Transmission electron microscopy study of carbon/metal oxide hybrid materials for Energy Storage Application

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Carbon-metal oxide nanohybrid materials are promising electrode materials for high-power electrochemical energy storage applications or also for capacitive deionization of water. A key aspect is the combination of the advantages of carbon substrates (high surface area and electrical conductivity) with the high Li- or Na-ion storage capacity of metal oxide nanomaterials. However, the controlled synthesis of such nanohybrids is still challenging. Different routes are explored, e.g. plasma ion assisted deposition (PIAD) or atomic layer deposition. The main aim of our study is the correlation of nanostructure and material properties in regard to the synthesis parameters. The nanomaterials synthesized in this work are mainly characterized using advanced C_s-corrected (scanning) transmission electron microscopy ((S)TEM) techniques as well as the according spectroscopy methods like energy-dispersive X-ray (EDX) spectroscopy and electron energy loss spectroscopy (EELS).

To develop a reliable and reproducible film deposition by a PIAD process vanadium oxide thin films are deposited on Si substrates. The deposition parameters are varied to investigate their influence on film growth, crystallinity and thickness. (S)TEM and EDX analysis revealed homogenous and uniform VO_x films with different thicknesses for different deposition parameters, an exemplary (S)TEM image is shown in Fig. 1. EDX and EELS confirmed a VO_x layer on Si (Fig. 1), which is passivated by an amorphous SiO_2 layer. X-ray diffraction and Raman experiments indicate the formation of V_2O_5 but the presence of additional phases like VO_2 cannot be excluded. A dependence of the crystallinity of the VO_x layers on deposition parameters during the plasma based synthesis was found. Furthermore, VO_x was deposited directly on free-standing carbon nanotubes (CNT) to obtain hybrid electrode materials that combine good redox activity and high electrical conductivity. First electrochemical characterizations show promising activities and potential for their usage as electrode materials in lithium-ion batteries.

Additionally, MoO_x was deposited directly on CNTs by atomic layer deposition and subsequently transformed to MoO_2 particles by thermal annealing. The particles can be partially or fully transformed to MoS_2 by sulfurization in H_2S atmosphere. This was confirmed by STEM EDS analysis and EELS measurements of the S L_{23} edge confirming the formation of the MoS_2 shell (Fig. 2). First electrochemical measurements of the nanohybrids as anodes in Li-ion batteries suggest that the MoO_2/MoS_2 core-shell material exhibits an improved stability during galvanostatic cycling between 0.01 V and 3 V vs. Li^+/Li compared to fully sulfurized MoS_2.

In future, detailed (S)TEM investigations, also post mortem on electrochemically tested samples, will be done to analyse the stability of the nanohybrids and to reveal possible degradation mechanisms. Here, focus will be laid on the interface as it is suggested that it strongly affects the electrochemical properties.

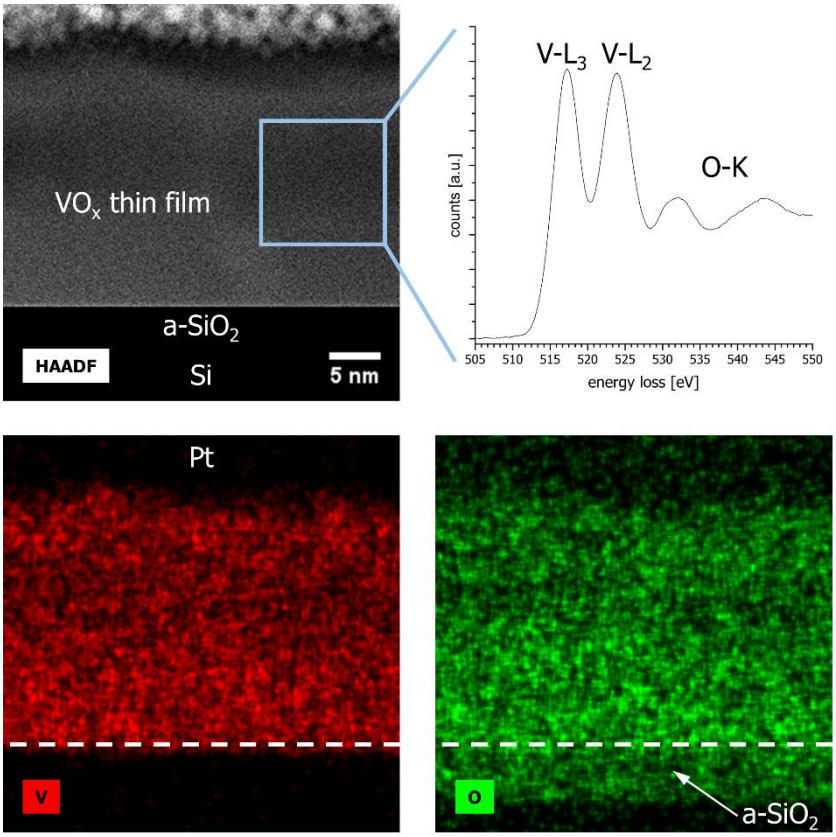

Figure 1: Cross-sectional HAADF STEM image (top left) and the corresponding V and O EDS mappings (bottom) of a ~20 nm thin VO_x film on a Si|amorphous-SiO_2 substrate. EEL spectrum of the VO_x film including the V-L_3, V-L_2 and the overlapping O-K edges (top right).

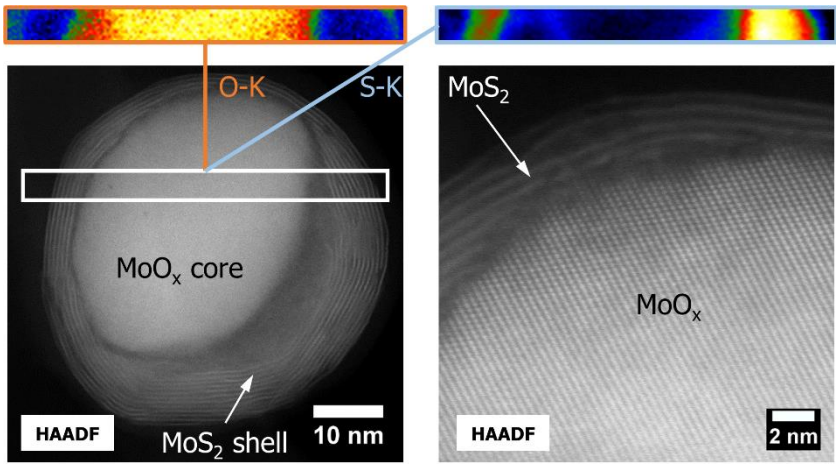

Figure 2: HAADF STEM images of a core-shell particle: overview (bottom left) and atomic column resolved micrograph (bottom right). EELS mappings of the O-K edge (top left) and the S-K edge (top right) reveal a MoO_x core and a MoS_2 shell structure.