



Review

Mechanochemical synthesis and physical–chemical properties of carbon–fluorocarbon nanocomposition materials. A review

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ABSTRACT

There are the described novel class of porous carbon–fluorocarbon nanocomposition materials “C–CF_{1+x}”, prepared via the mechanochemical activation (MA) in the heterogeneous mixed systems “nano-C–nano-CF_{1+x}”, having an atomic ratio C:F as 1.14–4.0. As nano-C it was used thermally expanded graphite TEG and mesoporous carbon material NUMS (free porosity 45–95% and specific area 25–400 m²/g). As nano-CF_{1+x} these were used a superstoichiometric fluorocarbons FS and FT (CF_{1.18–1.25}) having the coherent diffraction area (CDA) ~20–25 Å, free porosity 60–70%, sum O + H₂O in mixtures ~0.1–0.5 wt.%, and metals sum <0.01 wt.%.

Prepared nanocomposites “C–CF_{1+x}” were studied by FTIR, Raman, XPS C1s, O1s, F1s, X-ray diffraction and by chemical C, H, F-analyses. It was shown, that decrease of weight in systems “C–CF_{1+x}” does not exceed 0.5 wt.% and stated two main features of the temporary dynamics in changes for all MA-products. These are monotonous changes in bulk properties, such as decrease of C-nanophase relative amounts, confirmed with XRD. Simultaneously, a decrease of sp³-C–F and sp³-CF₂-groups at 1200 and 1320 cm⁻¹ and an origination of sp³-C–F-groups at 1080–1120 cm⁻¹, typical for C₂F-like structures are observed. Decrease of specific surface is corresponding to decrease in CDA sizes and density for all MA-products.

O-containing admixtures in starting materials have a key influence to interactions in nano-“C–CF_{1+x}” systems during MA-processing, despite to their low content. The main O-contained participant is H₂O and it is interaction with sp³-C–F-bonds is leading to primary hydrolytic substitution of F onto OH with the origin of surface sp³-C–OH-bonds and their subsequent transformations into edged sp²>C=O or/and into ester bridges C–O–C among basal and edged nano-C and nano-fluorocarbon blocks. The presence of basal sp³-C–OH and edged sp²>C=O (sp²>COOH)-groups is confirmed by FTIR and XPS C1s and O1s spectra for all MA-nanocomposites in “C–CF_{1+x}” systems. Changes in the surface properties of prepared MA-“C–CF_{1+x}” nanocomposites are corresponded to the origin of extrema in properties for MA-time 6–10 min, such as content of surface C-nanophases and surface F with the simultaneous appearance of extrema in the specific electro conductivities and capacitances. The nature of observed phenomena is explained by the origin of chemical carbon nanosized contacts on particle surface and it is possible to use for practical applications. The main difference among MA-“C–CF_{1+x}” nanocomposites is that the “FS–TEG” systems are dominated by sp²-C–sp³-C–F electroconductive bridges, whereas in “NUMS–FT” systems the character of conductivity is determined by contribution of ester bridges C–O–C.

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1. Introduction

Fluorocarbon materials (FCM) of general formula CF_x ($x = 0.9$ – 1.3) are a basic component for most of high-capacity cathodes, used in nonaqueous lithium chemical electrical sources (LCS) [1–4]. Because of CF_x high resistivity ($\rho \sim 10^{14-15} \Omega \text{ cm}$), FCMs are usually carefully mixed with electroconductive technical carbon materials (carbon black, soot, graphite etc.) in order to get good electroconductive LCS cathodes [1–3,5]. It was stated from an empirical way that expanded graphite (thermally expanded graphite: TEG) was the best current-conductive and pore-forming additive [6]. As a result of R&D carried out during 1993–2003 in collaboration with Nikolaev Institute of Inorganic Chemistry SB RAS and Joint Stock Novosibirsk Chemical Concentrates Plant Inc. (JS NCCP) it has been developed and patented as new generation of high-porosity cathode materials for LCS, having a specific capacity not less than 600 mAh/g [3,7,8]. In the mentioned works there was shown that the best effective and porous cathodes for lithium cells, having an excellent current density of about 1 mA/cm² could be prepared via mechanochemical activation (MA) of powdered mixtures of superstoichiometric $CF_{1.18-1.33}$ with TEG [3]. Meanwhile, detailed basic works [3,7,8], explaining the nature of such improvements in the properties of these novel FCM-based cathodes, were published in Russian scientific journals and therefore were not spread among the world specialists of fluorine chemistry and lithium batteries technology.

The aim of the presented review is the detailed description of syntheses and physico-chemical phenomena proceeds at mechanochemical interaction of the superstoichiometric fluorocarbon nanosized materials, mixed with some highly porous technical carbon materials, such as thermally expanded graphite (TEG) and mesoporous carbon material (NUMS).

2. Experimental

2.1. Initial carbon materials

Thermally expanded graphite TEG was prepared by thermolysis of graphite fluoroxide FOG-E at 400 °C (4 h). FOG-E was synthesized by electrochemical oxidation of previously purified graphite (Taiginskoye deposit, Russia) in 40–46% HF media [9], according to patent [10]. Because of peculiar physico-chemical properties, FOG-E met the technical specifications [11]. With respect to known TEGs prepared by thermolysis of graphite bisulphate, a product of oxidation of raw natural graphite in 100% hot H_2SO_4 , the carbon material TEG, synthesized from FOG-E precursor, contained two to three orders less impurities (0.05–0.08 wt.% vs. 4–8 wt.%, typical value of commercial TEGs). The present study used samples of TEG, exhibited a specific surface area $17.5 \pm 1 \text{ m}^2/\text{g}$ (BET under N_2) and

$\sim 95\%$ free pores volume (FPV). The total amount of impurities present in TEG, i.e. Fe, Si, Al, Ca, Na, Mg, Cu, Ni, Mn, Cr, etc., are determined by an atomic emission spectral analysis with use of a double-jet argon plasmatron and MAES registration technique (DJP MAES) [12], was about 0.025 wt.%. The content of absorbed moisture in TEG samples was ~ 0.36 wt.%. The chemical composition of TEG dried at 105 °C: C = 97.8 wt.%, H = 0.26 wt.%, F = 0.34 wt.%, O = 1.23 wt.%, as difference $[100\% - C - H - H_2O - \Sigma \text{impurities}]$.

The size of nanoblocks in starting TEG particles (Fig. 1), accordingly X-ray data on coherent diffraction area (CDA) was estimated as 400–800 Å.

Mesoporous carbon material NUMS was prepared by purification of starting semi-industrial carbon of the type “Tekhnosorb”, produced by Omsk Institute of Hydrocarbon Processing SB RAS, according to the technical specification TU 38 41538-94. For the studies it used “Tekhnosorb” fraction with particle sizes of 100–200 mcm, purified by processing with 37 wt.% HCl (extra pure grade) under heating at 70–80 °C (2 times for 3–4 h) for removal of impurities, washed by distilled water and finally dried for 5 h at 105 °C. A powdered mesoporous carbon material NUMS was then obtained, having a specific surface area $317 \pm 18 \text{ m}^2/\text{g}$ (method BET, N_2), a pycnometric density of $2.05 \pm 0.03 \text{ g/cm}^3$, and a volume of free pores $62.1 \pm 1.8\%$. The content of absorbed H_2O was 0.60 wt.%. Carbon in purified NUMS was found to be 97.8 wt.%, H = 0.20 wt.%, O = 1.38 wt.% as difference $[100\% - C - H - H_2O - \Sigma \text{impurities}]$. The total amount of impurities in purified NUMS powder was detected by DJP MAES as 116 ppm (Fe, Si, Al, Ca, Mg, Ni, Mn, etc.).

The size of nanoblocks in NUMS particles, determined from CDA of 0 0 2 and 0 0 4 XRD peaks was evaluated about ~ 25 – 45 Å.

Micrographs of morphology and images of both carbon materials particles, obtained with the raster electron microscope BS-350 (Brno, ČSSR) are shown in Fig. 1. Both TEG and NUMS powders before use were initially treated by 5 wt.% H_2O_2 (room temperature, 2 h) for oxidation of particles surface and then dried for 5 h at 105 °C. Summary content of O-groups (sp^3 -C-OH and sp^2 -COOH) + H_2O in TEG and NUMS-O was determined by titrimetry as 0.15 and 1.5 wt.% [13].

2.2. Initial fluorocarbon materials (FCMs)

For starting FCMs, samples of superstoichiometric polycarbonofluorides of the FS and FT types were used. They were prepared by the method described in Ref. [14]. Chemical composition and properties of FCM materials met the technical requirements of the official technical specifications [15]. Determination of F in FCMs, conducted by the Shoeniger–Fadееva method [16], gave 64.96 ± 0.36 wt.% in FS and 65.41 ± 0.56 wt.% in FT. Carbon in FCMs was determined by hydrogen thermogravimetry method [15,17] and its content was found as 33.04 ± 0.36 wt.% in FT and 34.20 ± 0.44 wt.%

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