

## ADVANCED NANOSTRUCTURED ANODE MATERIALS FOR LITHIUM-ION BATTERIES

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### ABSTRACT

The more popular active material for negative electrode is usually flake graphite due to its excellent cycle life (up to 1000 cycles). The main disadvantage of graphite is a relatively low specific capacity, because even the theoretical value is  $QC_{th} = 372$  mA·h/g.

Si, Sn, Al, hard carbons and some other materials are actively investigated as the alternate materials for lithium-ion batteries. However, they have not received a practical application, since their large theoretical capacity is accompanied by sharp drop of capacity (during the few cycles), high irreversible capacity (up to 50 % and more), non-horizontal shape of charge–discharge curves. The main reason of sharp capacity degradation is considerable (in 2-4 times) volume changes of these materials during intercalation-deintercalation of lithium ions.

We have formulated some theoretical principles and developed the experimental composite nanostructured anode materials for lithium-ion batteries with high level of specific capacity (up to 600 mA·h/g), quite stable cyclization, minimal irreversible capacity (ca 8 %), horizontal shape of charge–discharge curves.

**Key words:** nanocomposite, lithium-ion battery, negative electrode

### INTRODUCTION

Lithium-ion batteries are the most promising devices for electrochemical energy storage due to their high energy density and cycle life.

The more popular active material for negative electrode is usually flake graphite due to its excellent cycle life (up to 1000 cycles). The main disadvantage of graphite is a relatively low specific capacity, because even the theoretical value of capacity is  $QC_{th} = 372$  mA·h/g.

Si, Sn, Al, hard carbons and some other materials are able to intercalation-deintercalation of lithium ions. Nevertheless, they have not received a practical application, since a huge theoretical capacity (for example  $QS_{th} = 4,200$  mA·h/g for Si,  $QS_{th} = 994$  mA·h/g for Sn) is accompanied by sharp drop of capacity (during the few cycles), high irreversible capacity (up to 50 % and more), non-horizontal shape of charge–discharge curves. The main reason of

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sharp capacity degradation is considerable volume changes of these materials during intercalation-deintercalation of lithium ions in the structure of above mentioned active materials (AMs).

### **METHODS OF SAMPLE MANUFACTURING AND ANALYSIS**

Composite active materials (AMs) for lithium-ion battery electrodes were prepared mainly by mixing corresponding electrochemically active components with different-type nano-structured graphite and carbon materials [1], such as thermally expanded graphite (TEG), graphitized carbon-black (GC), special types of activated coal (AC) and their mixtures. The electrodes were produced by thoroughly mixing the AM with different-type polymer fillers (polytetrafluoroethylene (PTFE), carboxymethylcellulose (CMC), polyvinylidene fluoride (PVDF) and others) followed by applying a thin uniform layer of the suspensions to metal foil with the help of a special device, "Doctor Blade".

The lithium-ion battery assemblies were carried out in the Department of Electrochemical Power Engineering & Chemistry of Kiev National University of Technologies and Design in non-aqueous and oxygen-free atmosphere of the UNILAB (MBraun Inc., USA) glove-box.

Apart from general physical-chemical methods (light, transmission electron, scanning electron and energy-dispersion microscopy), atomic-adsorption spectroscopy with the automatic double-beam atomic-adsorption spectrometer SOLAAR S4 (ThermoElectron, USA) was used to determine the chemical composition of the materials.

Electrochemical characteristics of the materials were measured by cyclic voltammetry, chronoammetry and electrochemical impedance spectroscopy carried out with the multi-channel potentiostat-galvanostat VMP3 (Bio-Logic-Science Instruments, France).

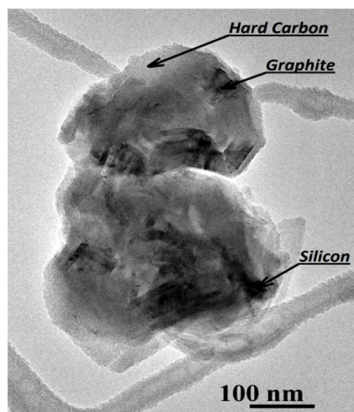
The performance of the electrode materials and battery models in long-term operation was studied using the automatic 32-channel system for testing batteries MSTAT 32 (Arbin Instruments, Texas, USA).

### **RESULTS AND DISCUSSION**

We have formulated the following principles of practical usage of above-mentioned materials for development of advanced composite anode materials for lithium-ion batteries [2, 3].

Anodes has to contain a composite of graphite with high-dispersed (as ideal – nano-dispersed) particles of AMs (like Si, Sn) as active additives;

Particles of AMs have to be surrounded by a quite elastic porous electroconductive matrix (ECM), like amorphous carbon, Al, etc. This ECM has to compensate the considerable volumetric changes of AMs particles during the cycling. It creates the possibilities to prevent a destruction of AM particles and to reach relatively stable cyclization of electrodes.

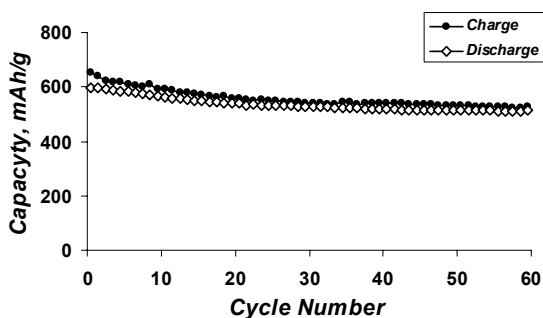


**Fig 1.** – TEM micrographs of carbon coated silicon - natural graphite composite (sample graphite/Si/C)

A concentration of AMs particles has not to be very high (not more than 10%).

We made some experimental investigations in our laboratory and have developed Si/C/graphite based composite nanostructured anode materials for lithium-ion batteries with high level of specific capacity (up to 550-600 mA·h/g), quite stable cyclization (during the hundred cycles), minimal irreversible capacity (ca 8 %), horizontal shape of charge–discharge curves.

The similar results we have achieved also with Sn - based composite nanostructured anodes. Both these nanostructured composites give possibility to exceed noticeably the maximal achieved capacity of graphite anodes (ca 350-370 mA·h/g).



**Fig. 2** – Specific capacity vs cycle number of the carbon coated silicon-graphite composite. Current density is 30 mA/g. The cut-off potentials were 1.5 V for charge and 0.01 V for discharge

### **CONCLUSIONS**

Nano-composites of graphite with silicon, tin and some other materials which can be involved in reversible intercalation of lithium ions have been developed. The use of such materials allows one to increase specific capacity of anodes of lithium-ion batteries by a minimum of 1.5-2 times and at the same time to provide the necessary stability of cycling.

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