

^{13}C enriched halogenated carbon materials

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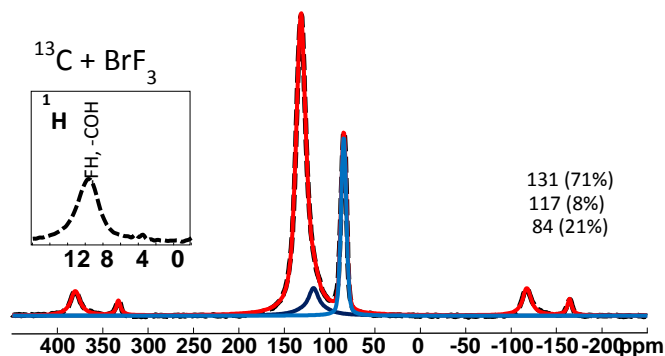
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Carbon-based materials are widely used as anode materials (graphite, hard and soft carbon) and conductive additives (super P[®] carbon, acetylene black, etc.) in Li-ion batteries. The process of Li intercalation in graphite has been thoroughly studied by a variety of physical and chemical methods, while in other promising carbon materials, such as hard and soft carbon, many chemical aspects of this process remain poorly understood. Particularly, presence of nanopores and defects in a hard carbon allows substantially exceeding the theoretical limit of 372 mAh/g in the specific capacity of graphite [1]. In addition, electrochemical performance of carbon-based materials can be improved by means of functionalization with halogens (fluorine or bromine). At a low functionalization degree, attachment of halogen atoms results in increase of electrical conductivity of carbon material and promotes a reversible faradaic reaction with Li [2]. In principle primary lithium-ion batteries could benefit from using fluorinated carbon as anode material, because of high voltage and capacity, produced in the process of lithium fluoride formation during lithium intercalation.

Solid-state NMR is known as a powerful tool to identify and quantify different structural species present in the material. Recently, fluorine patterning and distribution in the graphite layer with different fluorination degree was recognized using this method [3]. This method has been used for the *in situ* studies of electrochemical processes [4, 5]. But it has a limitation in applications to the study on carbon nuclei, as the only NMR-active ^{13}C isotope has a natural abundance of 1.1% and can not contribute essentially to the NMR signals. To solve this problem, in the present work we studied ^{13}C enriched materials with different texture and halogenation.

Starting hard carbon material, produced from hydrocarbons, and phenol formaldehyde resin at 2600°C with an initial ^{13}C content in the composite of ~70%, was recrystallized under high pressure and temperature. The material obtained, as well as starting material, was brominated and fluorinated through gas-phase reaction. All materials obtained were subjected for Li intercalation performance study as well as XPS, XRD, Raman, IR analysis, and ^{13}C , ^{19}F , ^1H NMR. According to NMR and XPS data recrystallized material has less oxygen containing groups in comparison to initial one, while preserving the same amount of graphitic phase. Halogenation of the samples leads to removal of sp^3 -bonded carbon component and oxygen containing groups and results in either partial fluorination or bromine molecules intercalation into the material. NMR spectra, presented in figure 1, suggests formation of graphene domains in fluorinated materials (red line is graphitic, blue one is C-F bonded and black is graphene domains).



The work was financially supported by Russian Science Foundation grant №16-13-00016 and German-Russian Research Interdisciplinary Center grant №C-2017a-6.

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