NANOSTRUCTURED (Sn, Ti)O_2 – NEW MATERIAL FOR NEGATIVE ELECTRODE OF LITHIUM-ION BATTERIES

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Since publication of Fuji [1] various materials based on SnO_2 are considered to be promising candidates for negative electrodes of lithium-ion batteries. In the wake of [2–4] the mechanism of functioning such electrodes can be described as follows. During the initial cathodic polarization SnO_2 is reduced to metal

$$SnO_2 + 4\,Li^+ + 4\,e \rightarrow Sn + 2\,Li_2O \qquad (1)$$

Then lithium is intercalated into tin metal

$$x\,Li^+ + Sn + x\,e \rightarrow Li_xSn \qquad (2)$$

The coefficient x can be, in principle, sufficiently high, up to 4.4. For this value of x the theoretical specific capacity of tin electrode is 991 mAh/g or 7234 mAh/cm^3. Even being calculated with respect to the initial SnO_2, the resulting values of specific capacity still remain as high as 781 mAh/g and 5428 mAh/cm^3.

Reaction (1) corresponds to inevitable irreversible capacity of the first cycle. However it is not sole origin of irreversible capacity. For instance, an electrolyte reduction leads to useless charge consumption, i.e. contributes to irreversible capacity as well. Therefore irreversible capacity must be at least more than 710 mAh/g what corresponds to eq. (1).

Various materials based on tin oxides are described, including amorphous composite oxides with a basic formula SnM_xO_y, where M = B, P, and/or Al; microcrystalline SnO_2 and SnO; nanostructured SnO_2; SnO_2–carbon composites.

The present work is devoted to investigation of novel material with net formula 90% SnO_2 + 10% TiO_2 (ST10), prepared by thermohydrolytic decomposition of $SnCl_2$ and $TiCl_4$ solutions, layer by layer applied to Ti substrates. According to STM ST10 films annealed at 450°C consist of globules 15 – 20 nm in size, which in turn have a fine nanostructure. XRD revealed that cores of the globules contain crystallites of (Sn,Ti)O_2 rutile solid solution (5-8 nm) pierced with amorphous SnO_2 strips, oriented along *c* axis of the rutile cell. A similar amorphous SnO_2 layers, containing up to 15% SnO, cover the globule surface. Such nanostructure in ST10 films is due to the formation as their precursor of the crystalline $SnCl_2$ intercalation phase containing inclusions of polynuclear titanium-tin oxohydroxo complexes.

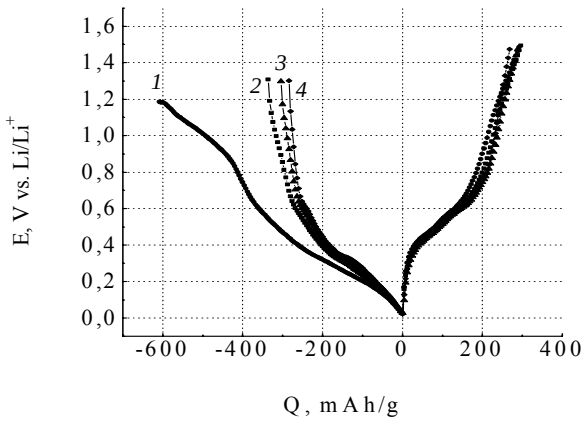

Fig.1. *Charge-discharge galvanostatic curves for the electrode with ST10 film. Cycle numbers are shown near curves.*

Fig. 1 shows galvanostatic charge-discharge curves for such an electrode in 1 M $LiN(CF_3SO_3)_2$ in dioxolane. The reversible capacity is close to 300 mAh/g. The irreversible capacity is close to this figure too. Curves shown in Fig. 1 were registered at current density 80 mA/g. It is noticeable that reversible capacity was invariant in the rather wide range of current densities, from 1 to 80 mA/g.

Charge-discharge cycling of ST10 electrodes resulted in some capacity fading.

During the first 30 cycles at current density 80 mA/g the rate of capacity fading amounted to a mere 0.6% per cycle (Fig. 2).

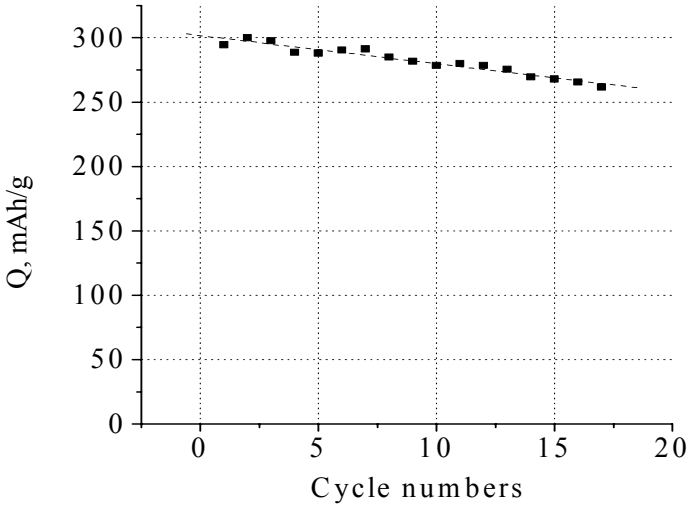

Fig.2. *Capacity decrease upon cycling of electrode with ST10 film*

Low values of irreversible capacity points to incomplete SnO_2 reduction in the course of the first cathodic polarization. This suggestion was confirmed by results of Mössbauer spectroscopy analysis (MSA). Indeed, XRD and MSA have revealed that $(Sn,Ti)O_2$ solid solution decomposed to strongly dispersed and amorphous in X-rays SnO_2 phase and TiO_2 (rutile), accompanied with metallic Sn formation. The average size of Sn crystallites was *ca.* 30 nm; no SnO being observed. More likely than not the cover layers and strips of amorphous SnO_2 (containing SnO) in the initial globules undergo to the reduction by lithium, deconstructing $(Sn,Ti)O_2$ solid solution to fine dispersed SnO_2 phase and TiO_2. At the same time, according to MSA minor share of tin presents in metal form, whereas the main amount remains as oxide. It must be stressed that such amorphous SnO_2 phase remained in an electrode after the reduction of another tin oxides was firstly observed.

Not so high irreversible capacity allows one to suggest that along with the alloying with tin another mechanism of Li insertion is available. Fine dispersed SnO_2 phase could be possible region where Li insertion occurs by the intercalation. This suggestion can be confirmed also by the fact that not all irreversible capacity disappeared after the first charge-discharge cycle. Irreversible capacity of the second cycle amounted up to 15% of that of the first cycle.

References

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