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Pulsed plasma chemical synthesis of $Si_xC_yO_z$ composite nanopowder

G Kholodnaya, R Sazonov, D Ponomarev and G Remnev
Institute of High Technology Physics, Tomsk Polytechnic University, 30 Lenin Avenue, 634050, Tomsk, Russia

E-mail: galina_holodnaya@mail.ru

Abstract. $Si_xC_yO_z$ composite nanopowder with an average size of particles about 10-50 nm was produced using the pulsed plasma chemical method. The experiments on the synthesis of nanosized composite were carried out using a TEA-500 pulsed electron accelerator. To produce a composite, $SiCl_4$, O_2, and CH_4 were used. The major part of experiments was conducted using a plasma chemical reactor (quartz, 140 mm diameter, 6 l volume). The initial reagents were injected into the reactor, then a pulsed electron beam was injected which initiated the chemical reactions whose products were the $Si_xC_yO_z$ composite nanopowder. To define the morphology of the particles, the JEOL-II-100 transmission electron microscope (TEM) with an accelerating voltage of 100 kV was used. The substances in the composition of the composite nanopowder were identified using the infrared absorption optical spectrum. To conduct this analysis, the Nicolet 5700 FT-IR spectrometer was used.

1. Introduction

In modern solid-state physics, the properties of nanocomposite structures are actively studied, which are applied for obtaining materials of pre given properties. The components of such combinations can be both metals and their oxides, as well as semiconductors and dielectrics. Regarding the increasing industrial production of hybrid automobiles and Li-ion battery (LIB) electromobiles [1-2], in recent years, a demand for manufacturing a new electrode material for a negative electrode with a higher specific capacity than synthetic graphites (theoretical quantity 372 mAh/g) and improved LIBs has increased. A great attention was paid to alloys of lithium with tin, aluminum, and silicon. A special interest was paid to silicon [3], which showed the highest theoretical specific capacity during electrochemical alloying with lithium (3579 mAh/g) for Li15Si4 [4], hardly yielding to a lithium metal - 4235 mAh/g [5].

The extraction of high amount of lithium is associated with great changes in a volume and structural transformations inducing significant inner mechanical stresses and particle cracking which result in a contact fault with a shunt. As a result, the electrodes based on lithium alloys quickly lose the reversible capacity during cycling. A possible solution of the problem of silicon electrode cyclability is the location of silicon particles inside a conducting matrix. The material for such matrix can be carbon with its high electron conductivity (as high as 10^3 S/cm), low specific weight, and insignificant increase in volume after lithium introduction. The silicon-carbon composites are obtained using grinding of the silicon and graphite mixture in a ball grinder [6-8], coating of silicon particles

with carbon, using the methods of chemical and thermal deposition from the gas phase [9-11], or high-energy plasma [12], the pyrolysis of a precursor mixture [13-14].

The purpose of the given work is the experimental production of $Si_xC_yO_z$ composite nanopowders using a pulsed plasma chemical method.

2. Methodology

The $Si_xC_yO_z$ composite nanopowder has been obtained using the pulsed plasma chemical method. The given method of synthesis is based on the bulk excitation of the reaction gas by a pulsed electron beam and organization of the process of reaction over the whole region of excitation.

The beam energy inputs are significantly lower than the energy of the chemical endothermic reactions of the synthesis. In this way, the potentially high performance in practical realization of the method was attained. The use of the plasma, which was generated by a pulsed electron beam, in the synthesis enabled to decrease a nonproductive energy loss, to vary the properties (the size of particles, crystal lattice) of the final product, to make the process more technological and easy-to-control. In Fig. 1, the scheme of the $Si_xC_yO_z$ composite production is presented.

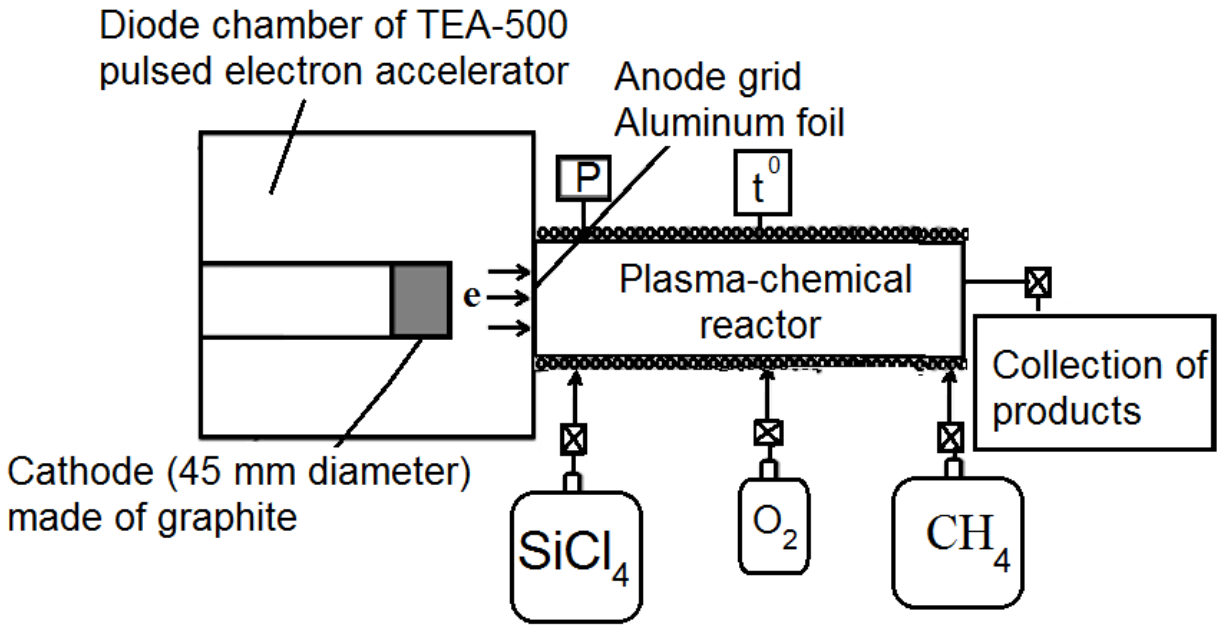

Figure 1. Scheme of an experimental facility

The experiments on the synthesis of the nanosized composite were carried out using a TEA-500 pulsed electron accelerator [15-17]. To obtain the $Si_xC_yO_z$ composite powder, $SiCl_4$, O_2, and CH_4 were used. Most experiments were done using the plasma chemical reactor (quartz, 140 mm diameter, 6 l volume). The reactor was equipped with a manometer, a vacuum meter, a pressure sensor, a shut-off and control valve of the initial reactant mixture inlet and the gas pumping out. The plasma chemical reactor was pumped out up to a pressure of ~ 1-5 Torr before puffing the gas. An electron beam was injected from the end of the reactor. A series of samples was manufactured, the inital concentration of CH_4 varying from sample to sample (the sample 1: SiCl4 170 Torr, O_2 152 Torr, CH_4 57 Torr; the sample 2: SiCl4 170 Torr, O_2 152 Torr, CH_4 76 Torr; the sample 3 SiCl4 170 Torr, O_2 152 Torr, CH_4 152 Torr).

3. Results and Discussion

A wide-spread method of analysis of a chemical composition and a solid substance strucute is the measurement of the optical reflection spectrum in the infrared region (400-4000) cm^{-1}. The use of this method to study the nanoparticles enables to conduct the bulk analysis of the matter, since the penetration depth of IR-radiation (several microns) exceeds the geometrical size of the particles. To carry out this analysis, the Nicolet 5700 FT-IR Spectrometer was used. The technical characteristics of the Nicolet 5700 FT-IR Spectrometer are: the spectral range is as high as (7400 – 350) cm^{-1}; the resolution is 0.09 cm^{-1}; a signal-noise ratio is 40 000:1 (peak-to-peak for 1 minute of scanning); the wavenumber precision is 0.01 cm^{-1} [18-22].

Fig. 2 demonstrates the typical infrared radiation absorption spectra of the $Si_xC_yO_z$ composite powders (samples 1 and 3). The powder under study was preliminary mixed with KBr and was pressed in the tablet. The reflection spectrum of pure KBr was subtracted from the mixture reflection spectrum.

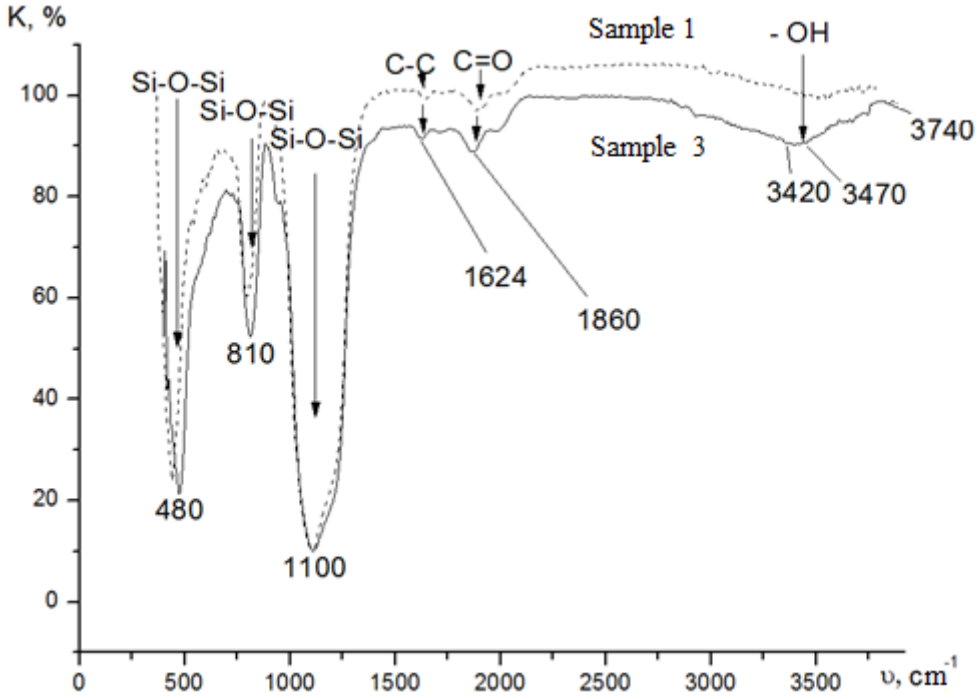

Figure 2. Infrared reflection spectrum of the synthesized $Si_xC_yO_z$ nanocomposites

For the studied samples, the peaks of 1100 and 480 cm^{-1} are typical, they are responsible for Si–O–Si and O–Si–O bond fluctuations. The peak of the C – C bond is recorded. A peak of 810 cm^{-1} can be referred both to the Si – C bond fluctuation (from 750 to 805 cm^{-1}) and to the Si – O – Si bond fluctuation (from 770 to 860 cm^{-1}).

The size of the powder particles was determined using the JEM-100CX II transmission electron microscope (TEM). Fig. 3 presents the histograms from the scanned slides obtained using TEM. The histograms were built with over 1000 particles.

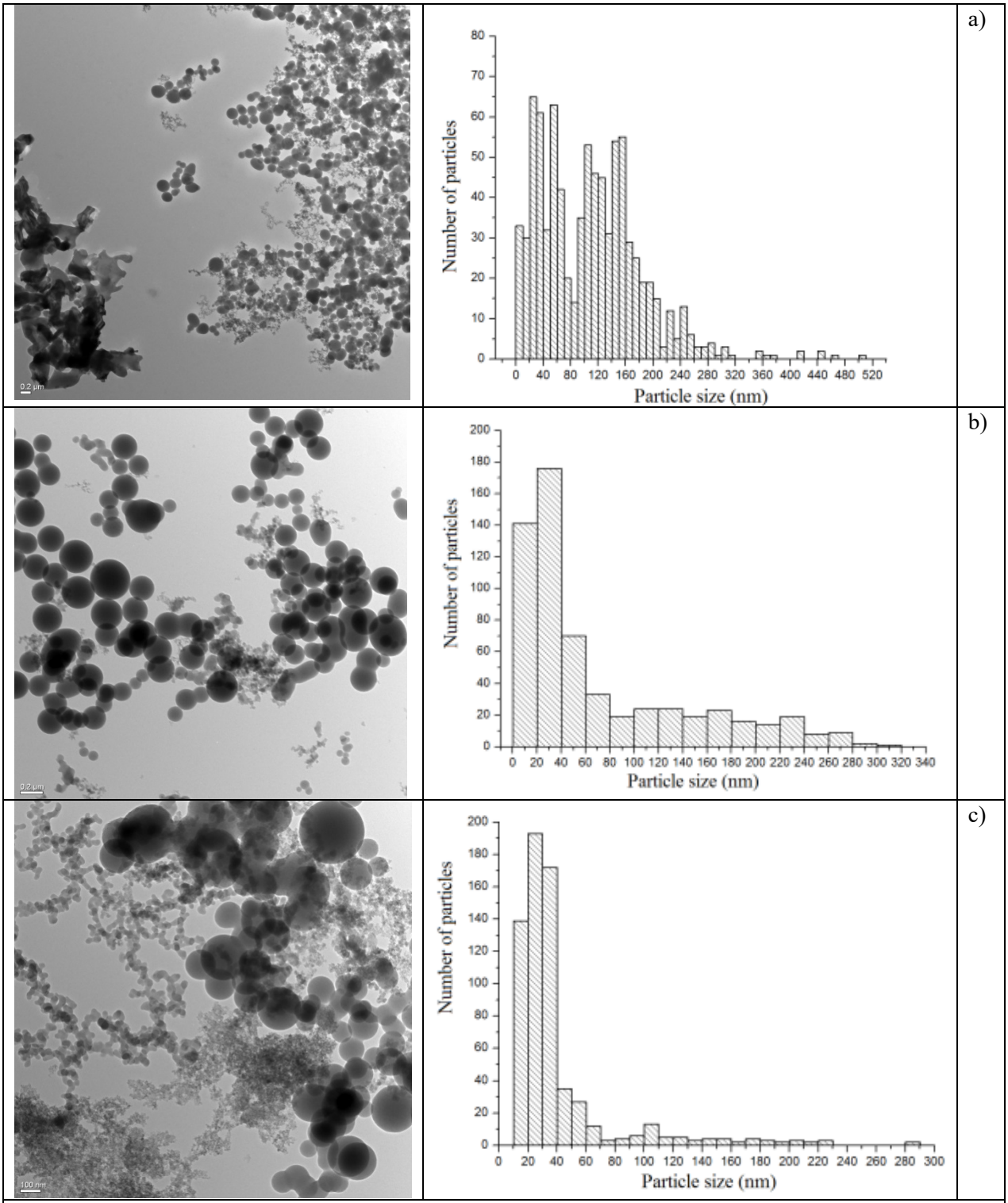

Figure 3. The images of the synthesized composite powder and particle size distribution bar chart: a) sample 1; b) sample 2; c) sample 3

Fig. 3 shows that the particles are spherical; the built bar charts make it possible to conclude that the size of particles varied from 20 to 200 nm. For sample 1, the presence of the irregularly-shaped particle agglomerations is typical. There are the particles of various sizes – large and very small. The

particles of sample 2 are uniform and spherical in morphology. There is a large amount of tiny particles in sample 3, larger particles are rare, compared to samples 1 and 2.

For every $Si_xC_yO_z$ sample, the micro-diffraction patterns were taken. In all studied samples, the weak reflexes are observed. But the brightest reflexes were observed in sample 3 - $Si_xC_yO_z$ (Fig.4) that enabled to conclude about the presence of the crystalline structure in the synthesized nanocomposite. The X-ray phase analysis also justified the presence of the crystal structure in the synthesized nanocomposite. Nevertheless, to specify the obtained data, additional investigations should be carried out.

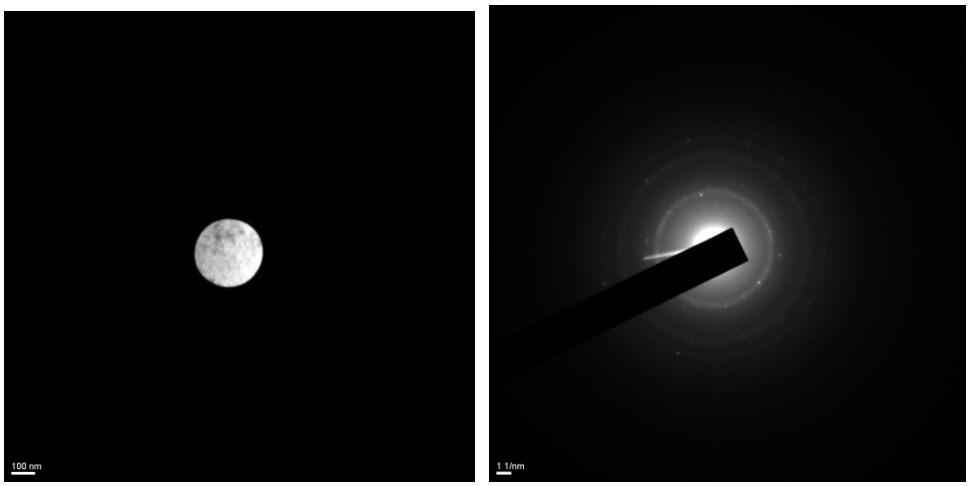

Figure 4. TEM-image of sample 3 - $Si_xO_yC_z$ and its microdiffraction pattern

The synthesized composite $Si_xC_yO_z$ nanopowders were studied using EDX method, which enabled to make a conclusion about the consistency of the chemical composition for the nanoparticles of the different size produced by the method of the plasma chemical synthesis (Fig. 5, sample 3).

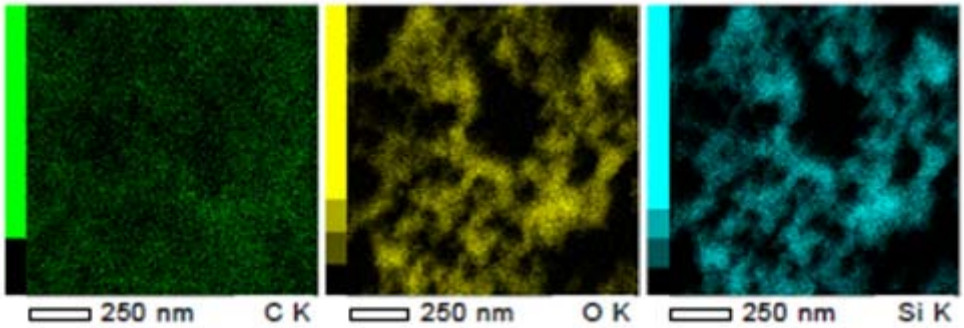

Figure 5. Color windows reflecting the elements of sample 3

EDX-analysis shows that the carbon distribution in powder is uniform.

4. Conclusion

Thus, in the plasma chemical process initiated by the pulsed electron beam, the $Si_xC_yO_z$ powders are synthesized, which are composed of the spherical particles with a diameter of 20-200 nm and with various carbon concentration. According to the results of the X-ray phase analysis and micro-diffraction patterns, we can conclude that the synthesized samples have a crystal lattice. For all composite powders obtained using pulsed plasma chemical synthesis, the presence of the Si–O–Si and C–C bonds is typical.

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