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

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A completely functional composite cathode material based on a VO_x aerogel was synthesized by a supercritical drying technique. The electrochemical performance of the resultant composite was characterized.

The development of lithium-ion battery systems has become a very important scientific achievement over recent years.[1] The capacity of known and used cathode materials is much smaller than that of anode materials; therefore, energy stored in the battery is determined by the cathode material, and it is very important to find a suitable material to improve the electrochemical performance.

Nowadays, attention is focused on cathode materials such as vanadium oxides. These oxides and their composites[2,3] attract great interest as cathode materials[4] because of their competitive characteristics, mainly high discharge capacity (up to 650 mAh g^{-1}).[5,6]

The electrochemical behaviour of a cathode material strongly depends on its morphology. The vanadium–oxygen system is able to form 1D,[7,8] 2D[9] and 3D[10] structures, including aerogels.[11] Owing to unique morphology[12,13] the aerogels are interesting objects for both fundamental investigation[14,15] and applied research,[16] especially in the field of electrochemistry.[17] The extended 3D structure of an aerogel of high porosity and thin walls gives to electrolyte better access to interior parts of the material (*cf.* a bulk phase). The material/electrolyte surface area increases and rate capability also increases. Whiskers electrode materials have also good electron conductivity and high specific surface area. Therefore, they can be an excellent reinforcing and electron conductive component of a composite.

Most of electrochemically active materials are not good electronic conductors; thus, it is necessary to add an electronically conductive material such as carbon black to them.[2] However, in the case of aerogels, the usage of carbon additives is undesirable because they close up pores in aerogel, which lowers the cathode effective surface. Consequently, the electrochemical efficiency of the cathode dramatically decreases.[3] For avoiding this surface blockage, a 1D material in the form of whiskers was used as a filler within an aerogel matrix instead of using carbon black. This component does not block the aerogel surface and, at the same time, forms an electron conductive framework.[3]

Here, we studied a novel composite material, in which all of the components are able to intercalate/deintercalate lithium. This can be made by adding $Ba_{0.25}V_2O_5$ whiskers as a 1D electron conductive additive to a VO_x aerogel. The whiskers can form a conductive framework similar to nanotubes;[5,6] on the other hand, whiskers act as a cathode material with a discharge capacity of about 145 mAh g^{-1} and a specific energy of about 130 Wh kg^{-1}.[18] Thus, we have obtained a completely functional composite cathode material (CFCCM) based on vanadium oxides for Li-ion batteries.[†]

The morphology of CFCCM was observed by scanning electron microscopy (SEM),[†] and it is quite alike to the morphology of a raw aerogel (Figure 1). The average diameter of the aerogel agglomerates is approximately 3 μm. The diameter of the whiskers filler, randomly extended throughout the aerogel, is about 1 μm; whereas the length is > 50 μm. The surface of the whisker is modified with aerogel particles, suggesting chemical affinity between the matrix and the filler (Figure 1, insert).

The microstructure of CFCCM was investigated by transmission electron microscopy (TEM).[†] The aerogel consists of 1D nanorods with a ~10 nm width and a 50–300 nm length (Figure 2). This is a typical morphology of aerogels based on vanadium oxides.[21] The nanorods have partial ordering that leads to agglomeration. The selected area electron diffraction (SAED) image shows that the observed area of the sample is polycrystalline because several nanorods were captured by an electron beam resulting in a ring ED pattern.

The powder X-ray diffraction (XRD)[†] pattern of the whiskers has very narrow and intense reflexes, confirming the high crystallinity of whiskers [Figure 3(*a*)]. All observed peaks belong to the $Ba_{0.25}V_2O_5$ phase[18] and there are no peaks of any secondary phases. As opposite to the whiskers, the XRD pattern from aerogel is just characterized by few broad and low-intensity peaks [Figure 3(*b*)]. This fact shows that the aerogel is a poorly

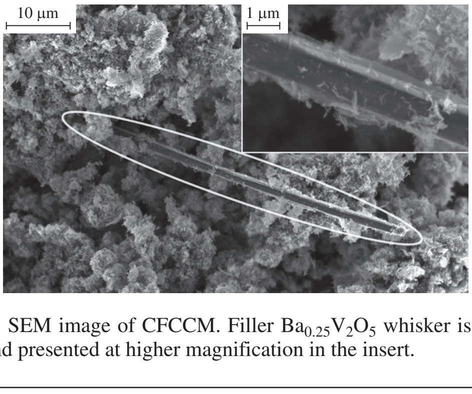

Figure 1 SEM image of CFCCM. Filler $Ba_{0.25}V_2O_5$ whisker is indicated by oval and presented at higher magnification in the insert.

[†] For experimental details, see Online Supplementary Materials and refs. 18–20.

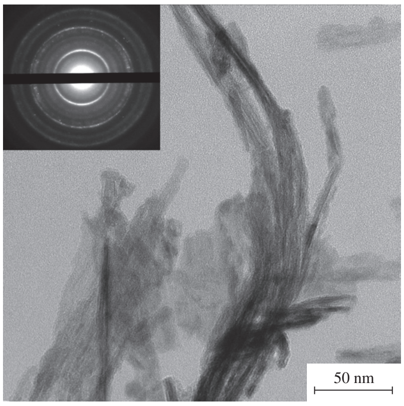

Figure 2 TEM image of the CFCCM matrix. SAED image is presented in the insert.

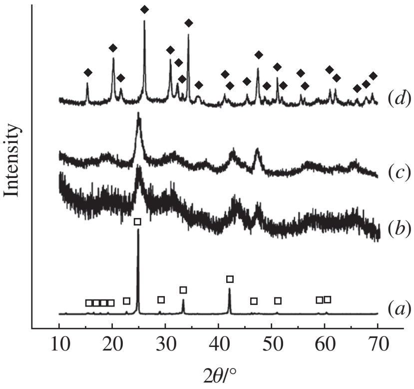

Figure 3 XRD patterns of CFCCM precursors: (*a*) $Ba_{0.25}V_2O_5$ whiskers, (*b*) raw aerogel, (*c*) whiskers/aerogel composite before annealing and (*d*) CFCCM after annealing. (◆) corresponds to V_2O_5 phase (ICDD no. 72-433) and (□) corresponds to $Ba_{0.25}V_2O_5$ phase.[18]

crystalline material.[21] From the XRD data, it is difficult to identify the exact phase composition of the aerogel; therefore, X-ray photoelectron spectroscopy (XPS) was applied (experimental details are not presented here). According to the XPS data, the aerogel formula is $VO_{2.23}$ (V^{5+}:V^{4+} ratio is 1:1.15, giving the content of V^{4+} cations of ~53.5%). The XRD pattern of whiskers/aerogel composite material is very similar to that from raw aerogel, demonstrating poorly resolved peaks due to the low content of a whisker phase [Figure 3(*c*)]. Thus, the XRD data confirm the poor crystallinity of the unannealed CFCCM.

Due to the elucidated presence of V^{4+} ions in the composite matrix, it was necessary to perform annealing under oxidative conditions to secure a maximal discharge capacity *via* achievement of a maximal V^{5+}/V^{4+} ratio in the sample. Indeed, annealing led to the formation of a composite material with a V_2O_5 matrix [Figure 3(*d*)]. Note that the above thermal treatment was carried out at 300 °C, when the structure of whiskers is stable.[18]

The fabrication of a whiskers/aerogel composite cathode material was motivated by the low electron conductivity of a matrix aerogel (*cf.* other materials based on vanadium oxides[22]). The values of the conductivity of both composite components, *viz.*, the aerogel matrix and the whisker filler, were estimated by electrochemical impedance spectroscopy (EIS).[†] A typical Nyquist plot of ac-impedance for matrix aerogel contains two semicircles which correspond to two different kinds of conductivity [Figure 4(*a*)]. We suggest that the resistance R1 in the presented equivalent circuit (at high frequencies) reflects the surface conductivity, while R2 refers to the bulk conductivity (low frequencies) [Figure 4(*a*)]. The impedance spectrum of a whiskers sample was fitted by a simple semicircle, from which the resistance R1 of the whiskers was estimated [Figure 4(*b*)]. Simulation parameters are given in Table 1. Whereas the total conductivity of the aerogel sample was estimated at 4 mS cm^{-1}, the calculated value of whiskers electrical conductivity was 10 mS cm^{-1}.

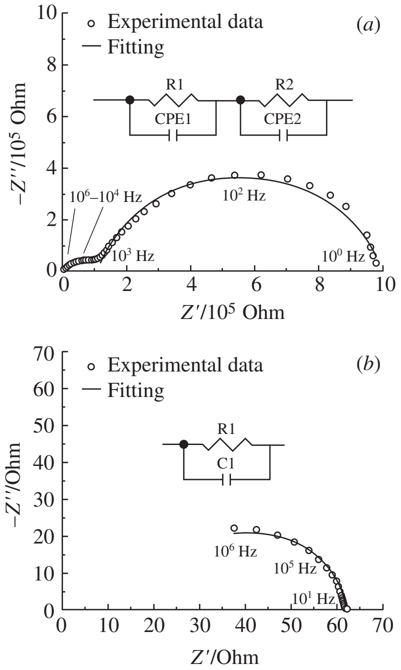

Figure 4 Experimental impedance spectra of (*a*) aerogel and (*b*) whiskers. Inserts: equivalent electrical circles.

Table 1 Fitting parameters of the impedance spectra.

Sample	Element of the circle	Value of the element	Estimated specific conductivity / mS cm^{-1}	Fitting parameter $\chi 2$
Whiskers	R1	43.8±0.3	10±1	0.01808
	C1	(412±7)×10^{-11}		
Aerogel	R1	(135±1)×10^{3}	3.6±0.4	4.9×10^{-5}
	Z_0[a]	(27±1)×10^{-10}		
	n[a]	0.653±0.003		
	R2	(868±5)×10^{3}		
	Z_0[a]	(38±1)×10^{-10}		
	n[a]	0.884±0.004		

[a] A constant phase element (CPE) can be expressed as $Z_{CPE} = Z_0(i\omega)^{-n}$, $-1 < n < 1$.

Both aerogel and whiskers[18] were investigated by the electrochemical testing of intercalation/deintercalation of lithium ions.[†] Discharge capacities of the materials were quite high. The capacity of the aerogel reaches ~350 mAh g^{-1} at the first cycle (Figure 5), then it slightly decreases with further cycles, and it is estimated as 250 mAh g^{-1} at the eighth cycle. Whiskers showed

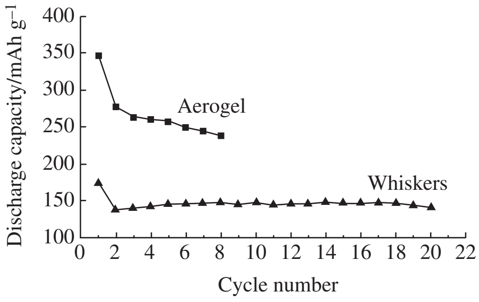

Figure 5 Discharge capacity *vs.* cycle number plots for $VO_{2.23}$ aerogel and $Ba_{0.25}V_2O_5$ whiskers.[19] Current density for cycling of both materials was 20 mA g^{-1}, corresponding to ~C/15.

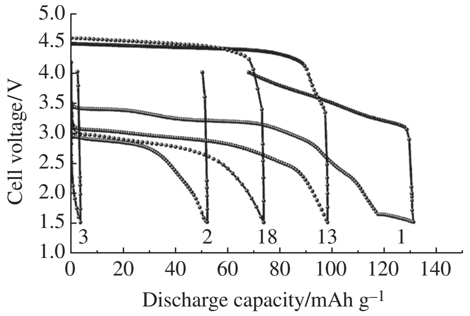

Figure 6 Charge–discharge curves of CFCCM. Numbers of cycles are indicated.

lower but stable capacity from second cycle which was about 145 mAh g^{-1}.

An active mass of the CFCCM electrode contains 10 wt% of the $Ba_{0.25}V_2O_5$ whiskers and has not any other conductive additives (*e.g.*, carbon black). The cycling was carried out at C/25 current. The charge–discharge curves (except one at the first cycle) contain two plateaus attributed to two different positions for lithium intercalation in the composite – the positions of whiskers and aerogel structures (Figure 6).

Initially, the electrode was cycled at a potential range of 1.5–4.0 V. The discharge capacity at the first cycle was ~130 mAh g^{-1} (a specific energy was ~180 Wh kg^{-1}) (Figure 7). During the further cycling, the capacity strongly decreased to almost zero. The appearance of charge–discharge curves allowed us to deduce that the extraction of Li^+ occurs at higher potentials. Therefore, anode limits were increased up to 4.4 V (at 8–10 cycles) and up to 4.5 V (at 11–22 cycles) during subsequent cycling. These changes led to increasing both charge and discharge capacities. The second one rises up to ~110 mAh g^{-1} and after that it smoothly falls to a stable value of ~80 mAh g^{-1} (the specific energy was ~85 Wh kg^{-1}).

The discharge capacity of the CFCCM is significantly lower than those of the separate components (Figure 5). We suggest that the reason for this is nonoptimal conditions of the electrode formation. Moreover, the testing regime applied during the first cycle leads to the degradation of the material, and accordingly the cathode was not able to show its maximal capacity.

The test material exhibited a worse electrochemical behaviour than that of $LiCoO_2$ or $LiFePO_4$.[4] However, the main achievement of the current work is the development of a novel kind of composite material, wherein all the components take part in the electrochemical reaction of intercalation/deintercalation of lithium ions.

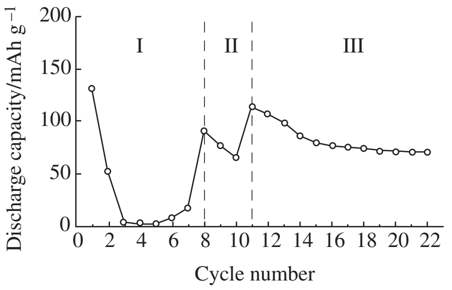

Figure 7 Discharge capacity *vs.* the number of cycle plot for CFCCM. Different ranges of potential were applied: (I) 1.5–4.0, (II) 1.5–4.4 and (III) 1.5–4.5 V.

In summary, the completely functional composite cathode material based on a vanadia aerogel was synthesized by supercritical drying. The $Ba_{0.25}V_2O_5$ whiskers were used as a simultaneous 1D conductive additive, reinforcing filler and cathode components, instead of carbon black blocking the matrix surface. Electrochemical measurements showed strong dependence on the applied range of potential, therefore, only the charging of the electrode up to 4.5 V at C/25 current allowed revealing a stable capacity value of ~80 mAh g^{-1} (specific energy, ~85 Wh kg^{-1}).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.11.007.

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