NANOMATERIALS IN SUPERCAPACITORS WITH APROTIC ELECTROLYTES

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Introduction

Supercapacitors draw considerable attention due to their remarkable properties, specifically higher cyclability and power density in comparison with batteries, and higher energy density in comparison with common capacitors. The most of supercapacitors are based on aqueous electrolytes. Meanwhile, supercapacitors with non-aqueous electrolytes have certain advantages, first of all, higher voltage. In the present work we investigate possibility to create such supercapacitors with two nanostructured electrode materials, namely single-wall carbon nanotubes (SWNTs) and mixed tin-titanium oxide ST10.

Experimental

SWNTs were fabricated by the arc discharge process and purified by removing by-products (metal catalyst, soot particles and amorphous carbon) to the final product containing up to 80 – 90 mass. % of SWNTs and metal content no more than 0.5 mass. % [1]. The main impurity in the purified SWNT material was graphite microparticles. Purified SWNTs were mostly aggregated in microcrystals of ribbon-like morphology [2]. The mean diameter of SWNTs was about 1.4 nm. Electrodes from SWNT were manufactured by common technology. Active mass of the electrodes consisting of 90% SWNT material and 10% PVdF binder was applied onto nickel current collectors.

Electrodes from ST10 (net formula 90% SnO_2 + 10% TiO_2) were 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^{o}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 [3].

All electrochemical cells contained the electrode under investigation and counter and reference electrodes made from Li-foil, all electrodes being separated with Celgard-like material. Besides two-electrode cells were tested as supercapacitors. Such cells contained identical electrodes with opposite charging degree. All cells were assembled in a CO_2-filled glove box. Two various electrolytes were used: (i) 1M $LiN(CF_3SO_2)_2$ in dioxolane, and (ii) 1M $LiPF_6$ in a mixture of ethylene carbonate, diethyl carbonate, and dimethyl carbonate.

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Results and discussion

Fig. 1 depicts cycling voltammograms (CVA) for an electrode from SWNTs in the electrolyte (ii). Wide potential range from 0.8 to 2.5 V vs Li/Li^+ corresponds to pure capacitive behavior of the carboneous electrode. Corresponding specific capacity is close to 60 $F.g^{-1}$. It is rather good figure for non-aqueous electrolyte. Potential range from 0.0 to 0.8 V corresponds to sum of double layer capacity and pseudocapacity of process of lithium intercalation-deintercalation. The sum is equal to 1500 $F.g^{-1}$.

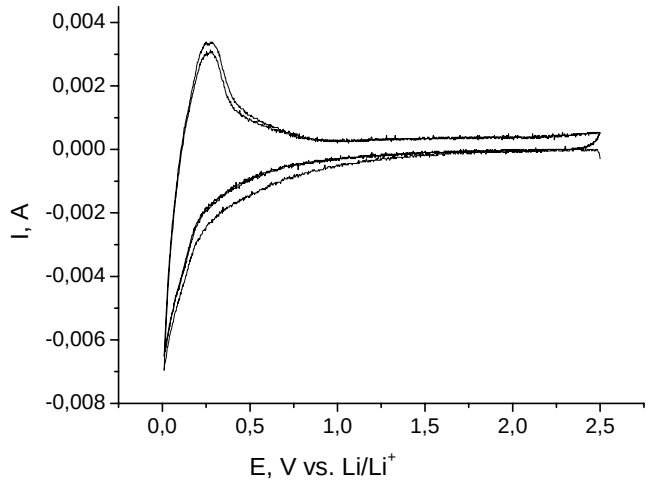

Fig.1 *CVA for electrode from SWNT (scan rate 1 $mV.s^{-1}$)*

Result of testing supercapacitor made from two SWNT-electrodes is shown in Fig. 2. The plot is typical to capacitors' cycling but every charge-discharge line is slightly curved due to contribution of faradaic process of lithium intercalation-deintercalation. Averaged capacity in this case is close to 450 $F.g^{-1}$. At the same time one can see a certain degradation of the capacitor in the course of cycling. True origin of the degradation is unclear.

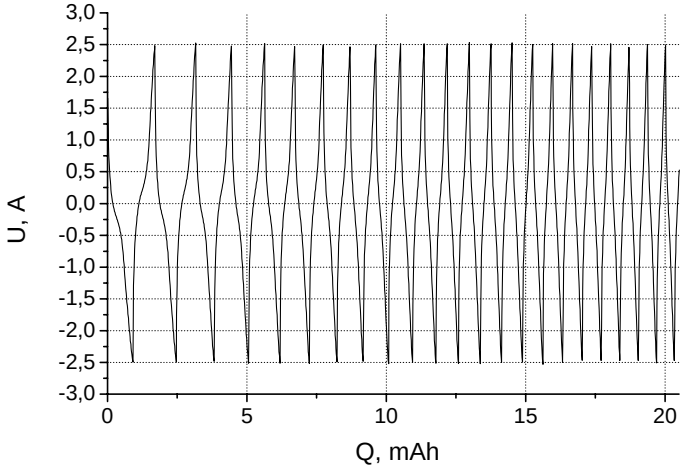

Fig.2 *The cycling history of SWNT-supercapacitor with current density 0.5 $A.g^{-1}$.*

Fig. 3 demonstrates CVA for an electrode with ST10 film in the electrolyte (i). Double layer portion in this case covers the potential range from 0.8 to 1.5 V. Potential range from 0.0 to 0.8 V also corresponds to sum of double layer capacity and pseudocapacity. Average capacity of supercapacitor based on ST10 is more than that of supercapacitors with SWNT-electrodes and amounted up to 600 $F.g^{-1}$.

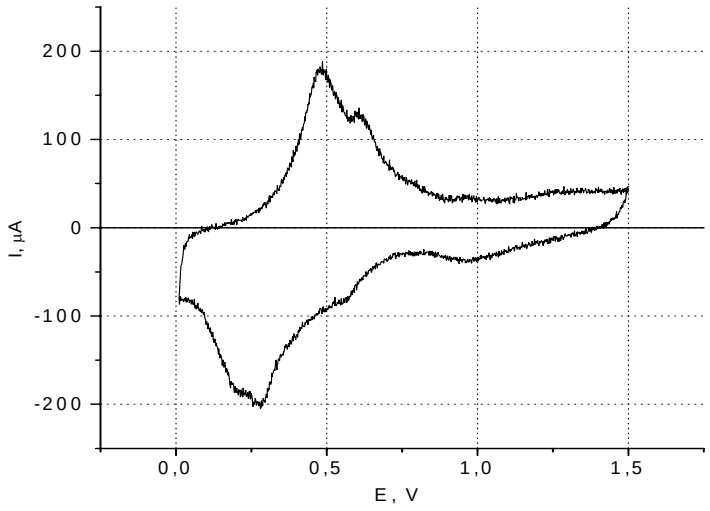

Fig.3 *CVA for electrode from ST10 (scan rate 0.075 $mV.s^{-1}$, weight of ST10 0.6 mg)*

Conclusion

Single wall carbon nanotubes as well as nanostructured (Sn, Ti)O_2 thin films are promising candidates for manufacturing supercapacitors with non-aqueous electrolytes.

References

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