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Completely functional composite cathode material based on an aerogel of vanadium oxides

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For the synthesis of the CFCCM, analytical-grade vanadium(v) oxide, hydrogen peroxide (30% solution), acetone and *n*-hexane were used.

A vanadia-based gel, used as a main precursor, was synthesized according to a known technique.[18–20] An exothermal reaction between V_2O_5 powder (0.5 g) and H_2O_2 solution (15 ml) yielded a $V_2O_5 \cdot nH_2O$ gel. Hydrothermally synthesized $Ba_{0.25}V_2O_5$ whiskers[18] (0.025 g) were added to the freshly prepared $V_2O_5 \cdot nH_2O$ gel mass (0.25 g) and stirred for 30 min. Thus, the whisker content of the product composite was 10 wt%. The mixture was centrifuged and subsequently washed with acetone three times.

Supercritical drying was carried out using a Parr 4593 microreactor (USA) equipped with a Knauer K-120 high-pressure pump (Germany). The precursor was placed in a stainless steel autoclave, which was filled with acetone as a primary solvent (90 vol% filling). After that, the autoclave was closed and heated to 250 °C. The inner pressure was raised to 10.0 MPa by *n*-hexane (a secondary solvent) pumping. The system was kept for 30 min under supercritical conditions. Then, the primary solvent was replaced by a secondary one with the online mechanism (*i.e.*, the inlet and outlet velocities of the solvent streams were equal to keep the inner pressure constant). After the full replacement of acetone by *n*-hexane, the system was kept at 250 °C for 30 min, and then the slow removal of the secondary solvent was carried out (approximately 0.1–0.5 MPa s^{-1}). The resultant product of supercritical drying was finaly calcined at 300 °C for 10 h in air.

The microstructure of the whiskers was observed by TEM [JEOL JEM-2000FX(II), Japan] with an accelerating voltage 200 kV and SEM (Leo Supra 50 VP, Germany) with an INCA Energy + EDX analyzer (Oxford, UK).

XRD was measured using a Rigaku D/MAX 2500 powder diffractometer (Japan) operated in the standard Bragg–Brentano geometry with $CuK_{1,2}$ radiation of λ = 1.54176 Å (graphite monochromator). Data were collected from 5 to 75° (step: 0.02°) in 2θ.

EIS was performed using a two-electrode cell with a Solartron SI 1255B frequency response analyzer and a Solartron SI 1287 potentiostat in the frequency range of 1–10^6 Hz and at

an amplitude of 10 mV. Samples were pressed to pellets with a diameter of 6 mm and a thickness of 1.1–1.4 mm. Copper wires were attached to the sides of the pellet by silver paste. Finally, the pellets were dried at 80 °C for 30 min and subjected to the measurement. Fitting of the impedance spectra was performed using the Zview-Impedance Software (Scribner Associates).

The composite (the active material, 95%) and polyvinylidene difluoride dissolved in *N*-methylpyrrolidone (a binder, 5%) were mixed together and homogenized using a UZDN-4D ultrasonic disperser. The working electrode was made with coating this slurry on a stainless steel gauze and subsequent pressing and drying in a vacuum. Lithium foil was used as a counter electrode and a reference electrode. A standard mixture of 1 M $LiClO_4$ solution in propylene carbonate/dimethoxyethane (7:3) was used as an electrolyte. The cell assembling was carried out in a glove box under argon; the quantity of oxygen and water vapor was < 5 ppm. Galvanostatic charge-discharge characteristics were recorded using a multichannel PC-controlled setup for cell cycling. The working (positive) electrode was cycled at 1.5–4.0, 1.5–4.4 and 1.5–4.5 V potential ranges. The current density was 10 mA g^{-1}.