Supporting information

High capacity vertical aligned carbon nanotube / sulfur composite cathodes for lithium sulfur batteries

Susanne Dörfler,[a,b] Markus Hagen,[c] Holger Althues,[a] Jens Tübke,[c] Stefan Kaskel[a,b] *, Michael J. Hoffmann[d]

Experimental Section

The detailed catalyst coating procedure and subsequent CVD deposition process for the preparation of VA-CNT-electrodes is described elsewhere[14]. Nickel foil (50 µm, $R_a = 25$ nm) (Alfa Aesar, 99 % Ni) was used as substrate for the growth of CNT. The foil was cut into 3.5 x 3.5 cm^2 pieces and dip-coated firstly with Al_2O_3 a process based on a modified sol-gel synthesis. For the catalyst layer $Fe(2\text{-ethylhexanoate})_3$ (Alfa Aesar, 50 % in mineral spirits), $Mo(2\text{-ethylhexanoate})_4$ (Strem Chemicals) and $Co(2\text{-ethyhexanoate})_2$ (Sigma Aldrich, 65 % in mineral spirits) were dissolved in appropriate ratio in 2-propanol (Berkel) to obtain a 0.22 mol l^{-1} solution. Catalyst and the buffer layer were deposited by a dip coating technique. CNT growth by APCVD was performed with a quartz tube (40 mm diameter) positioned in a split tube furnace (HTM Reetz). At a process temperature of 730 °C argon, ethene as carbon precursor and hydrogen (Linde AG) as in situ reductant for the oxidized catalyst layer were used for the carbon nanotube deposition. A small amount of water (85 ppm) as soft oxidant for in situ emerging amorphous carbon enhances the catalyst activity. A growth time of 20 min was applied for all samples being described in this work.

For the sulfur infiltration of CNT-electrodes, Sulfur (SigmaAldrich, > 99.5 %) is dissolved in toluene (Sigma Aldrich, 99.8 %, anhydrous) and infiltrated into the electrodes using a µ-liter injection. The sulfur content is controlled by the temperature: 40 ml toluene at room temperature (RT) contain 0.5 g sulfur, and 40 ml toluene at 80 °C contains 2 g sulfur. By heating the CNT-electrode to 120 °C, the solution is soaked completely in the VA-CNT film and finally dried by solvent evaporation.

The present state of the art for the electrode size in regard of cycle testing is 1 cm^2 with a weight of few mg. In this context, weight differences of 2 and 4 % (65% was the target sulfur content) represent comparable values given the limited accuracy of weighing. Thus the experiments compared in our contribution represent comparable sulfur loadings.

Materials characterization

The CNT film or rather the CNT/sulfur composite electrode morphology is characterized by a scanning electron microscope (SEM) (ZEISS type DSM 982 GEMINI) with a heat-able field emission tungsten cathode.

Cell assembly and analysis

All tests are examined versus metallic lithium (SIGMA ALDRICH, 99.9 % purity) as counter electrode. The lithium is scraped with a ceramic knife to remove surface layers and afterwards pressed through a calendar to obtain a homogeneous and comparable surface. As test cells, glass tubes with screw threads on both sides are used. A sandwich-like cell assembly consisting of lithium foil, separator and VA-CNT/S electrode is used: The lithium foil is cut with a round hollow punch of 10 mm diameter and pressed on a stainless steel stamp with a gasket, which was put in the glass tube. A CELGARD 2400 polypropylene separator (thickness: 25 µm, porosity: 37 %) and alternatively, a WHATMAN glass fibre separator (GF/C, thickness: 260 µm) was applied. The separator was wetted by 8 – 50 µm of the respective electrolyte. The applied organic electrolytes consists of 1 mol l^{-1} LiTFSI (SIGMA ALDRICH, 99.95%) in DME:DIOX (1:1, v:v) (SIGMA ALDRICH, anhydrous) or 1 mol l^{-1} LiTFSI in DME:DIOX (1:1, v:v) with 0.25 mol l^{-1} $LiNO_3$ (ABCR 99.98%; metals basis). Subsequently, a sulfurized CNT-electrode and a stainless steel disk are placed on the wet separator. A pressure spring put a defined pressure on the electrodes and to an electrical connection with the second stainless steel stamp. Plastic caps were screwed onto the glass threads to prevent the steel stamps from being pushed out of the cell and to guarantee a proper sealing. The assembly of the test cells took place in an argon-filled glove box (MBRAUN) with an O_2 and H_2O content of less than 1 ppm. The VA-CNT/S electrodes were cycled between 1.0 V and 3.0 V at constant currents with a SOLARTRON MODU LAB 1450E or a BASYTEC CTS Lab system.

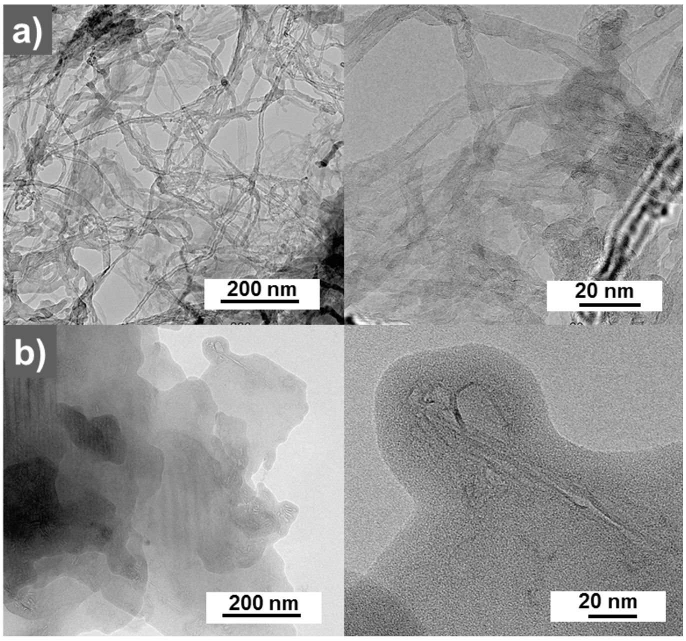

Figure1: TEM image of as-grown scratched-off CNT (a) and sulfur infiltrated CNT (b)

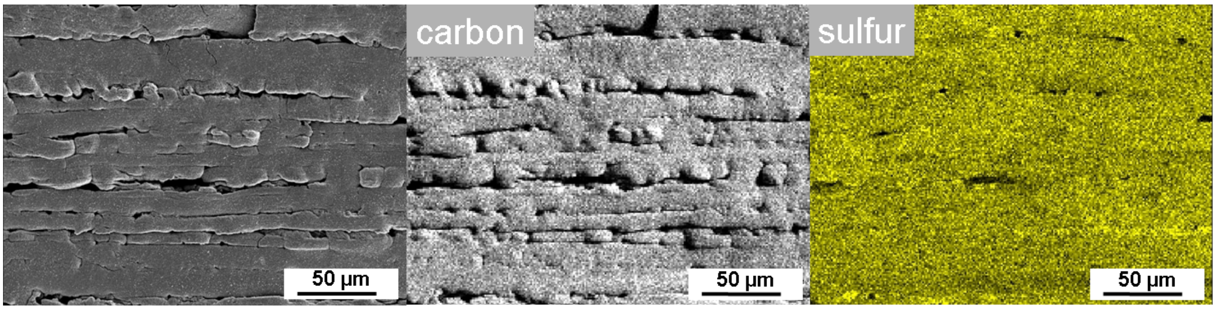

Figure 2: secondary electron image, EDX mapping of carbon (white spots) and sulfur (yellow spots)

The shadowing effects in the carbon EDX map result from the microscope/detector geometry and rough surface morphology of the VA-CNT film.

[14] S. Dörfler, A. Meier, S. Thieme, P. Németh, H. Althues, S. Kaskel, *Chem. Phys. Lett.* 2011, **511**, 288-293.