sealed and the suspension treated hydrothermally for 15 h at 200 °C. Pristine  $V_2O_5\cdot nH_2O$  was prepared by the same reaction but treated hydrothermally for a shorter time, i.e. 6 h at 200 °C.

At the end of the reactions, the solid products were filtered, washed with water and isopropanol and dried at 80 °C for 3 h in air.

### 2.2. Physicochemical characterizations

The crystal structure was evaluated by XRD. The powder diffraction patterns were obtained using a PANalytical X'Pert PRO system equipped with a copper tube, a Johansson monochromator (Cu-K $\alpha$ 1 radiation, 1.5406 Å) and a X'Celerator linear detector operating in Bragg-Brentano geometry ( $\theta/2\theta$ ). The diffraction patterns were recorded between 5° and 80° (2 $\theta$ ). *In-situ* temperature dependent XRD patterns were recorded using a PANalytical X'Pert MRD system with Cu-K $\alpha$ 1,2 radiation ( $\lambda = 1.5418$  Å) and PIXCel detector. The sample was sealed in a gas-tight Anton Paar XRK-900 heating chamber to control the temperature and the atmosphere. The diffraction patterns were recorded from 5° to 50° (2 $\theta$ ) under synthetic air (100 mL min<sup>-1</sup>) from room temperature to 500 °C with a heating rate of 10 °C min<sup>-1</sup>. The diffraction patterns were collected for 10 min at every 25 °C.

A TEM in imaging mode equipped with a LaB<sub>6</sub> filament and an acceleration voltage of 300 kV (Philips CM30) was used for morphology characterization and to assess the local crystallinity of the samples by selected area diffraction (SAD). The SAD aperture cut out an illuminated area with a diameter of 654 nm. The obtained diffraction patterns were analyzed by comparison to simulated patterns obtained by the JEMS software. Further morphology and chemical analysis was performed using a JEM 2000FS TEM/STEM equipped with a Schottky field emission electron source with an acceleration voltage of 200 kV and an EDX detector. High resolution images and the corresponding EDX spectra were acquired in TEM mode where the illuminated area was restricted to a monocrystalline zone using a small C2 aperture. The morphology of the fibers was further evaluated by SEM using a FEI Nova NanoSEM 230 with an EDX detector.

XPS spectra were acquired using a PHI Quantum 2000 spectrometer with monochromatic AlK $\alpha$  X-ray radiation (1486.6 eV).

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