The influence of the coherent domain size on the Li-insertion behavior of nanocrystalline RuO_2

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Although the nanocrystalline insertion hosts were intensively studied with respect to the applications in rechargeable Li-ion power cells, the influence of the particle size on the insertion behavior did not attract adequate attention yet. Only one paper dealing with this approach was published on the activity of anatase with respect to the BET area [1]. However, the size of coherent domain plays an important role mainly if a phase transition takes a place during reduction or oxidation. This work shows coherent domain size effect on the Li insertion into nanocrystalline RuO_2.

A set of samples of nanocrystalline ruthenium dioxide was prepared by sol-gel method from $RuNO(NO_3)_3$ according to Musić et al. [2] The samples were analyzed using X-ray diffraction (XRD) and transmission electron microscopy (TEM). All samples were phase pure RuO_2 (rutile) and contained no amorphous impurities. From TEM images results that the size of particles of RuO_2 is around 100 nm and it is almost the same for all temperatures of annealing. The size of coherent domain determined from XRD spectra ranged between 5-16 nm.

Cyclic voltammograms differ for RuO_2 samples of different coherent domain size (see Fig. 1). Samples with small coherent domain (< 8 nm) insert Li in single step characterized by single cathodic peak at ca. 2.1 V. The materials with bigger coherent domain size, on the other hand, show two additional cathodic peaks attributable to Li insertion process. The position of the first peak is insensitive to actual coherent domain size (ca. 2.03 V) ,the position of the second additional peak moves with increasing coherent domain size from 1.9 V to more negative potentials. The complementary anodic process remains unaffected by the variation of the coherent domain size.

The presence of the cathodic peaks located at 2.1 and 2.03 in the voltammograms is in accordance with the mechanism proposed for reduction of the microcrystalline RuO_2 by Ohzuku et al.[3]. In this model the host undergoes a phase transition from tetragonal to rhomboedric symmetry. The most negative cathodic peak indicates a possibility of an irreversible process during RuO_2 reduction. The specific capacity of the nanocrystalline RuO_2 does not increase monotonously with decreasing scan rate, but shows a maximum at scan rate of ca. 0.1 mV/s (see Fig.2). Similar type of dependence one gets also for relationship between specific capacity and coherent domain size (see Fig. 2). The voltammetric and specific capacity data can be rationalized in such a way that the smaller coherent domain size stabilizes the tetragonal rutile-type structure in the partially reduced RuO_2.

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References:

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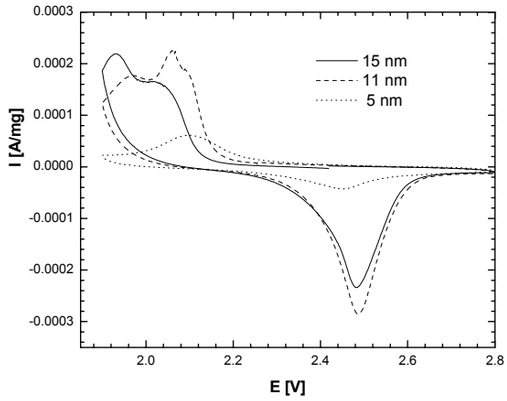

Figure 1. Cyclic voltammograms of nanocrystallin RuO_2 electrodes. The coherent domain size of the materials is shown in the inset. The voltammograms were recorded in 0.5 M $Li(CF_3SO_2)_2N$ EC/DME (1:1) electrolyte at scan rate 0.1 mV/s.

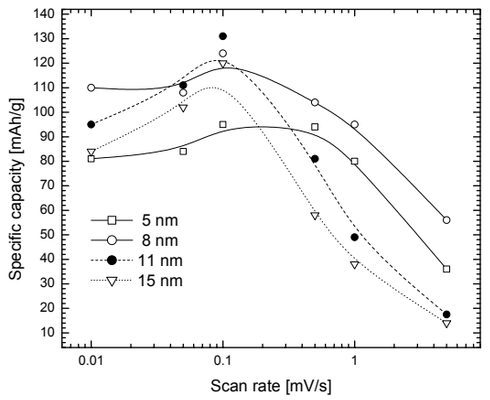

Figure 2. Specific capacity as a function of scan rate for RuO_2 samples of different coherent domain size(see Figure inset).

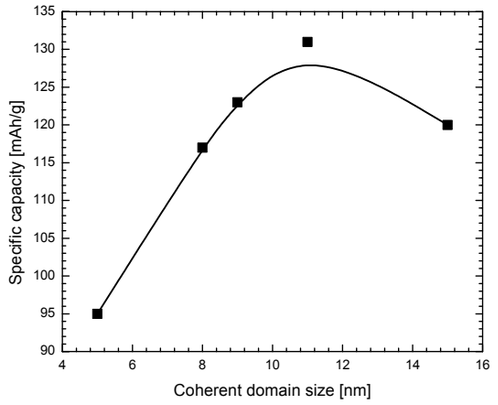

Figure 3 Specific capacity as a function of coherent domain size. Data were extracted from cyclic voltammograms measured at 0.1 mV/s.